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Finite-size scaling method for the stability of atomic and molecular ions

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Abstract

Phase transitions at absolute zero temperature can take place as some parameter in the Hamiltonian of the system is varied. For the Hamiltonian of N-electron atoms, this parameter is taken to be the nuclear charge. As the nuclear charge reaches a critical point, the quantum ground state changes its characters from being bound to being degenerate or absorbed by a continuum. We describe the large-dimension approximation and the finite-size scaling method to calculate the critical nuclear charge for which an atom can bind an extra electron to form a stable negative ion. Results show that, at most, only one electron can be added to a free atom in the gas phase. The existence of doubly charged atomic negative ions in a strong magnetic field will be discussed.

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1. Introduction

The isomorphism between quantum theory and classical statistical mechanics makes many statistical mechanical techniques very important to various different areas of the physical sciences. Constructing analogies between different systems is a method of great value to solve new problems in theoretical physics. In particular, we will have the solution of one model problem if we knew the mapping to another model with a known solution.

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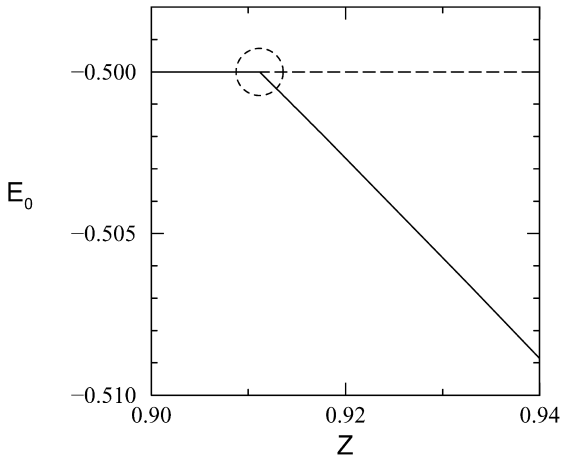

Fig. 1. The ground state energy (in atomic units) vs. nuclear charge for the two-electron atoms. The dashed line correspond to the hydrogen atom ground state energy. The non-analytical point is shown by a circle.

Along these lines, one interesting problem in atomic and molecular physics is to calculate singularities in the ground state energy of a few-body quantum system as a function of the parameters of the Hamiltonian. For example Fig. 1 illustrates the behavior of the ground state energy for a two-electron atom as a function of the nuclear charge. The critical nuclear charge, which is denoted by a circle, is the minimum charge necessary to bind two electrons. A directly related problem in statistical mechanics, is the study of phase transitions and critical phenomena which is characterized by singularities in the free energy. This is an important field in statistical mechanics and many powerful techniques have been developed to calculate and classify singularities in the different thermodynamics quantities.

This paper is organized as follows: in the next section we show that using a particular semiclassical limit, the large dimension limit for a quantum few-body system is equivalent to a mean-field calculation of a classical model. This analogy allows us to describe stability and symmetry breaking of electronic structure configurations as phase transitions and critical phenomena. In Section 3, we use the finite size scaling method to calculate critical parameters for three-dimensional problems, and in Section 4 we discuss the existence of free doubly charged atomic ions in the gas phase. Finally, we give the conclusions in Section 5.

2. The large dimension limit

In many physical theories, the *large-N limit* gives a simplification in the analysis of a wide range of problems and quite often an exact solution can be obtained. Then, the inverse of the parameter N can be used to obtain an asymptotic expansion for finite values of N.

One of the first examples is the spherical model, the exact solution was given by Berlin and Kac in 1952 [1]. Here the parameter N is the number of components of a spin in the N-vector model of magnetism [2]. This spherical model remains as a unique model with exact solution at $D = 3$ with a critical point with non-classical exponents: $\alpha = -1;\ \beta = \frac{1}{2};\ \gamma = 2;\ \delta = 5$.

In quantum mechanics, we use the spatial dimension D as a free parameter. As Yaffe showed in the early 1980s [3], the large-D limit is a classical limit in the sense that it is a limit in which all quantum interference effects disappear. One can then show that the limit $D \to \infty$ is a classical approximation to the ground state energy. This limit is completely different from the "conventional" $\hbar \to 0$ classical limit, which is good for large quantum numbers.

The large-D limit was first applied to electronic structure problems by Herschbach and co-workers [4]. They showed that the symmetry breaking solutions can occur in the ground state electronic configuration when parameters of the Hamiltonian are varied.

When $D \to \infty$ the radial part of the kinetic energy operator vanishes, the wave function becomes a δ-function and the $D = \infty$ Hamiltonian takes the following simple form:

$$\mathscr{H}_\infty = \text{"centrifugal term"} + V(\{\lambda_i\}, \{x_j\})\,. \tag{1}$$

Then the ground state energy is given as the global minimum of the Hamiltonian (1):

$$\mathscr{E}_\infty(\{\lambda_i\}) = \min_{\{x_j\}} \mathscr{H}_\infty(\{\lambda_i\}, \{x_j\})\,. \tag{2}$$

An example that shows a symmetry breaking solution is the two Coulomb center molecule. If the nuclei are located at $x = \pm R/2$ the Hamiltonian at $D = \infty$ takes the form

$$\mathscr{H}_\infty = \frac{1}{2\rho^2} - \frac{1-\Delta}{r_-} - \frac{1+\Delta}{r_+}\,, \tag{3}$$

where ρ is the distance of the electron from the symmetry axis, and Δ is the scaled difference of charge between nuclei [5]. For $\Delta = 0$ a symmetric solution with $x = 0;\ r_- = r_+$ exists. This solution is stable for $R \leqslant R_c = \frac{3\sqrt{3}}{4}$.

The numerical study of the $\Delta = 0$ solutions leads to [5]:

(i) There are no stable solutions with $x \neq 0$ for $R < R_c$.

(ii) There are only two equivalent stable solutions with $x \neq 0$ for $R > R_c$.

With the definitions [5],

$$\psi \equiv -\frac{\partial \mathscr{E}_\infty(R, \Delta)}{\partial \Delta}, \qquad \varepsilon \equiv \frac{1/R - 1/R_c}{1/R_c}\,. \tag{4}$$

We can define "critical exponents" as

$$\psi(\varepsilon, \Delta = 0) \sim (-\varepsilon)^\beta, \quad \varepsilon \to 0^-\,,$$

$$\mathscr{E}_\infty(\varepsilon, \Delta = 0) \sim |\varepsilon|^{2-\alpha}, \quad \varepsilon \to 0\,,$$

$$\Delta(\varepsilon = 0, \psi) \sim \psi^{\delta} sg(\psi), \quad \psi \to 0 ,$$

$$\left.\frac{\partial \psi}{\partial \Delta}\right|_{\Delta=0} \sim |\varepsilon|^{-\gamma}, \quad \varepsilon \to 0 . \tag{5}$$

We obtain the critical exponents for the H_2^+ molecule, which are the same as the mean-field critical exponents

$$\beta = \frac{1}{2}, \qquad \alpha = 0_{\mathrm{dis}}, \qquad \delta = 3, \qquad \gamma = 1 . \tag{6}$$

More complicated systems with two or more free parameters can give rich "phase diagrams" [6,7].

3. "Real world": finite size scaling

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*, in this limit the volume (V) and particle number (N) go to infinity, with a constant density ($\rho = N/V$). This fact could be understood by analyzing the partition function. For a finite system, the partition function is a finite sum of analytical terms, and therefore it is itself an analytical function. It is necessary to take an infinite number of terms in order to obtain a singularity. The question of why a finite system can apparently describe phase transitions and the relation of this phenomena with true phase transitions in infinite systems is the main subject of FSS theory. However, FSS is not only a formal way to understand the asymptotic behavior of a system when the size goes to infinity. In fact, the theory gives us numerical methods capable of obtaining accurate results for infinite systems only by studying very small systems.

There are excellent review articles about FSS in statistical mechanics in the literature [8–10] and here we will develop similar techniques useful for few-body quantum problems.

Let us consider a Hamiltonian of the general form

$$\mathscr{H} = \mathscr{H}_0 + V_\lambda , \tag{7}$$

where $\mathscr{H}_0$ is λ-independent. We will assume that the Hamiltonian has a bound state E_λ for $\lambda > \lambda_c$ which becomes equal to zero (the bottom of the continuum) at $\lambda = \lambda_c$. One of the most widely used methods to obtain approximated solutions is the linear variational method [11]. This method uses a complete λ-independent basis set $\{\Phi_n\}$, where n is an appropriate set of quantum numbers. The expansion is truncated at order N and then the Hamiltonian is replaced by $M(N) \times M(N)$ matrix $\mathscr{H}^{(N)}$, where $M(N)$ is the number of elements in the truncated basis set.

The Nth-order approximations for the ground state energy and the wave function are given by

$$E_\lambda^{(N)} = \min_{\{i\}} \{\Lambda_i^{(N)}\} , \tag{8}$$

$$\Psi_{\lambda}^{(N)} = \sum_{n}^{M(N)} a_n^{(N)}(\lambda)\Phi_n \tag{9}$$

and the expectation value of an operator $\mathcal{O}$ at order N is given by

$$\langle \mathcal{O} \rangle_{\lambda}^{(N)} = \sum_{n,m}^{N} a_n^{(N)}(\lambda)^* a_m^{(N)}(\lambda)\mathcal{O}_{n,m} \,. \tag{10}$$

In general, an expectation value $\langle \mathcal{O} \rangle$ will be non-analytical at $\lambda = \lambda_c$. But because the basis-set is λ-independent and N is finite, as in statistical mechanics, it is easy to prove that any expectation value truncated at order N is analytical at $\lambda = \lambda_c$ [12].

As $\langle \mathcal{O} \rangle$ is non-analytical at $\lambda = \lambda_c$, we can define an associated critical exponent, $\mu_{\mathcal{O}}$:

$$\langle \mathcal{O} \rangle_{\lambda} \underset{\lambda \to \lambda_c^+}{\sim} (\lambda - \lambda_c)^{\mu_{\mathcal{O}}} \,. \tag{11}$$

As in the FSS ansatz in statistical mechanics, we will assume that there exists a scaling function for the truncated magnitudes

$$\langle \mathcal{O} \rangle_{\lambda}^{(N)} \sim \langle \mathcal{O} \rangle_{\lambda} F_{\mathcal{O}}(N|\lambda - \lambda_c|^{\nu}) \tag{12}$$

with a different scaling function $F_{\mathcal{O}}$ for each different operator but with a *unique* scaling exponent ν. Because $\langle \mathcal{O} \rangle_{\lambda}^{(N)}$ is analytical in $\lambda = \lambda_c$

$$F_{\mathcal{O}}(x) \sim x^{-\mu_{\mathcal{O}}/\nu} \,. \tag{13}$$

Now we define the following function:

$$\Delta_{\mathcal{O}}(\lambda; N, N') = \frac{\ln(\langle \mathcal{O} \rangle_{\lambda}^{(N)} / \langle \mathcal{O} \rangle_{\lambda}^{(N')})}{\ln(N'/N)} \,. \tag{14}$$

At the critical point, $\langle \mathcal{O} \rangle \sim N^{-\mu_{\mathcal{O}}/\nu}$; thus one obtains an equation for the ratio of the critical exponents

$$\Delta_{\mathcal{O}}(\lambda_c; N, N') = \frac{\mu_{\mathcal{O}}}{\nu} \tag{15}$$

independent of the values of N and N'. For three different values N, N' and N'' the curves intersect at the critical point

$$\Delta_{\mathcal{O}}(\lambda_c; N, N') = \Delta_{\mathcal{O}}(\lambda_c; N'', N) \,. \tag{16}$$

The energy-critical exponent α is obtained putting $\mathcal{O} = \mathscr{H}$ and, $\mu_{\mathcal{O}} = \alpha$,

$$\frac{\alpha}{\nu} = \Delta_{\mathscr{H}}(\lambda_c; N, N') \,. \tag{17}$$

A second equation for ν and α is obtained from the Hellmann–Feynman theorem

$$\frac{\partial E_{\lambda}}{\partial \lambda} = \left\langle \frac{\partial \mathscr{H}}{\partial \lambda} \right\rangle_{\lambda} = \left\langle \frac{\partial V_{\lambda}}{\partial \lambda} \right\rangle_{\lambda} \,. \tag{18}$$

Then, replacing $\mathcal{O}$ by $\partial V_{\lambda}/\partial\lambda$ in Eq. (14) together with Eq. (17) we can define the function

$$\Gamma_{\alpha}(\lambda; N, N') = \frac{\Delta_{\mathscr{H}}(\lambda; N, N')}{\Delta_{\mathscr{H}}(\lambda; N, N') - \Delta_{\partial \mathscr{V}_{\lambda}/\partial\lambda}(\lambda; N, N')} \,. \tag{19}$$

The value of the function Γ_α at the critical point $\lambda = \lambda_c$ does not depend on the values of N and N' [13]:

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

Of course, the ansatz to get an estimation of λ_c at order N is not unique, another useful technique developed in statistical mechanics by Nightingale [14] is the phenomenological renormalization. In analogy with classical statistical mechanics, the equivalent equation for the critical parameters in quantum few-body problems is [15,16]

$$\left(\frac{E_1^{(N)}(\lambda^{N,N'})}{E_0^{(N)}(\lambda^{N,N'})}\right)^N = \left(\frac{E_1^{(N')}(\lambda^{N,N'})}{E_0^{(N')}(\lambda^{N,N'})}\right)^{N'} \,, \tag{21}$$

where $E_0^{(N)}$ and $E_1^{(N)}$ are the ground state and first excited energies for a given value of N.

To illustrate the applications of the FSS Eq. (20) in quantum mechanics, let us study the exactly solvable one-particle potential, the Pösch–Teller potential

$$V_\lambda(r) = -\frac{\lambda}{\cosh^2(r)} \,. \tag{22}$$

The three-dimensional (3-d) states are given by the odd states of the 1-d Pösch–Teller potential. In particular, the 3-d ground state corresponds to the first excited 1-d level. Using the transformation $y = \tanh(x)$; $-1 \leqslant y \leqslant 1$; the Schrödinger equation for bound states takes the form

$$\left[-(1-y^2)\frac{\mathrm{d}}{\mathrm{d}y}(1-y^2)\frac{\mathrm{d}}{\mathrm{d}y} - \lambda(1-y^2)\right] \Psi_n = -E_n \Psi_n \tag{23}$$

with $E > 0$. The eigenfunctions have a defined parity, and we are interested in the lowest odd eigenfunction. In order to apply FSS we used the following complete (odd) basis set in the $[-1, 1]$ interval:

$$\phi_k(y) = \sqrt{1-y^2}\sin k\pi y \,, \tag{24}$$

where k is a positive integer. The matrix elements are calculated analytically using Mathematica, and the eigenvalues are calculated numerically.

The exact critical value of λ is $\lambda_c = 2$ and the exact critical exponent is $\alpha = 2$ [17]. As we show in Fig. 2, the value λ^* obtained as approximation to λ_c with one-hundred functions using the usual approximation $E_0(\lambda^*) = 0$ is $\lambda^* = 3.345$. The value obtained for λ_c *with the same computational effort* using FSS Eq. (20) with $N = 100, N' = 98$ is $\lambda_{\mathrm{fss}} = 2.137$. In Fig. 3 we show the function Γ_α vs. λ for several values of N. Note that the curves cross at $\Gamma_\alpha \simeq 2$.

4. Many-electron atoms

Since the size of the variational basis set grows exponentially with the increase of the number of electrons, we choose to follow a simpler path. Recently with

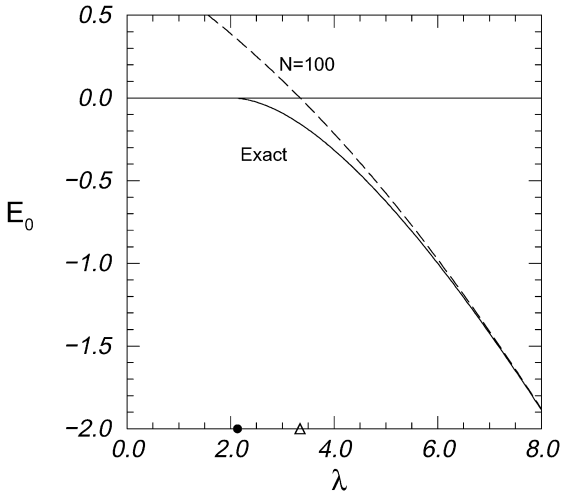

Fig. 2. The ground state energy vs. λ for the Pösch–Teller potential. The solid line corresponds to the exact solution, and the dashed line corresponds to a $N = 100$ basis functions expansion. The exact value $\lambda_c = 2$ is also compared with $\lambda_{\mathrm{fss}} = 2.137$ (●) and with $\lambda^* = 3.345$ defined by $E_0^{(100)}(\lambda^*) = 0$ (△).

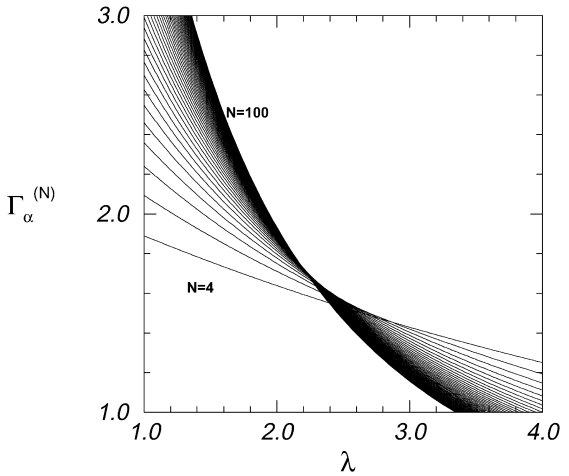

Fig. 3. $\Gamma_\alpha(\lambda, N-2, N)$ as a function of λ for the Pösch–Teller potential for even values of $N = 4, 6, \ldots, 98, 100$.

Sergeev [18], we used the reliable data for the ionization energy of a negative ion and a neutral atom, which were calculated or experimentally measured to develop a simple one-particle potential in order to model the movement of a loosely bound valence electron that is going to dissociate when the charge approaches its critical value. This model is realistic in the vicinity of the critical charge and effectively reproduces the non-trivial singularity of the ionization energy at the critical charge.

For a given atom with N electrons and a nuclear charge Z, we considered a spherically symmetric potential of the form

$$V(r) = -\frac{1}{r} + \frac{\gamma}{r}(1 - e^{-\delta r}) \tag{25}$$

with $\gamma = (N-1)/Z$. This model potential is asymptotically correct both at small and at large distances from the nucleus where the scaled atomic core potential tends to $-1/r$ and to $-(Z-N+1)/(Zr)$, respectively. In this way, we map an arbitrary atom, which is characterized by a pair of numbers (N,Z) to the model one-particle system which is characterized by a pair of parameters (γ,δ). Results of fitting the parameter δ for elements with $N \leqslant 86$ is given in our previous study [18].

For the N-electron atom, using theoretical and experimental results, Morgan and co-workers [19] concluded that the critical charge obeys the following inequality

$$N - 2 \leqslant Z_c \leqslant N - 1\,. \tag{26}$$

The numerical results, using the above simple one-dimensional potential, confirm this inequality and show that at most, only one electron can be added to a free atom in the gas phase. However, doubly charged atomic negative ions might exist in a strong magnetic field. We have found that dianions with closed shell configurations such as O^{-2}, S^{-2}, Se^{-2}, Te^{-2}, and Po^{-2} became stable at about 1–2 a.u. (1 a.u. $= 2.35\ 10^9$ G) [18].

5. Conclusions and perspectives

In this paper, we have shown that one can use ideas and methods from statistical mechanics to solve problems in the field of atomic and molecular physics. In particular, we established an analogy between mean-field theory of phase transitions and symmetry breaking of electronic structure configurations at the large-D limit. We interpreted the ionization and dissociation as phase transitions phenomena. Moreover, we have shown that the finite-size scaling method can be used to obtain critical parameters for quantum Hamiltonians. This approach was successfully used to obtain the critical charges for two and three-electron atoms, and simple molecular systems. The knowledge of critical charges can be used to understand and predict the stability of atomic and molecular negative ions.

Many electron atoms and molecular systems are challenging from a critical phenomena point of view. Research is still underway to develop a good basis set which can be combined with the finite-size scaling method for large-scale calculations. There are also new calculations underway for atoms and molecules in external fields, resonance states of atomic anions, and scattering properties such as electron impact ionization cross section for atoms. This field is still in its infancy and there are many open questions about the interpretations of the results. In particular: what is the Physical meaning of the "*correlation length*".

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