

# Finite Size Scaling for Criticality of the Schrödinger Equation

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By solving the Schrödinger equation one obtains the whole energy spectrum, both the bound and the continuum states. If the Hamiltonian depends on a set of parameters, these could be tuned to a transition from bound to continuum states. The behavior of systems near the threshold, which separates bound-states from continuum states, is important in the study of such phenomenon as: ionization of atoms and molecules, molecule dissociation, scattering collisions and stability of matter. In general, the energy is non-analytic as a function of the Hamiltonian parameters or a bound-state does not exist at the threshold energy. The overall goal of this chapter is to show how one can predict, generate and identify new class of stable quantum systems using large-dimensional models and the finite size scaling approach. Within this approach, the finite size corresponds not to the spatial dimension but to the number of elements in a complete basis set used to expand the exact eigenfunction of a given Hamiltonian. This method is efficient and very accurate for estimating the critical parameters,  $\{\lambda_i\}$ , for stability of a given Hamiltonian,  $H(\lambda_i)$ . We present two methods of obtaining critical parameters using finite size scaling for a given quantum Hamiltonian: The finite element method and the basis set expansion method. The long term goal of developing finite size scaling is treating criticality from first principles at quantum phase transitions. In the last decade considerable attention has concentrated on a new class of phase transitions, transitions which occur at the absolute zero of temperature. These are quantum phase transitions which are driven by quantum fluctuations as a consequence of Heisenberg's uncertainty principle. These new transitions are tuned by parameters in the Hamiltonian. Finite size scaling might be useful in predicting the quantum critical parameters for systems going through quantum phase transitions.

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## I. INTRODUCTION

Weakly bound states represent an interesting field of research in atomic and molecular physics. The behavior of systems near the binding threshold is important in the study of ionization of atoms and molecules, molecule dissociation and scattering collisions. Moreover, the stability of atomic and molecular systems in external electric, magnetic and laser fields is of fundamental importance in atomic and molecular physics and has attracted considerable experimental and theoretical attention over the past decades[1–4]. A superintense laser field can change the nature of atomic and molecular systems and their anions; the stabilization in superstrong fields is accompanied by splitting of the electron distribution into distinct lobes, with locations governed by the quiver amplitude and polarization of the laser field. This localization markedly alters electron-nucleus interactions as well as reduces electron-electron repulsions and hence suppresses autoionization. In molecules, it can also enhance chemical bonding. This localization markedly reduces the ionization probability and can enhance chemical bonding when the laser strength becomes sufficiently strong and can give rise to new stable multiply charged negative ions such as  $\text{H}^{--}$ ,  $\text{He}^-$  and  $\text{H}_2^-$  [3, 5–7].

In general, the energy is non-analytical, an analytic function is a function that is locally given by a convergent power series, as a function of the Hamiltonian parameters or a bound-state does not exist at the threshold energy. It has been suggested for some time, based on large-dimensional models, that there are possible analogies between critical phenomena and singularities of the energy [8–10].

Phase transitions are associated with singularities of the free energy. These singularities occur only in the thermodynamic limit[11, 12] where the dimension of the system approaches infinity. However calculations are done only on finite systems. A Finite Size Scaling (FSS) approach is needed in order to extrapolate results from finite systems to the thermodynamic limit[13]. FSS is not only a formal way to understand the asymptotic behavior of a system when the size tends to infinity, but a theory that also gives us numerical methods[14–20] capable of obtaining accurate results for infinite systems by studying the corresponding small systems[21–32]. Applications include expansion in Slater-type basis functions[30], Gaussian-type basis functions[33] and recently finite elements[34].

## II. CRITICALITY FOR LARGE-DIMENSIONAL MODELS

Large dimension models were originally developed for specific theories in the fields of nuclear physics, critical phenomena and particle physics[35, 36]. Subsequently, with the pioneering work of Herschbach[10, 37], they found wide use in the field of atomic and molecular physics[38]. In this method one takes the dimension of space,  $D$ , as a variable, solves the problem at some dimension  $D \neq 3$  where the physics becomes much simpler, and then uses perturbation theory or other techniques to obtain an approximate result for  $D = 3$ [10].

It is possible to describe stability and symmetry breaking of electronic structure configurations of atoms and molecules as phase transitions and critical phenomena. This analogy was revealed by using dimensional scaling method and the large dimensional limit model of electronic structure configurations[39–42].

To study the behavior of a given system near the critical point, one has to rely on model calculations which are simple, capture the main physics of the problem and which belong to the same universality class[16, 17]. Here we will illustrate the phase transitions and symmetry breaking using the large dimension model. In the application of dimensional scaling to electronic structure, the large-D limit reduces to a semi-classical electrostatic problem in which the electrons are assumed to have fixed positions relative both to the nuclei and to each other in the D-scaled space[10]. This configuration corresponds to the minimum of an effective potential which includes Coulomb interactions as well as centrifugal terms arising from the generalized D-dependence kinetic energy. Typically, in the large-D regime the electronic structure configuration undergoes symmetry breaking for certain ranges of nuclear charges or molecular geometries[46].

In order to illustrate the analogy between symmetry breaking and phase transitions we present as an example: the results for the two-electron atoms in the Hartree-Fock (HF) approximation[39]. In the HF approximation at the  $D \rightarrow \infty$  limit, the dimensional-scaled effective Hamiltonian for the two-electron atom in an external weak electric field  $\mathcal{E}$  can be written as[47, 48],

$$\mathcal{H}_\infty = \frac{1}{2} \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) - Z \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{(r_1^2 + r_2^2)^{1/2}} - \mathcal{E} (r_1 - r_2) \quad (1)$$

where  $r_1$  and  $r_2$  are the electron-nucleus radii, and  $Z$  is the nuclear charge. The ground state energy at the large-D limit is then given by  $E_\infty(Z, \mathcal{E}) = \min_{\{r_1, r_2\}} \mathcal{H}_\infty$ .

In the absence of an external electric field,  $\mathcal{E} = 0$ , Herschbach and coworkers[49] have found that these equations have a symmetric solution with the two electrons equidistant from the nucleus, with  $r_1 = r_2 = r$ . This symmetric solution represents a minimum in the region where all the eigenvalues of the Hessian matrix are positive,  $Z \geq Z_c = \sqrt{2}$ . For values of  $Z$  smaller than  $Z_c$ , the solutions become unsymmetrical with one electron much closer to the nucleus than the other ( $r_1 \neq r_2$ ). In order to describe this symmetry breaking, it is convenient to introduce new variables  $(r, \eta)$  of the form:  $r_1 = r$ ;  $r_2 = (1 - \eta)r$ , where  $\eta = (r_1 - r_2)/r_1 \neq 0$  measures the deviation from the symmetric solution.

By studying the eigenvalues of the Hessian matrix, one finds that the solution is a minimum of the effective potential for the range,  $1 \leq Z \leq Z_c$ . We now turn to the question of how to describe the system near the critical point. To answer this question, a complete mapping between this problem and critical phenomena in statistical mechanics is readily feasible with the following analogies:

- nuclear charge ( $Z$ )  $\leftrightarrow$  temperature ( $T$ )
- external electric field ( $\mathcal{E}$ )  $\leftrightarrow$  ordering field ( $h$ )
- ground state energy ( $E_\infty(Z, \mathcal{E})$ )  $\leftrightarrow$  free energy ( $f(T, h)$ )
- asymmetry parameter ( $\eta$ )  $\leftrightarrow$  order parameter ( $m$ )
- stability limit point ( $Z_c, \mathcal{E} = 0$ )  $\leftrightarrow$  critical point ( $T_c, h = 0$ )

Using the above scheme, we can define the critical exponents ( $\beta, \alpha, \delta$  and  $\gamma$ ) for the electronic structure of the two electron atom in the following way:

$$\begin{aligned} \eta(Z, \mathcal{E} = 0) &\sim (-\Delta Z)^\beta ; \Delta Z \rightarrow 0^- \\ E_\infty(Z, \mathcal{E} = 0) &\sim |\Delta Z|^\alpha ; \Delta Z \rightarrow 0 \\ \mathcal{E}(Z_c, \eta) &\sim \eta^\delta \text{sgn}(\eta) ; \eta \rightarrow 0 \\ \frac{\partial \eta}{\partial \mathcal{E}} |_{\mathcal{E}=0} &\sim |\Delta Z|^{-\gamma} ; \Delta Z \rightarrow 0 \end{aligned} \quad (2)$$

where  $\Delta Z \equiv Z - Z_c$ . These critical exponents describe the nature of the singularities in the above quantities at the critical charge  $Z_c$ . The values obtained for these critical exponents are known as classical or mean-field critical exponents:  $\beta = \frac{1}{2}$  ;  $\alpha = 2$  ;  $\delta = 3$  ;  $\gamma = 1$ .

This analogy between symmetry breaking and phase transitions was also generalized to include the large dimensional model of the N-electron atoms[40], simple diatomic molecules[41, 43], both linear and planar one-electron systems[42] as well as three-body Coulomb systems of the general form  $ABA$ [44].

The above simple large-D picture helps to establish a connection to phase transitions. However, the next question to be addressed is: How to carry out such an analogy to  $D = 3$ ? This question will be examined in the subsequent sections using the finite size scaling approach.

### III. FINITE SIZE SCALING: A BRIEF HISTORY

Ice tea, boiling water and other aspects of two-phase coexistence are familiar features of daily life. Yet phase transitions do not exist at all in finite systems! They appear in the thermodynamic limit: The volume  $V \rightarrow \infty$  and particle number  $N \rightarrow \infty$  in such a way that their ratio, which is the density  $\rho = N/V$ , approaches a finite quantity. In statistical mechanics, the existence of phase transitions is associated with singularities of the free energy per particle in some region of the thermodynamic space. These singularities occur only in the *thermodynamic limit*[11, 12]. This fact could be understood by examining the partition function  $Z$ .

$$Z = \sum_{\text{microstate } \Omega} e^{-E(\Omega)/k_B T}, \quad (3)$$

where  $E(\Omega)$  is the energies of the states,  $k_B$  is the Boltzmann constant and  $T$  is the temperature. For a finite system, the partition function is a finite sum of analytical terms, and therefore it is itself an analytical function. The

Boltzmann factor is an analytical function of  $T$  except at  $T = 0$ . For  $T > 0$ , it is necessary to take an infinite number of terms in order to obtain a singularity in the thermodynamic limit[11, 12].

In practice, real systems have a large but finite volume and particle numbers ( $N \sim 10^{23}$ ), and phase transitions are observed. More dramatic even is the case of numerical simulations, where sometimes systems with only a few number (hundreds, or even tens) of particles are studied, and “critical” phenomena are still present. Finite size scaling theory, which was pioneered by Fisher[13], addresses the question of why finite systems apparently describe phase transitions and what is the relation of this phenomena with the true phase transitions in corresponding infinite systems. Moreover, finite-size scaling is not only a formal way to understand the asymptotic behavior of a system when the size tends to infinity. In fact, the theory gives us numerical methods capable of obtaining accurate results for infinite systems by studying the corresponding small systems (see [15–17] and references therein).

In order to understand the main idea of finite size scaling, let us consider a system defined in a  $D$ -dimensional volume  $V$  of a linear dimension  $L$  ( $V = L^D$ ). In a finite size system, If quantum effects are not taken into consideration, there are in principle three length scales: The finite geometry characteristic size  $L$ , the correlation length  $\xi$ , which may be defined as the length scale covering the exponential decay  $e^{-r/\xi}$  with distance  $r$  of the correlation function, and the microscopic length  $a$  which governs the range of the interaction. Thermodynamic quantities thus may depend on the dimensionless ratios  $\xi/a$  and  $L/a$ . The finite size scaling hypothesis assumes that, close to the critical point, the microscopic length drops out.

If in the thermodynamic limit,  $L \rightarrow \infty$ , we consider that there is only one parameter (say temperature  $T$ ) in the problem and the infinite system has a second order phase transition at a critical temperature  $T_c$ , a thermodynamic quantity  $G$  develops a singularity as a function of the temperature  $T$  in the form:

$$G(T) = \lim_{L \rightarrow \infty} G_L(T) \sim |T - T_c|^{-\rho} , \quad (4)$$

whereas it is regular in the finite system,  $G_L(T)$  has no singularity.

When the size  $L$  increases, the singularity of  $G(T)$  starts to develop. For example, if the correlation length diverges at  $T_c$  as:

$$\xi(T) = \lim_{L \rightarrow \infty} \xi_L(T) \sim |T - T_c|^{-\nu} , \quad (5)$$

then  $\xi_L(T)$  has a maximum which becomes sharper and sharper, then FSS ansatz assumes the existence of scaling function  $F_K$  such that:

$$G_L(T) \sim G(T) F_K \left( \frac{L}{\xi(T)} \right) , \quad (6)$$

where  $F_K(y) \sim y^{\rho/\nu}$  for  $y \sim 0^+$ . Since the FSS ansatz, Eq. (6), should be valid for any quantity which exhibits an algebraic singularity in the bulk, we can apply it to the correlation length  $\xi$  itself. Thus the correlation length in a finite system should have the form:

$$\xi_L(T) \sim L \phi_\xi(L^{1/\nu} |T - T_c|) . \quad (7)$$

The special significance of this result was first realized by Nightingale [51], 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  $L$  and  $L'$  is given by:

$$\frac{\xi_L(T)}{L} = \frac{\xi_{L'}(T')}{L'} , \quad (8)$$

and has a fixed point at  $T^{(L,L')}$ . It is expected that the succession of points  $\{T^{(L,L')}\}$  will converge to the true  $T_c$  in the infinite size limit.

The finite-size scaling theory combined with transfer matrix calculations had been, since the development of the phenomenological renormalization in 1976 by Nightingale[51], one of the most powerful tools to study critical phenomena in two-dimensional lattice models. For these models the partition function and all the physical quantities of the system (free energy, correlation length, response functions, etc) can be written as a function of the eigenvalues of the transfer matrix[52]. In particular, the free energy takes the form:

$$f(T) = -T \ln \lambda_1 \quad (9)$$

and the correlation length is:

$$\xi(T) = -\frac{1}{\ln(\lambda_2/\lambda_1)} \quad (10)$$

where  $\lambda_1$  and  $\lambda_2$  are the largest and the second largest eigenvalues of the transfer matrix. In this context, critical points are related with the degeneracy of these eigenvalues. For finite transfer matrix the largest eigenvalue is isolated (non degenerated) and phase transitions can occur only in the limit  $L \rightarrow \infty$  where the size of the transfer matrix goes to infinity and the largest eigenvalues can be degenerated. In the next section, we will see that these ideas of finite size scaling can be generalize to quantum mechanics, in particular addressing the criticality of the Schrödinger equation.

#### IV. FINITE SIZE SCALING FOR THE SCHRÖDINGER EQUATION

The finite size scaling method is a systematic way to extract the critical behavior of an infinite system from analysis on finite systems[30]. It is efficient and accurate for the calculation of critical parameters of the Schrödinger equation. Let's assume we have the following Hamiltonian:

$$\mathcal{H} = \mathcal{H}_0 + V_\lambda \quad (11)$$

where  $\mathcal{H}_0$  is  $\lambda$ -independent and  $V_\lambda$  is the  $\lambda$ -dependent term. We are interested in the study of how the different properties of the system change when the value of  $\lambda$  varies. A critical point,  $\lambda_c$ , will be defined as a point for which a bound state becomes absorbed or degenerate with a continuum.

Without loss of generality, we will assume that the Hamiltonian, Eq. (11), has a bound state,  $E_\lambda$ , for  $\lambda > \lambda_c$  which becomes equal to zero at  $\lambda = \lambda_c$ . As in statistical mechanics, we can define some critical exponents related to the asymptotic behavior of different quantities near the critical point. In particular, for the energy we can define the critical exponent  $\alpha$  as:

$$E_\lambda \underset{\lambda \rightarrow \lambda_c^+}{\sim} (\lambda - \lambda_c)^\alpha. \quad (12)$$

The existence or absence of a bound state at the critical point is related to the type of the singularity in the energy. Using statistical mechanics terminology, we can associate “first order phase transitions” with the existence of a normalizable eigenfunction at the critical point. The absence of such a function could be related to “continuous phase transitions”[30].

In quantum calculations, the variational method is widely used to approximate the solution of the Schrödinger equation. To obtain exact results one should expand the exact wave function in a complete basis set and take the number of basis functions to infinity. In practice, one truncates this expansion at some order  $N$ . In the present approach, the finite size corresponds not to the spatial dimension, as in statistical mechanics, but to the number of elements in a complete basis set used to expand the exact eigenfunction of a given Hamiltonian. We will compare two methods to obtain the matrix elements needed to apply the FSS ansatz. The size of our system for the basis set expansion will correspond to the dimension of the Hilbert space. For a given complete basis set  $\Phi_n$ , the ground-state eigenfunction has the following expansion:

$$\Psi_\lambda = \sum_n a_n(\lambda) \psi_n, \quad (13)$$

where  $n$  is the set of quantum numbers. We have to truncate the series at order  $N$  and the expectation value of any general operator  $O$  at order  $N$  is given by:

$$\langle O \rangle^N = \sum_{n,m} a_n^{(N)} a_m^{(N)} O_{n,m}, \quad (14)$$

where  $O_{n,m}$  are the matrix elements of  $O$  in the basis set  $\{\psi_n\}$ .

For the finite element method (FEM), the wavefunction  $\psi_n(r)$  in the  $n$ -th element is expressed in terms of local shape functions. For our calculations, we use Hermite interpolation polynomials with two nodes and three degrees of freedom. This choice ensures the continuity of the wavefunction and its first two derivatives. Then in  $n$ -th element the wavefunction is[34]:

$$\psi_n(r) = \sum_{i=1}^2 \left[ \phi_i(r) \psi_n^i + \bar{\phi}_i(r) \psi_n'^i + \bar{\bar{\phi}}_i(r) \psi_n''^i \right], \quad (15)$$

with  $\alpha$  indicating the nodal index of the element;  $i = 1$  for the left and  $i = 2$  for the right border of the element. The functions  $\phi_i(r)$ ,  $\bar{\phi}_i(r)$ , and  $\bar{\bar{\phi}}_i(r)$  are the (fifth degree) Hermite interpolation polynomials. Then  $\psi_n^i$ ,  $\psi_n'^i$ , and  $\psi_n''^i$  are the undetermined values of the wavefunction and its first and second derivative on the nodal points. The size for the case of solving the equation with the FEM will be the number of elements used.

Since  $\langle O \rangle_\lambda$  is not analytical at  $\lambda = \lambda_c$ , then we define a critical exponent,  $\mu_O$ , if the general operator has the following relation:

$$\langle O \rangle_\lambda \approx (\lambda - \lambda_c)^{\mu_O} \text{ for } \lambda \rightarrow \lambda_c^+, \quad (16)$$

where  $\lambda \rightarrow \lambda_c^+$  represents taking the limit of  $\lambda$  approaching the critical point from larger values of  $\lambda$ . As in the FSS ansatz in statistical mechanics [16, 53], we will assume that there exists a scaling function for the truncated magnitudes such that:

$$\langle O \rangle_\lambda^{(N)} \sim \langle O \rangle_\lambda F_O(N|\lambda - \lambda_c|^\nu), \quad (17)$$

with the scaling function  $F_O$  being particular for different operators but all having the same unique scaling exponent  $\nu$ .

To obtain the critical parameters, we define the following function:

$$\Delta_O(\lambda; N, N') = \frac{\ln(\langle O \rangle_\lambda^N / \langle O \rangle_\lambda^{N'})}{\ln(N'/N)}. \quad (18)$$

At the critical point, the expectation value is related to  $N$  as a power law,  $\langle O \rangle \sim N^{\mu_O/\nu}$ , and Eq. (18) becomes independent of  $N$ . For the energy operator  $O = H$  and using the critical exponent  $\alpha$  for the corresponding exponent  $\mu_O$  we have:

$$\Delta_H(\lambda_c; N, N') = \frac{\alpha}{\nu}. \quad (19)$$

In order to obtain the critical exponent  $\alpha$  from numerical calculations, it is convenient to define a new function[30]:

$$\Gamma_\alpha(\lambda, N, N') = \frac{\Delta_H(\lambda; N, N')}{\Delta_H(\lambda; N, N') - \Delta_{\frac{\partial \nu_\lambda}{\partial \lambda}}(\lambda; N, N')}, \quad (20)$$

which at the critical point is independent of  $N$  and  $N'$  and takes the value of  $\alpha$ . Namely, for  $\lambda = \lambda_c$  and any values of  $N$  and  $N'$  we have

$$\Gamma_\alpha(\lambda_c, N, N') = \alpha, \quad (21)$$

and the critical exponent  $\nu$  is readily given by Eq. (19).

## V. THE HULTHEN POTENTIAL

To illustrate the application of the FSS method in quantum mechanics, let us give an example of the criticality of the Hulthen potential. The Hulthen potential behaves like a Coulomb potential for small distances whereas for large distances it decreases exponentially so that the ‘‘capacity’’ for bound states is smaller than that of Coulomb potential. Thus, they have the same singularity but shifted energy levels. They always lie lower in the Coulomb case than in the Hulthen case, where there remains only space for a finite number of bound states[55]. Here, we present the FSS calculations using two methods: finite elements and basis set expansion; each used to obtaining quantum critical parameters for the Hulthen Hamiltonian. First, we give the analytical solution, then FSS with basis set expansion and finite element solution.

### A. Analytical Solution

The Hulthen potential has the following form[54, 55]:

$$V(r) = -\frac{\lambda}{a^2} \frac{e^{-r/a}}{1 - e^{-r/a}} \quad (22)$$

where  $\lambda$  is the coupling constant, and  $a$  is the scaling parameter. For small values of  $r/a$  the potential  $V(r) \rightarrow -\frac{1}{a}\lambda/r$ , whereas for large values of  $r/a$  the potential approaches zero exponentially fast, therefore the *scale*  $a$  in the potential regulates the infinite number of levels that would otherwise appear with a large-distance *Coulomb* behavior.

Shrödinger radial differential equation in the dimensionless variable  $r = r/a$  becomes:

$$\frac{1}{2} \frac{d^2 \chi}{dr^2} + (-\alpha^2 + \lambda \frac{e^{-r}}{1 - e^{-r}}) \chi = 0. \quad (23)$$

We only consider the case for  $l = 0$  for the Hulthen potential. Here we used the abbreviations  $\alpha^2 = -Ea^2 \geq 0$  (in atomic units  $m = \hbar = 1$ ). The complete solutions for the wavefunctions are written in term of hypergeometric functions as follows[55]:

$$\chi = N_0 e^{-\alpha r} (1 - e^{-r}) {}_2F_1(2\alpha + 1 + n, 1 - n, 2\alpha + 1; e^{-r}), \quad (24)$$

where the normalization factor is given by  $N_0 = [\alpha(\alpha + n)(2\alpha + n)]^{\frac{1}{2}} [\Gamma(2\alpha + n)/\Gamma(2\alpha + 1)\Gamma(n)]$ . It follows that the energy levels are given by:

$$E_n = -\frac{1}{a^2} \frac{(2\lambda - n^2)^2}{8n^2}; \quad n = 1, 2, 3, \dots, n_{max}. \quad (25)$$

We can make the following comments concerning the energy levels obtained for the Hulthen potential. There exists a *critical* value for the coupling  $\lambda_c$  to have the given energy levels,  $\lambda_c = n^2/2$ . It follows directly from the first observation that the number of levels  $n_{max}$  allowed is *finite* and it depends on the size of the coupling constant  $n_{max}^2 \leq 2\lambda$ . As  $\lambda \rightarrow \infty$  the potential is well behaved, which can be seen as follows: In this limit we get the obvious inequality  $\alpha^2 \ll 2\lambda \Rightarrow \sqrt{2\lambda} \approx n$ . It follow that we can set  $\alpha \approx 0$  in Eq. (24) to obtain:

$$\chi_{\alpha \rightarrow 0} = (1 - e^{-r}) {}_2F_1(1 + n, 1 - n, 1; e^{-r}), \quad (26)$$

which is the wave function at threshold. This wave function is not normalizable as expected when the energy exponent  $\alpha = 2$ ,  $E \sim (\lambda - \lambda_c)^\alpha$ . For the ground state, the asymptotic limit of the probability density for  $r \gg 1$  and  $\lambda \rightarrow \lambda_c$  becomes:

$$P(r) \sim e^{-r/\xi}, \quad \xi \sim |\lambda - \lambda_c|^{-\nu}, \quad (27)$$

with a characteristic length  $\xi$  and exponent  $\nu = 1$ . The Hulthen potential has a finite capacity determined by the critical coupling,  $\lambda_c$ . The potential admits bound states between the range of values for the coupling:  $\lambda = [1/2, \infty)$ .

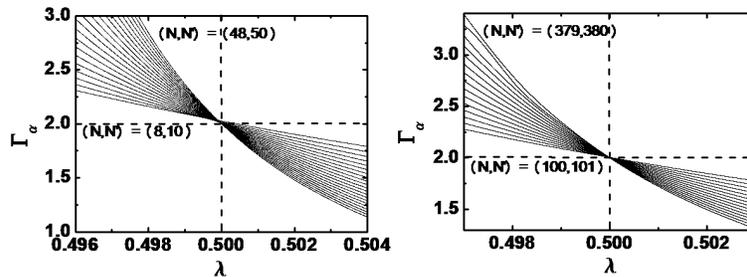


FIG. 1. Plot of  $\Gamma_\alpha$ , obtained by FSS method, as a function of  $\lambda$ . Using the number of basis  $N$  from 8 to 48 in steps of 2. For FEM the number elements used were from 100 to 380 in steps of 20.

### B. Basis Set Expansion

For the Hulthen potential, the wavefunction can be expanded in the following Slater basis ( see Chapter 7 for details [56]):

$$\Phi_n(r) = \sqrt{\frac{1/4\pi}{(n+1)(n+2)}} e^{-r/2} L_n^{(2)}(r). \quad (28)$$

$L_n^{(2)}(r)$  is the Laguerre polynomial of degree  $n$  and order 2. The kinetic term can be obtained analytically. However, the potential term need to be calculated numerically[57].

Figure 1, show the results for the plot  $\Gamma_\alpha(\lambda, N, N')$  as a function of  $\lambda$  with different  $N$  and  $N'$ , all the curves will cross exactly at the critical point.

### C. Finite Element Method

The FEM is a numerical technique which gives approximate solutions to differential equations. In the case of quantum mechanics, the differential equation is formulated as a boundary value problem[61, 62]. For our purposes, we are interested in solving the time-independent Schrödinger equation with finite elements. We will require our boundary conditions to be restricted to the Dirichlet type. For this problem, we will use two interpolation methods: linear interpolation and Hermite Interpolation polynomials to solve for this potential.

We start by integration by parts and impose the boundary conditions for the kinetic energy and reduce it to the weak form[34]:

$$\frac{1}{2} \int_0^\infty r^2 \psi^{*'}(r) \psi'(r) dr. \quad (29)$$

For the potential energy:

$$\int_0^\infty r^2 \psi^*(r) \psi(r) \lambda \frac{-e^{-r}}{1 - e^{-r}} dr. \quad (30)$$

We calculated the local matrix elements of the potential energy by using a four point Gaussian Quadrature to evaluate the integral. We set the cutoff for the integration to  $r_c$ . To include the integration to infinity, we added an infinite element approximation. To do so, we approximate the solution of the wave function in the region of  $[r_c, \infty)$  to be an exponentially decaying function with the form  $\psi(r) = \psi(r_c) e^{-r}$ .

The local matrices are then assembled to form the complete solution and by invoking the variational principle on

the nodal values  $\psi_i$  we obtain a generalized eigenvalue problem representing the initial Schrödinger equation:

$$H_{ij}|\psi_j\rangle = \epsilon U_{ij}|\psi_j\rangle. \quad (31)$$

Solution of Eq. (31) is achieved using standard numerical methods (see Chapter 10 for details [63]).

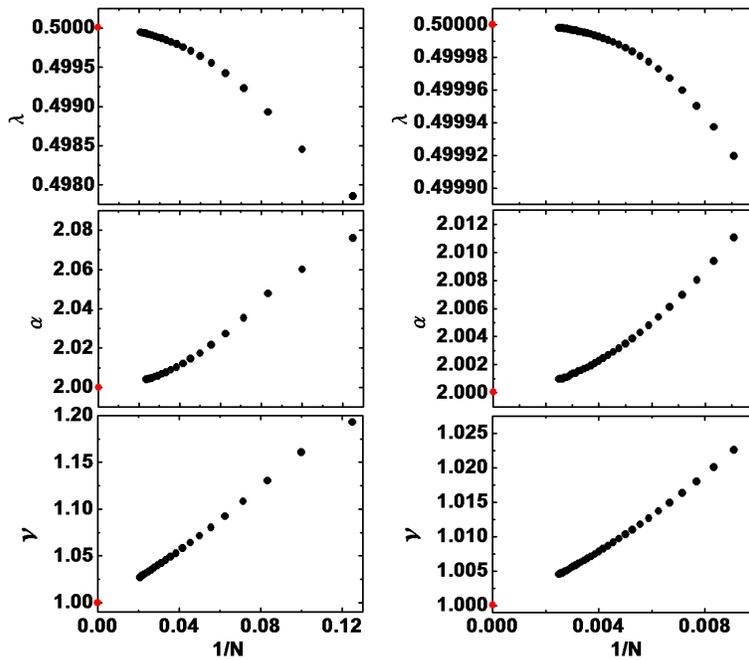


FIG. 2. Extrapolated values for the critical exponents and the critical parameter  $\lambda$ . The solid red dots at  $1/N = 0$  are the extrapolated critical values. The left side is the basis set method while the right is the FEM with Hermite interpolation polynomials.

#### D. Finite Size Scaling Results

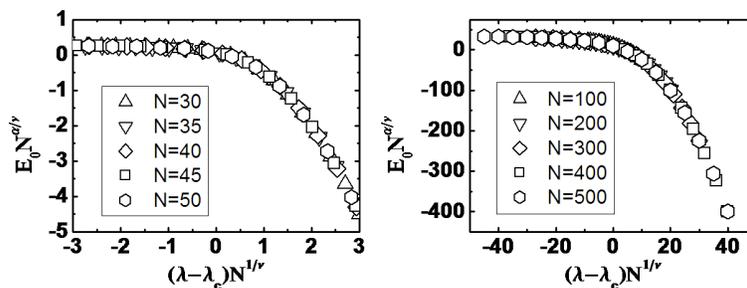


FIG. 3. Data collapse study of the basis set method and FEM. The left is the basis set method and the right being the FEM.

The finite size scaling equations are valid only as asymptotic expressions, but unique values of  $\lambda_c$ ,  $\alpha$ , and  $\nu$  can be obtained as a succession of values as a function of  $N$ . The lengths of the elements are set  $h = 0.5$ . The plots of  $\Gamma_\alpha$ , figure 1, the basis set expansion is giving values very close to the analytical solution of the Hulthen potential. For the plot of  $\Gamma_\alpha$  for the FEM estimation of  $\lambda_c$  is producing results very close to the exact values using Hermite interpolation.

The intersection of these curves indicate the  $\lambda_c$  on the abscissa. The ordinate gives the critical exponents  $\alpha$  (in  $\Gamma_\alpha$  plots). In Figure 2, we observed the behavior of the pseudocritical parameters,  $\lambda_c^{(N)}$ ,  $\alpha_c^{(N)}$ ,  $\nu_c^{(N)}$ , as a function of  $1/N$ . The three curves monotonically converge to limiting values for the Hermite interpolation and the basis set expansion.

To check the validity of our finite size scaling assumptions, we performed a data collapse[64] calculation of the Hulthen potential. In the data collapse analysis, we examine the main assumption we have made in Eq. (17) for the existence of a scaling function for each truncated magnitude  $\langle \mathcal{O} \rangle_\lambda^{(N)}$  with a unique scaling exponent  $\nu$ .

Since the  $\langle \mathcal{O} \rangle_\lambda^{(N)}$  is analytical in  $\lambda$ , then from Eq. (17) the asymptotic behavior of the scaling function must have the form:

$$F_{\mathcal{O}}(x) \sim x^{-\mu_{\mathcal{O}}/\nu}. \quad (32)$$

For large values of  $N$ , at the  $\lambda_c$ , we have

$$\langle \mathcal{O} \rangle_\lambda^{(N)}(\lambda_c) \sim N^{-\mu_{\mathcal{O}}/\nu}. \quad (33)$$

Because the same argument of regularity holds for the derivatives of the truncated expectation values, we have:

$$\left. \frac{\partial^m \langle \mathcal{O} \rangle_\lambda^{(N)}}{\partial \lambda^m} \right|_{\lambda=\lambda_c} \sim N^{-(\mu_{\mathcal{O}}-m)/\nu}, \quad (34)$$

$\langle \mathcal{O} \rangle_\lambda^{(N)}$  is analytical in  $\lambda$ , then using Eq. (34), the Taylor expansion could be written as:

$$\langle \mathcal{O} \rangle_\lambda^{(N)}(\lambda) \sim N^{-\mu_{\mathcal{O}}/\nu} G_{\mathcal{O}}(N^{1/\nu}(\lambda - \lambda_c)), \quad (35)$$

where  $G_{\mathcal{O}}$  is an analytical function of its argument. This equivalent expression for the scaling of a given expectation value has a correct form to study the data collapse in order to test FSS hypothesis. If the scaling Eq. (17) or Eq. (35) holds, then near the critical point the physical quantities will collapse to a single universal curve when plotted in the appropriate form  $\langle \mathcal{O} \rangle_\lambda^{(N)} N^{\mu_{\mathcal{O}}/\nu}$  against  $N^{1/\nu}(\lambda - \lambda_c)$ . If the operator  $\mathcal{O}$  is the Hamiltonian then we will have a data collapse when plotting  $E_0 N^{-\alpha/\nu}$  against  $N^{1/\nu}(\lambda - \lambda_c)$ . In Figure 3 we plot the results corresponding to the basis set method (right panel) and Hermite interpolation (left panel), which have been calculated with  $\lambda_c = 0.49999$ ,  $\alpha = 1.9960$  and  $\nu = 0.99910$  for the basis set method and for the Hermite interpolation we have  $\lambda_c = 0.50000$ ,  $\alpha = 2.00011$  and  $\nu = 1.000322$ . The data collapse study do in fact support our FSS assumptions. We have conveniently summarized our results for the critical parameters for the analytical, linear interpolation, Hermite interpolation and the basis set expansion in table I.

TABLE I. Critical Parameters for the Hulthen Potential

	Analytical	Linear	Hermite	Basis Set
$\lambda$	0.5 (exact)	0.50184	0.50000	0.49999
$\alpha$	2 (exact)	1.99993	2.00011	1.9960
$\nu$	1 (exact)	1.00079	1.00032	0.99910

We have successfully obtained the critical exponents and the critical parameter for the Hulthen potential using FSS with the basis set method and the FEM. The results are in excellent agreement with the analytical solution even for the very simplistic linear interpolation used for the FEM calculations. However, the ability of the FEM to describe the wavefunction locally in terms of elements affords a very natural way to extend its use for FSS purposes.

## VI. FINITE SIZE SCALING AND CRITICALITY OF M-ELECTRON ATOMS

Let us examine the criticality of the N-electrons atomic Hamiltonian as a function of the nuclear charge  $Z$ . The scaled Hamiltonian takes the form:

$$\mathcal{H}(\lambda) = \sum_{i=1}^M \left[ -\frac{1}{2} \nabla_i^2 - \frac{1}{r_i} \right] + \lambda \sum_{i<j=1}^M \frac{1}{r_{ij}}, \quad (36)$$

where  $r_{ij}$  are the interelectron distances, and  $\lambda = 1/Z$  is the inverse of the nuclear charge. For this Hamiltonian, a critical point means the value of the parameter,  $\lambda_c$ , for which a bound state energy becomes absorbed or degenerate with the continuum.

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. For  $M = 2$ , one can choose the following basis set functions:

$$\Phi_{ijk,\ell}(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \left( r_1^i r_2^j e^{-(\gamma r_1 + \delta r_2)} + r_1^j r_2^i e^{-(\delta r_1 + \gamma r_2)} \right) r_{12}^k F_\ell(\theta_{12}, \mathbf{\Omega}) \quad (37)$$

where  $\gamma$  and  $\delta$  are fixed parameters, we have found numerically that  $\gamma = 2$  and  $\delta = 0.15$  is a good choice for the ground state[21],  $r_{12}$  is the interelectronic distance and  $F_\ell(\theta_{12}, \mathbf{\Omega})$  is a suitable function of the angle between the positions of the two electrons  $\theta_{12}$  and the Euler angles  $\mathbf{\Omega} = (\Theta, \Phi, \Psi)$ . This function  $F_\ell$  is different for each orbital-block of the Hamiltonian. For the ground state  $F_0(\theta_{12}, \mathbf{\Omega}) = 1$  and  $F_1(\theta_{12}, \mathbf{\Omega}) = \sin(\theta_{12}) \cos(\Theta)$  for the  $2p^2 \ ^3P$  state. These basis sets are complete for each  $\ell$ -subspace. The complete wave function is then a linear combination of these terms multiplied by variational coefficients determined by matrix diagonalization [21]. In the truncated basis set at order  $N$ , all terms are included such that  $N \geq i + j + k$ . Using FSS calculations with  $N = 6, 7, 8, \dots, 13$  gives the extrapolated values of  $\lambda_c = 1.0976 \pm 0.0004$  which is in excellent agreement with the best estimate of  $\lambda_c = 1.09766079$  using large-order perturbation calculations[65]. Since the critical charge  $Z_c = 1/\lambda_c \sim 0.91$  indicates that the hydrogen anion  $H^-$  is stable,  $Z = 1 > Z_c$ .

For three-electron atoms,  $M = 3$ , one can repeat the FSS procedure with the following Hylleraas-type basis set[22]:

$$\Psi_{ijklmn}(\vec{x}_1, \vec{x}_2, \vec{x}_3) = \mathcal{C} \mathcal{A} \left( r_1^i r_2^j r_3^k r_{12}^l r_{23}^m r_{31}^n e^{-\alpha(r_1+r_2)} e^{-\beta r_3} \chi_1 \right), \quad (38)$$

where the variational parameters,  $\alpha = 0.9$  and  $\beta = 0.1$ , were chosen to obtain accurate results near the critical charge  $Z \simeq 2$ ,  $\chi_1$  is the spin function with spin angular momentum 1/2:

$$\chi_1 = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3), \quad (39)$$

$\mathcal{C}$  is a normalization constant and  $\mathcal{A}$  is the usual three-particle antisymmetrizer operator[22]. The FSS calculations gives  $\lambda_c = 0.48 \pm 0.03$ . Since  $Z_c \sim 2.08$  the anions  $He^-$  and  $H^{--}$  are unstable.

One can extend this analysis and calculate the critical charges for M-electron atoms in order to perform a systematic check of the stability of atomic dianions. In order to have a stable doubly negatively charged atomic ion one should require the surcharge,  $S_e(N) \equiv N - Z_c(N) \geq 2$ . We have found that the surcharge never exceeds two. The maximal surcharge,  $S_e(86) = 1.48$ , is found for the closed-shell configuration of element Rn and can be related to the peak of electron affinity of the element  $N = 85$ . The FSS numerical results for M-electron atoms show that at most, only one electron can be added to a free atom in the gas phase. The second extra electron is not bound by singly charged negative ion because the combined action of the repulsive potential surrounding the isolated negative ion and the Pauli exclusion principle. However, doubly charged atomic negative ions might exist in a strong magnetic field of the order few atomic units, where  $1a.u. = 2.3505 \cdot 10^9 G$  and superintese laser fields.

## VII. CONCLUSIONS

In this chapter, we show how the finite size scaling ansatz can be combined with the variational method to extract information about critical behavior of quantum Hamiltonians. This approach is based on taking the number of elements in a complete basis set or the finite element method as the size of the system. As in statistical mechanics, finite size scaling can then be used directly to the Schrödinger equation. This approach is general and gives very

accurate results for the critical parameters, for which the bound state energy becomes absorbed or degenerate with a continuum. To illustrate the applications in quantum calculations, we present detailed calculations for the simple case of Hulthen potential and few electron atoms. For atomic systems we have shown that finite size scaling can be used to explain and predict the stability of atomic anions: At most, only one electron can be added to a free atom in the gas phase.

Recently, there has been an ongoing experimental and theoretical search for doubly charged negative molecular dianions[1]. In contrast to atoms, large molecular systems can hold many extra electrons because the extra electrons can stay well separated. However, such systems are challenging from both theoretical and experimental points of view. The present finite size scaling approach might be useful in predicting the general stability of molecular dianions.

The approach can be generalized to complex systems by calculating the matrix elements needed for FSS analysis by ab initio, density functional methods, orbital free density functional (OF-DFT) [66, 67] approach, density matrices[68, 69] and other electronic structure methods[70]. The implementation should be straightforward. We need to obtain the matrix elements to calculate  $\Gamma_a$  as a function of the number of elements used in solving for the system. In the finite element using mean field equations (like Hartree-Fock or Kohn Sham methods) the solution region will be discretized into elements composed of tetrahedrons.

The field of quantum critical phenomena in atomic and molecular physics is still in its infancy and there are many open questions about the interpretations of the results including whether or not these quantum phase transitions really do exist. The possibility of exploring these phenomena experimentally in the field of quantum dots[71] and systems in superintense laser fields[72] offers an exciting challenge for future research. This finite size scaling approach is general and might provide a powerful way in determining critical parameters for the stability of atomic and molecular systems in external fields, and for design and control electronic properties of materials using artificial atoms.

The critical exponents calculated with finite size scaling indicate the nature of the transitions from bound to continuum states. Study of the analytical behavior of the energy near the critical point show that the open shell system, such as the lithium like atoms, is completely different from that of a closed shell system, such as the helium like atoms. The transition in the closed shell systems from a bound state to a continuum resemble a “first-order phase transition”,  $E \sim (\lambda - \lambda_c)^1$ , while for the open shell system, the transition of the valence electron to the continuum is a “continuous phase transition”,  $E \sim (\lambda - \lambda_c)^2$ . For closed shell systems, one can show that  $\mathcal{H}(\lambda_c)$  has a square-integrable eigenfunction corresponding to a threshold energy, the existence of a bound state at the critical coupling constant  $\lambda_c$  implies that for  $\lambda < \lambda_c$ ,  $E(\lambda)$  approaches  $E(\lambda_c)$  linearly in  $(\lambda - \lambda_c)$  as  $\lambda \rightarrow \lambda_c^-$ . However, for open shell systems, the wave function is not square-integrable at  $\lambda_c$ . This difference in critical exponents might be helpful in developing a new atomic classification schemes based on the type of phase transitions and criticality of the system.

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