



## Quantum critical phenomena and stability of atomic and molecular ions

SABRE KAIS<sup>†</sup>

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, USA

and PABLO SERRA

Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba,  
Ciudad Universitaria, 5000 Córdoba, Argentina

In this review we discuss quantum phase transitions and the mapping between symmetry breaking of electronic structure configurations at the large-dimension limit and mean-field theory of phase transitions. We show that the finite size scaling method can be used for the calculations of the critical parameters of the few-body Schrödinger equation. In this approach, the finite size corresponds to the number of elements in a complete basis set used to expand the exact eigenfunction of a given Hamiltonian. The critical parameters such as the critical nuclear charges will be used to explain and predict the stability of atomic and molecular negative ions. For  $N$ -electron atoms with  $2 \leq N \leq 86$ , results 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.

### 1. Introduction

A wide variety of physical systems exhibit phase transitions and critical phenomena such as liquid–gas, ferromagnetic–paramagnetic, fluid–superfluid and conductor–superconductor transitions [1]. Phase transitions can be classified mainly as first-order and second-order phase transitions. First-order phase transitions are generally defined to be those that involve a non-zero latent heat and radical change in the structure of the material at the transition points. Second-order phase transitions are continuous phase changes where the properties of the system do not change discontinuously at the critical point, but at least one of their rates of change does [2]. One striking aspect of critical phenomena is the hypothesis of the universality of the critical exponents [3]. According to this hypothesis, only two quantities determine the critical behaviour of most systems: the dimensionality of space and the dimensionality of the order parameter. All systems that have the same values of these two quantities are said to be members of the same universality class. Systems in the same universality class have the same critical exponents independent of the model systems or the details of the forces.

Recently, we have found that one can describe stability and symmetry breaking of electronic structure configurations as phase transitions and critical phenomena. This analogy was revealed by using the dimensional scaling method and the large-dimension limit model of electronic structure configurations [4]. Large-dimension models were originally developed for specific theories in the fields of nuclear physics,

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<sup>†</sup> Email: kais@power1.chem.purdue.edu.

critical phenomena and particle physics (for reviews, see [5]). Subsequently, with the pioneering work of Herschbach *et al.* [6], they found wide use in the field of atomic and molecular physics [7]. In this method one takes the dimension  $D$  of space, 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  $D = 3$  [6]. For electronic structure of the  $N$ -electron atoms, the pseudoclassical  $D \rightarrow \infty$  limit is simple and gives unique geometrical configurations [8]. This provides a rigorous version of the electron-dot formula, *Lewis structure*, where the electrons assume fixed positions relative to the nuclei and each other. This simple qualitative picture opens the door to establishing a very interesting connection between symmetry breaking of the large- $D$  limit configurations, as the nuclear charge is varied, and the standard mean-field theory of phase transitions and critical phenomena in statistical mechanics. For atoms [4], the mapping between symmetry breaking of electronic structure configurations and mean-field theory of phase transitions was shown by allowing the nuclear charge to play a role analogous to temperature in statistical mechanics.

The large- $D$  picture helps to establish a connection to phase transitions. However, the questions which remain to be addressed are: how to carry out such an analogy to the  $N$ -electron atoms at  $D = 3$  and what are the physical consequences of this analogy? These questions can be answered by studying the analytical behaviour of the energies of atoms as a function of the nuclear charge. For the two-electron atoms, we used the finite-size scaling method to obtain the critical nuclear charge. In this context, critical means the minimum nuclear charge necessary to bind two electrons [9]. In statistical mechanics, the finite-size scaling (FSS) method gives a way to extrapolate information obtained from a finite (or partially infinite) system to the thermodynamic limit. In the present 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. In this method we assumed that the two lowest eigenvalues of the quantum Hamiltonian can be taken as the leading eigenvalues of a transfer matrix of a classical pseudosystem. Using FSS arguments [10, 11], the phenomenological renormalization (PR) equation [12] was used to obtain the critical properties of the classical pseudosystem and therefore of the quantum system. By searching for a fixed point of the PR equation, the critical charge is found  $Z_c \approx 0.911$ , which is in complete agreement with previous calculations [13]. The fact that this critical charge is below  $Z = 1$  explains why  $H^-$  is a stable negative ion. For the three-electron atoms, the critical nuclear charge for the ground state was found to be  $Z_c \approx 2$ , which explains why  $He^-$  is an unstable ion [14].

The analytical behaviour of the energy as a function of parameters for a given system has been the subject of study for many years; in particular, the study of the analytical behaviour of the energy as a function of the nuclear charge  $Z$ . Morgan and co-workers [13] have performed a 401st-order perturbation calculation to resolve the controversy over the radius of convergence of the  $\lambda = 1/Z$  expansion for the ground-state energy of the helium-like ions. Such high-order calculations were necessary to study the asymptotic behaviour of the perturbation series and to determine that the radius  $\lambda^*$  of convergence, is equal to  $\lambda_c$ , the critical value of  $\lambda$  for which the Hamiltonian has a bound state with zero binding energy. Estimating the critical charge  $Z_c$ , is very important in determining whether a negative ion is stable or not.

Almost all elements in the periodic table, except rare gases and a few other atoms, have stable ground-state negative-ion configurations in the gas phase. However, there

is no experimental or theoretical evidence of any doubly charged atomic negative ions in the gas phase. Recently [15], with a simple model potential, we estimated the critical nuclear charge, the minimum charge necessary to bind  $N$  electrons, for  $N$ -electron atoms with  $2 \leq N \leq 86$ . Results 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 ( $10^9$  G or greater) [15].

In the next section we shall review the symmetry breaking at the large-dimension limit for the  $N$ -electron atoms and simple molecular systems. In section 3 the finite-size scaling method will be briefly reviewed in classical statistical mechanics. In section 4, we present a direct FSS approach to study the critical behaviour of the quantum Hamiltonian without the need to use any explicit analogy to classical statistical mechanics. This approach assumes an explicit form for the asymptotic behaviour of the quantum mean values near the critical point. The results of FSS for the calculations of critical parameters for simple model Hamiltonians as well as the two- and three-electron atoms will be discussed in section 5. We present a new classifications of atoms according to their type of phase transitions in section 6, and in section 7 we discuss the existence of free doubly charged atomic negative ions in the gas phase. Finally, we give the conclusions and discuss the possibility of generalizing this approach to large atomic and molecular systems.

## 2. Phase transitions at the large-dimension limit

To study the behaviour of a given system near the critical point, one has to rely on model calculations which are simple, which capture the main physics of the problem and which belong to the same universality class. For electronic structure calculations of atoms and molecules, there are three exactly solvable models: the Thomas–Fermi statistical model (the limit  $N \rightarrow \infty$  for fixed  $N/Z$ , where  $N$  is the number of electrons and  $Z$  is the nuclear charge); the non-interacting electron model, the limit of infinite nuclear charge ( $Z \rightarrow \infty$ , for fixed  $N$ ); the large-dimension model ( $D \rightarrow \infty$  for fixed  $N$  and  $Z$ ) [16]. Here we shall 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 semiclassical electrostatic problem in which the electrons are assumed to have fixed positions relative to the nuclei and to each other in the  $D$ -scaled space [6]. This configuration corresponds to the minimum of an effective potential which includes Coulomb interactions as well as centrifugal terms arising from the generalized  $D$ -dependent kinetic energy. Typically, in the large- $D$  regime the electronic structure configuration undergoes symmetry breaking for certain ranges of nuclear charges or molecular geometries [17].

Recently [4], we have shown that symmetry breaking of electronic structure configurations at the large-dimension limit for Hartree–Fock (HF) two-electron atoms and the two-electron Coulomb problems is completely analogous to standard phase transitions. This analogy was shown by allowing the nuclear charge for atoms and the inverse internuclear distance for the two-electron Coulomb problem to play a role analogous to temperature in statistical mechanics. These systems exhibit critical points with mean-field critical exponents. In the next section we shall use the large-dimension limit model for the general  $N$ -electron atom to study symmetry breaking of electronic structure configurations leading to ionization. This model is simple, has an analytical solution for highly symmetric configurations [8] and yet contains a great deal of information about the ‘real’ atom. This model of the atom

is just the zeroth-order approximation and can be improved upon by a systematic perturbation expansion in  $1/D$  [18].

### 2.1. $N$ -electron atoms

For the exact solution of the  $N$ -electron atom at the  $D \rightarrow \infty$  limit, the dimension-scaled effective Hamiltonian can be written as [8]

$$\mathcal{H}_\infty = \frac{1}{2} \sum_{i=1}^N \frac{\Gamma_N^{(i)}}{\Gamma_N} \frac{1}{r_i^2} - Z \sum_{i=1}^N \frac{1}{r_i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{(r_i^2 + r_j^2 - 2r_i r_j \gamma_{ij})^{1/2}}. \quad (1)$$

Here,  $r_i$  are the electron-nucleus radii,  $Z$  is the nuclear charge,  $\gamma_{ij}$  are the cosines of the angles between electrons  $i$  and  $j$ ,  $\Gamma_N$  is the Grammian determinant  $|\gamma_{ij}|$  for all  $N$  electrons, and  $\Gamma_N^{(i)}$  is the Grammian determinant for all but the  $i$ th electron [8].

The  $N$  radii  $\{r_i\}$  together with  $N(N-1)/2$  cosines of the angles  $\{\gamma_{ij}\}$  between electrons, are the  $N(N+1)/2$  variational parameters. The large- $D$  limit ground-state energy is given by the minimum of the effective Hamiltonian:

$$E_\infty(N, Z) = \min_{\{r_i; \gamma_{ij}\}} \mathcal{H}_\infty \quad (2)$$

Loeser [8] obtained the totally symmetric solution of equation (2)  $r_i = r$  and  $\gamma_{ij} = \gamma \forall i, j$ . However, for fixed values of  $N$ , this symmetric solution is not the unique solution of equation (2) for all values of the charge  $Z$ . In general, there exist many local minima corresponding to different configurations. By studying the eigenvalues of the Hessian matrix, one can describe the stability of the different solutions.

In particular, for small values of  $N$  ( $N \leq 13$ ), we found there are two stable solutions of equation (2). One is the symmetric solution  $r_i = r$  and  $\gamma_{ij} = \gamma \forall i, j$ ; the second corresponds to one electron at a larger distance from the nucleus than the other  $N-1$  electrons  $r_1 > r_i, i > 1$  and  $\gamma_{1,i} = \gamma_1, \gamma_{ij} = \gamma, i, j > 1$ . A coexistence region exist where both solutions are stable and a first-order critical point is defined by the condition

$$E_\infty^{\text{sym}}(N, Z) = E_\infty^{\text{ns}}(N, Z) \quad (3)$$

When  $Z$  decreases, the asymmetric solution with  $N$  electrons goes in a continuous way to the symmetric solution with  $N-1$  electrons. Therefore, the transition from the neutral atom to the ionized atom is a first-order transition between the symmetric and the asymmetric configuration while it is a second-order transition between the asymmetric  $N$ -electron configuration to the symmetric ionized ( $N-1$  electrons) atom. This behaviour is shown in figure 1 for  $N = 3$ . In the HF approximation, there is no coexistence region between the symmetric and the asymmetric configuration, and both transitions are of a continuous type.

In order to present details of the calculation, for simplicity, let us take as an example the two-electron atoms in the HF approximation. In this approximation, there are only two variational parameters  $r_1$  and  $r_2$ ; the stability analysis takes a much simpler form and the results can be obtained analytically.

In the HF approximation at the  $D \rightarrow \infty$  limit, the dimension-scaled effective Hamiltonian for the two-electron atom in an external weak electric field  $\mathcal{E}$  can be

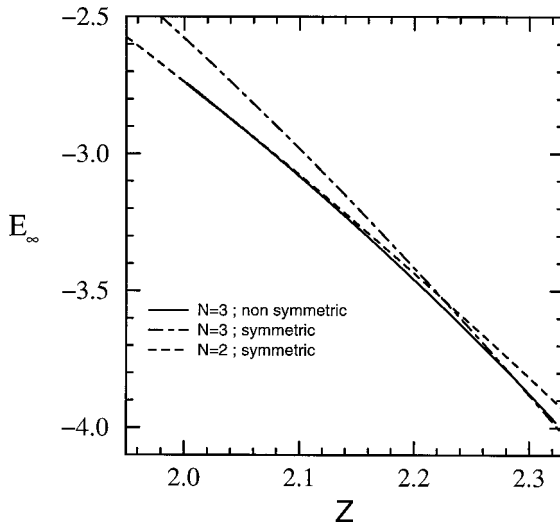


Figure 1. Energy versus  $Z$  at fixed value of  $N$  for the  $N$ -electron atom at the large  $D$  limit. The  $N = 3$  symmetric and asymmetric solutions and the  $N = 2$  symmetric solution are shown. The  $N = 3$  solutions cross at  $Z \approx 2.29$ . The symmetric  $N - 1 = 2$  solution merges continuously to the asymmetric  $N = 3$  solution at  $Z = 2$ .

written as [19]

$$\mathcal{H}_\infty = \frac{1}{2} \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) - Z \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{(r_1^2 + r_2^2)^{1/2}} - \mathcal{E} (r_1 - r_2), \quad (4)$$

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

$$E_\infty(Z, \mathcal{E}) = \min_{\{r_1, r_2\}} \mathcal{H}_\infty \quad (5)$$

This condition yields the equations

$$-\frac{1}{r_i^3} + \frac{Z}{r_i^2} - \frac{r_i}{(r_1^2 + r_2^2)^{3/2}} = \sigma_i \mathcal{E}, \quad i = 1, 2, \quad \sigma_1 = 1, \quad \sigma_2 = -1. \quad (6)$$

In the absence of an external electric field,  $\mathcal{E} = 0$ , Herschbach and co-workers [20] have found that these equations have a symmetric solution with the two electrons equidistant from the nucleus, with  $r_1 = r_2 = r = 2^{3/2}/(2^{3/2}Z - 1)$ . This symmetric solution represents a minimum in the region where all the eigenvalues of the Hessian matrix are positive,  $Z \geq Z_c = 2^{1/2}$ , and the ground-state energy is given by

$$E_\infty(Z) = - \left( Z - \frac{1}{2^{3/2}} \right)^2. \quad (7)$$

For values of  $Z$  smaller than  $Z_c$ , the solutions of the variational equations (6) become asymmetric 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

$$r_1 = r, \quad r_2 = (1 - \eta)r, \quad (8)$$

where  $\eta \neq 0$  measures the deviation from the symmetric solution.

By studying the eigenvalues of the Hessian matrix, we have found 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:

- (a) nuclear charge  $Z \leftrightarrow$  temperature  $T$ ;
- (b) external electric field  $\mathcal{E} \leftrightarrow$  ordering field  $h$ ;
- (c) ground-state energy  $E_\infty(Z, \mathcal{E}) \leftrightarrow$  free energy  $f(T, h)$ ;
- (d) asymmetry parameter  $\eta \leftrightarrow$  order parameter  $m$ ;
- (e) 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:

$$\begin{aligned} \eta(Z, \mathcal{E} = 0) &\sim (-\Delta Z)^\beta, & \Delta Z \rightarrow 0^-, \\ E_\infty(Z, \mathcal{E} = 0) &\sim |\Delta Z|^{2-\alpha}, & \Delta Z \rightarrow 0, \\ \mathcal{E}(Z_c, \eta) &\sim \eta^\delta \text{sgn}(\eta), & \eta \rightarrow 0, \\ \left. \frac{\partial \eta}{\partial \mathcal{E}} \right|_{\mathcal{E}=0} &\sim |\Delta Z|^{-\gamma}, & \Delta Z \rightarrow 0, \end{aligned} \quad (9)$$

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 critical exponent  $\beta$  determines the rate of vanishing of the order parameter, which is the asymmetry parameter  $\eta$ . In the absence of external electric fields, the value was found to be  $\beta = \frac{1}{2}$ . The  $\alpha$  exponent gives the rate of divergence of the second derivative of the energy with respect to the nuclear charge, which is analogous to the divergence of the heat capacity near the critical temperature. In this case,  $\alpha = 0_{\text{dis}}$ , the subscript dis, meaning discontinuity, is necessary in order to distinguish this case from other known systems where the divergence is logarithmic with  $\alpha = 0$  as in the two-dimensional Ising model. At the critical charge, the external field varies with the  $\delta$  power of the asymmetry parameter  $\eta$ . For our example, we have found that,  $\mathcal{E} \sim [9/(64 \times 2^{1/2})]\eta^3$  [4]. Thus the response to a small electric field is highly nonlinear with  $\delta = 3$ . Finally, in the standard phase transition, the exponent  $\gamma$  determines the rate of divergence of the susceptibility, or more generally, the divergence of the rate of change in the field with the order parameter. We have found that  $\gamma = 1$ .

The values obtained for these critical exponents are known as classical or mean-field critical exponents with

$$\beta = \frac{1}{2}, \quad \alpha = 0_{\text{dis}}, \quad \delta = 3, \quad \gamma = 1. \quad (10)$$

Only two of the four are independent because of the two relations between them known as the Rushbrooke and the Griffiths laws [2]

$$\alpha + 2\beta + \gamma = 2, \quad \alpha + \beta(\delta + 1) = 2 \quad (11)$$

The results of the asymmetry parameter  $\eta$  as a function of nuclear charge at  $\mathcal{E} = 0$  is shown in figure 2(a). This curve of the asymmetry parameter shown is completely analogous to curves representing the behaviour of magnetization as a function of the temperature in mean-field models of ferromagnetic systems [2] as shown in figure 2(b).

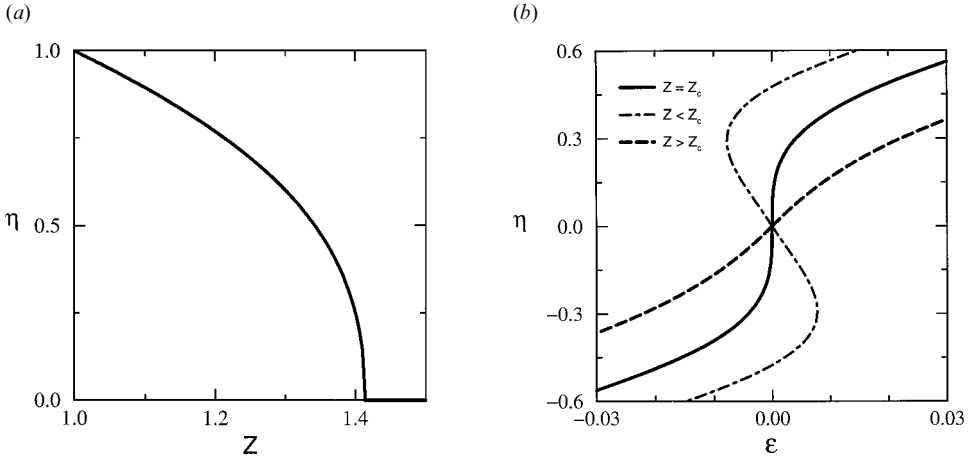


Figure 2. (a) The asymmetry parameter  $\eta$  as a function of the nuclear charge  $Z$  for the HF two-electron atom. (b) The asymmetry parameter  $\eta$  as a function of the external electric field for three values of the nuclear charge.

Finally, we consider the effect of a uniform magnetic field on the symmetry breaking and phase transitions of the HF two-electron atoms. In the external magnetic field, the value of the critical charge will change with the magnetic field but not the order of the phase transition. By examining the phase diagram for two-electron atoms in an external magnetic field, we note that, at  $Z = 1$  and critical field  $B_c = \frac{3}{16} [3(2^{1/2} - 1)]^{1/2} \approx 0.20901$ , the electrons are confined to a quadratic potential. With higher fields  $B > B_c$ , there is only a single phase, which is the symmetric phase [21].

## 2.2. Simple molecular systems

Symmetry breaking of the molecular electronic structure configurations at the large-dimension limit shows similar phase transitions. For the hydrogen molecular ion the analogy to standard phase transitions was shown by allowing the inverse internuclear distance to play a role analogous to temperature in statistical mechanics. As for the  $N$ -electron atoms, to calculate the critical exponents we performed the following mapping [4]:

- (a) inverse nuclear distance  $1/R \leftrightarrow$  temperature  $T$ ;
- (b) difference between the nuclear charges  $\Delta \leftrightarrow$  ordering field  $h$ ;
- (c) ground-state energy  $E_\infty(R, \Delta) \leftrightarrow$  free energy  $f(T, h)$ ;
- (d) asymmetry parameter  $\Psi \equiv -(\partial E_\infty[R, \Delta])/\partial \Delta \leftrightarrow$  order parameter  $m \equiv -(\partial f(T, h))/\partial h$ ;
- (e) stability limit point  $(R_c, \Delta = 0) \leftrightarrow$  critical point  $(T_c, h = 0)$ .

The critical exponents are now defined as

$$\begin{aligned}
 \Psi(\epsilon, \Delta = 0) &\sim (-\epsilon)^\beta, & \epsilon \rightarrow 0^-, \\
 E_\infty(\epsilon, \Delta = 0) &\sim |\epsilon|^{2-\alpha}, & \epsilon \rightarrow 0, \\
 \Delta(\epsilon = 0, \Psi) &\sim \Psi^\delta \text{sgn}(\Psi), & \Psi \rightarrow 0, \\
 \frac{\partial \Psi}{\partial \Delta} \Big|_{\Delta=0} &\sim |\epsilon|^{-\gamma}, & \epsilon \rightarrow 0,
 \end{aligned} \tag{12}$$

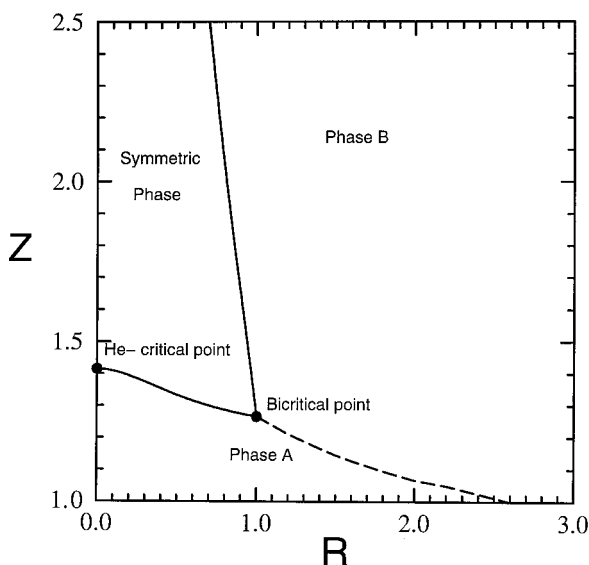


Figure 3. Phase diagram for the HF  $H_2$  molecule. Phase A is a pre-ionization phase with an electron closer to the symmetry axis than the other axis. Phase B is a pre-dissociation phase with one electron near one nucleus and the other electron near the second nucleus.

where  $\epsilon$  plays the role of the reduced temperature:  $\epsilon \equiv (1/R - 1/R_c)/(1/R_c)$ . As for the two-electron atom, we obtain the same mean-field critical exponents [4].

This analogy was used to treat the HF hydrogen molecule at the large- $D$  limit [22]. Symmetry breaking of the electronic structure configurations was also described as standard phase transitions. The phase diagram in the internuclear distance–nuclear charge plane shows three different stable phases, as in figure 3, corresponding to different electronic structure configurations. This phase diagram was characterized by a bicritical point where the two continuous phase transition lines join a first-order transition line. This approach was generalized to examine symmetry breaking for one-electron molecules. Rich phase diagrams with multicritical points were reported for both linear and planar one-electron systems. Detailed calculations for  $H_2^+$  and  $H_3^{2+}$  and four-atom molecules have been given in [23].

### 3. Finite size scaling in statistical mechanics

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 in such a way that the density  $\rho = N/V$  stays constant. This could be understood by examining 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 in the thermodynamic limit.

In practice, real systems have a large but finite volume and particle numbers ( $N \approx 10^{23}$ ), 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. The

question of why finite systems apparently describe phase transitions and the relation of this phenomena with the 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 behaviour 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 even by studying the corresponding small systems.

There are many excellent review articles on this subject in the literature [10, 11, 24]. However, in this review article we are going to discuss only the general idea of FSS in statistical mechanics, which is closely related to the application of these ideas in quantum mechanics.

In order to understand the main idea of FSS, let us consider a system defined in a  $d$ -dimensional volume  $V$  of a linear dimension  $L$  ( $V = L^d$ ). Then, the singular part of the free energy will be a function of the microscopic parameters, the temperature and also the inverse size of the system  $L^{-1}$ .  $L^{-1}$  plays a role of a relevant field, and phase transitions will occur at  $L^{-1} = 0$  (infinite volume or the thermodynamic limit).

If in the thermodynamic limit  $L \rightarrow \infty$  a quantity  $K$  develops a singularity as a function of the temperature  $T$  in the form

$$K(T) = \lim_{L \rightarrow \infty} K_L(T) \sim |T - T_c|^{-\rho} \quad (13)$$

and in particular for the correlation length

$$\xi(T) = \lim_{L \rightarrow \infty} \xi_L(T) \sim |T - T_c|^{-\nu}, \quad (14)$$

then the FSS *Ansatz* assumes the existence of the scaling function  $F_K$  such that

$$K_L(T) \sim K(T) F_K \left( \frac{L}{\xi(T)} \right), \quad (15)$$

where  $F_K(y)$  is an analytical function. Since the FSS *Ansatz*, equation (15), 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 [25]

$$\xi_L(T) \sim L \phi_\xi(L^{1/\nu} |T - T_c|). \quad (16)$$

The special significance of this result was first realized by Nightingale [12], who showed how it could be reinterpreted as a renormalization group transformation of the infinite system. The PR equation for finite systems of sizes  $L$  and  $L'$  is given by

$$\frac{\xi_L(T)}{L} = \frac{\xi_{L'}(T')}{L'} \quad (17)$$

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 PR in 1976 by Nightingale [12], one of the most powerful tools for studying 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 (see for example [26]). In particular, the

free energy takes the form

$$f(T) = -T \ln \lambda_1, \quad (18)$$

and the correlation length is

$$\xi(T) = -\frac{1}{\ln(\lambda_2/\lambda_1)}, \quad (19)$$

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 the finite transfer matrix, the Perron–Frobenius theorem [27] asserts that 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. It is important to note that in the Perron–Frobenius theorem all the matrix elements are positive.

For quasi-one-dimensional systems of size  $L$ , it is possible to calculate all the eigenvalues of the finite transfer matrix, and therefore, using scaling *Ansatz* such as PR (equation (17)) it is possible to obtain critical parameters and critical exponents for bidimensional systems. The transfer matrix with FSS theory was successfully applied to the study of a wide variety of two-dimensional lattice systems such as magnetic models [28], modulated phases [29], polymer models [30, 31], percolation [32, 33], long-range interactions [34], etc.

Now, we have a method to calculate singularities in the eigenvalues of certain class of infinite square matrix by studying the eigenvalues of systematic approximations with finite matrices. In order to apply these ideas to quantum few-body problems, we can use one of the widely used approximation methods in quantum mechanics, the variation method [35], to obtain the necessary approximations to the (infinite) exact Hamiltonian matrix by finite matrices. This is the subject of the next section.

#### 4. Finite size scaling in quantum mechanics

In quantum mechanics, when using variation methods, one encounters the same finite-size problem in studying the critical behaviour of a quantum Hamiltonian  $\mathcal{H}(\lambda_1, \dots, \lambda_k)$  as a function of its set of parameters  $\{\lambda_i\}$ . In this context, critical means the values of  $\{\lambda_i\}$  for which a bound state energy is non-analytic. In many cases, as in this study, this critical point is the point where a bound-state energy becomes absorbed or degenerate with a continuum. In this case, 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 wavefunction of a given Hamiltonian.

In order to apply FSS to quantum mechanics problems, let us consider the Hamiltonian of the form

$$\mathcal{H} = \mathcal{H}_0 + V_\lambda, \quad (20)$$

where  $\mathcal{H}_0$  is the  $\lambda$ -independent term 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. In this study, 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 shall assume that the Hamiltonian (20) 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 behaviour of different quantities near the critical point. In particular, for the energy we can

define the critical exponent  $\alpha$  as

$$E_\lambda \underset{\lambda \rightarrow \lambda_c^+}{\sim} (\lambda - \lambda_c)^\alpha. \quad (21)$$

For general potentials of the form  $V_\lambda = \lambda \overline{V}$ , Simon [36] showed that the critical exponent  $\alpha$  is equal to one if and only if  $\mathcal{H}(\lambda_c)$  has a normalizable eigenfunction with eigenvalue equal to zero. 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’.

In quantum calculations, the variation method is widely used to approximate the solution of the Schrödinger equation. To obtain exact results, one should expand the exact wavefunction 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. For a given complete orthonormal  $\lambda$ -independent basis set  $\{\Phi_n\}$ , the ground-state eigenfunction has the following expansion:

$$\Psi_\lambda = \sum_n a_n(\lambda) \Phi_n, \quad (22)$$

where  $n$  represents the set of quantum numbers. In order to approximate the different quantities, we have to truncate the series (22) at order  $N$ . Then the Hamiltonian is replaced by the  $M(N) \times M(N)$  matrix  $\mathcal{H}^{(N)}$ , with  $M(N)$  being the number of elements in the truncated basis set at order  $N$ . Using the standard linear variation method, the  $N$ th-order approximation for the energies are given by the eigenvalues  $\{A_i^{(N)}\}$  of the matrix  $\mathcal{H}^{(N)}$ ,

$$E_\lambda^{(N)} = \min_{\{i\}} \{A_i^{(N)}\}. \quad (23)$$

The corresponding eigenfunctions are given by

$$\Psi_\lambda^{(N)} = \sum_n^{M(N)} a_n^{(N)}(\lambda) \Phi_n, \quad (24)$$

where the coefficients  $a_n^{(N)}$  are the components of the ground-state eigenvector. In this representation, the expectation value of any operator  $\mathcal{O}$  at order  $N$  is given by

$$\langle \mathcal{O} \rangle_\lambda^{(N)} = \sum_{n,m}^N a_n^{(N)}(\lambda)^* a_m^{(N)}(\lambda) \mathcal{O}_{n,m}, \quad (25)$$

where  $\mathcal{O}_{n,m}$  are the matrix elements of  $\mathcal{O}$  in the basis set  $\{\Phi_n\}$ . In general, the mean value  $\langle \mathcal{O} \rangle$  is not analytical at  $\lambda = \lambda_c$ , and we can define a critical exponent  $\mu_{\mathcal{O}}$  by the relation

$$\langle \mathcal{O} \rangle_\lambda \underset{\lambda \rightarrow \lambda_c^+}{\sim} (\lambda - \lambda_c)^{\mu_{\mathcal{O}}}. \quad (26)$$

In statistical mechanics, the singularities in thermodynamic functions associated with a critical point occur only in the thermodynamic limit. In the variation approach,

singularities in the different mean values will occur only in the limit of infinite basis functions.

As in the FSS *Ansatz* in statistical mechanics [32], we shall assume that there exists a scaling function for the truncated magnitudes such that

$$\langle \mathcal{O} \rangle_{\lambda}^{(N)} \sim \langle \mathcal{O} \rangle_{\lambda} F_{\mathcal{O}}(N|\lambda - \lambda_c|^{\nu}), \quad (27)$$

with a different scaling function  $F_{\mathcal{O}}$  for each different operator but with a unique scaling exponent  $\nu$ .

Now we are in a position to obtain the critical parameters by defining the following function

$$\Delta_{\mathcal{O}}(\lambda; N, N') = \frac{\ln \left( \langle \mathcal{O} \rangle_{\lambda}^{(N)} / \langle \mathcal{O} \rangle_{\lambda}^{(N')} \right)}{\ln (N' / N)}. \quad (28)$$

At the critical point, the mean value depends on  $N$  as a power law,  $\langle \mathcal{O} \rangle \sim N^{-\mu_{\mathcal{O}}/\nu}$ , thus one obtains an equation for the ratio of the critical exponents:

$$\Delta_{\mathcal{O}}(\lambda_c; N, N') = \frac{\mu_{\mathcal{O}}}{\nu}, \quad (29)$$

which is independent of the values of  $N$  and  $N'$ . Thus, for three different values  $N, N'$  and  $N''$  the curves defined by equation (28) intersect at the critical point

$$\Delta_{\mathcal{O}}(\lambda_c; N, N') = \Delta_{\mathcal{O}}(\lambda_c; N'', N). \quad (30)$$

In order to obtain the critical exponent  $\alpha$ , which is associated with the energy, we can take  $\mathcal{O} = \mathcal{H}$  in equation (29) with  $\mu_{\mathcal{O}} = \alpha$ ,

$$\frac{\alpha}{\nu} = \Delta_{\mathcal{H}}(\lambda_c; N, N'). \quad (31)$$

By using the Hellmann–Feynman theorem (see for example [37]) we obtain

$$\frac{\partial E_{\lambda}}{\partial \lambda} = \left\langle \frac{\partial \mathcal{H}}{\partial \lambda} \right\rangle_{\lambda} = \left\langle \frac{\partial V_{\lambda}}{\partial \lambda} \right\rangle_{\lambda}. \quad (32)$$

Taking  $\mathcal{O} = \partial V_{\lambda} / \partial \lambda$  in equation (29) gives an equation for  $(\alpha - 1) / \nu$ , which together with equation (31) give the exponents  $\alpha$  and  $\nu$ .

The FSS equations are valid only as an asymptotic expression,  $N \rightarrow \infty$  but, with a finite basis set, unique values of  $\lambda_c, \alpha$  and  $\nu$  can be obtained as a succession of values as functions of  $N, N'$  and  $N''$ . The relation between  $N, N'$  and  $N''$  was extensively studied in FSS in statistical mechanics [11], and it is known that the fastest convergence is obtained when the difference between these numbers is as small as possible. In this study we took  $\Delta N = 1$ , and when there are parity effects we used  $\Delta N = 2$ . In order to obtain the extrapolated values for  $\lambda^{(N)}, \alpha^{(N)}$  and  $\nu^{(N)}$  at  $N \rightarrow \infty$  we used the algorithm of Bulirsch and Stoer [38] with  $N' = N + \Delta N$  and  $N'' = N - \Delta N$ . This algorithm was also studied in detail and gives very accurate results for both statistical mechanics problems [39] as well as electronic structure critical parameters [9, 14, 40].

## 5. Numerical calculations

To illustrate the applications of the FSS method in quantum mechanics, two cases with qualitatively different behaviours near the critical point have been reviewed: one with short-range exponential potentials and one with long-range Coulomb interactions.

### 5.1. Short-range potentials

There are many rigorous results known about the critical behaviour of short-range one-body potentials. Klaus and Simon [41] consider a family of Schrödinger operators,  $-\nabla^2 + \lambda V$ , with the coupling constant  $\lambda$  and short-range potential  $V$ . Their results address two general questions: is the eigenvalue  $E(\lambda)$  analytic at  $\lambda = \lambda_c$ , and what is the leading order of the expansion in  $(\lambda - \lambda_c)^\alpha$ ?

These two questions were analysed in detail for the Hamiltonian of the screened Coulomb potential in previous studies [42, 44]. Here, we shall summarize our main results using the FSS equations for this model.

In scaled atomic units the Hamiltonian can be written as

$$\mathcal{H}(\lambda) = -\frac{1}{2}\nabla^2 - \lambda \frac{\exp(-r)}{r}. \quad (33)$$

This Hamiltonian has bound states for large values of  $\lambda$ , and the exact value of the critical exponent  $\alpha$  is  $\alpha = 2$  for states with zero angular momentum and  $\alpha = 1$  for states with non-zero angular momentum [41].

We used FSS in order to obtain the pseudocritical  $\lambda^{(N)}$ ,  $\alpha^{(N)}$  and  $v^{(N)}$ . For  $l = 0$  the energy curve goes smoothly to zero as a function of  $\lambda$  but the second-derivative function develops a discontinuity in the neighbourhood of the critical point  $\lambda_c \approx 0.8399$  [42]. This behaviour is different from that of  $l = 1$  results, where the energy curve bends sharply to zero at the critical point  $\lambda_c \approx 4.5409$ . As one should expect, there is a discontinuity in the first derivative as a function of  $\lambda$  [42].

For the case  $l = 0$ , the eigenfunction is not normalizable at  $\lambda = \lambda_c$ . It is interesting to note that for the Hülten Hamiltonian, another potential with an exponential decay and exact solution for the ground state [44], the expansion coefficients of the wavefunction have the asymptotic form

$$a_n(\lambda) \sim_{\lambda \rightarrow \lambda_c^+} (\lambda - \lambda_c)^{1/2} \quad (34)$$

independent of the basis set and the value of  $n$ . It seems that this result is general and suggests that there is a unique critical exponent for the expansion coefficients. We assume that, with  $\alpha \neq 1$ , there is a unique critical exponent  $\mu_a$  defined by

$$a_n(\lambda) \sim_{\lambda \rightarrow \lambda_c^+} (\lambda - \lambda_c)^{\mu_a}. \quad (35)$$

Assuming that this is a universal behaviour for the coefficients  $\{a_n\}$  it is straightforward to show using the Hellmann–Feynman theorem that  $\mu_a = (\alpha - 1)/2$ .

To verify these results, numerical studies show that the curves of the leading coefficients  $a_0^{(N)}$  and  $a_1^{(N)}$  as functions of  $\lambda$  bend to zero at  $\lambda_c$  and in the limit of  $N \rightarrow \infty$  both  $a_0$  and  $a_1$  take the value zero for all  $\lambda$  below  $\lambda_c$ . Our conjecture is that the exact value of  $\mu_n$  is equal to  $(\alpha - 1)/2$  for all  $n$ , and in particular for  $\alpha = 2$ ,  $\mu = \frac{1}{2}$ . That is  $\mu$  is a ‘universal exponent’ for the coefficients independent of the value of  $n$  or the basis set [43].

In order to test the method in an exactly solvable problem, we apply FSS to the Pösch–Teller Hamiltonian

$$\mathcal{H}(\lambda) = -\frac{1}{2}\nabla^2 - \frac{\lambda(\lambda + 1)}{\cosh^2(r)}, \quad (36)$$

where we wrote  $\lambda(\lambda + 1)$  instead of  $\lambda$  as is usual in the literature. The exact value of the ground state is [44]  $E_0 = -(\lambda - 1)^2$  for  $\lambda > 1$ , then the exact value of the  $\alpha$  exponent is two.

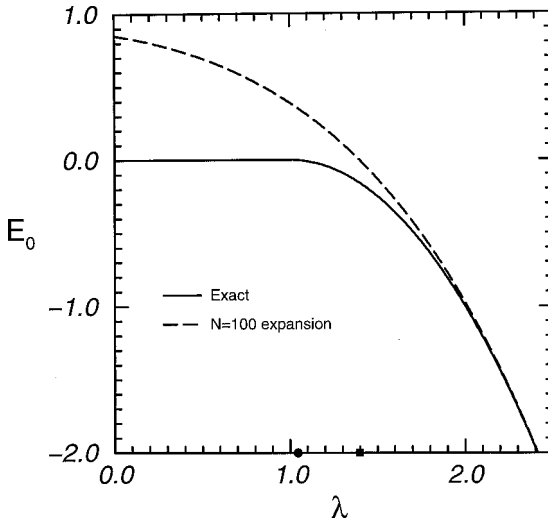


Figure 4. The exact ground state of the Pösch–Teller potential in comparison with the  $N = 100$  basis functions expansion. The exact value  $\lambda_c = 1$  is also compared with  $\lambda^{(100)} = 1.045$  (●) and with  $\lambda^*$  defined by  $E_0^{(100)}(\lambda^*) = 0$  (■).

For this potential, we used a Fourier-like orthonormal basis set with appropriate boundary conditions for  $y \in (0, 1)$ , where  $y = \tanh(r)$ . In this basis set we obtained an analytical expression for the matrix elements of the Hamiltonian. In figure 4 we compare the exact ground state with the variational approximation obtained from the truncated expansion at  $N = 100$  basis set functions. This approximate eigenvalue crosses the bottom of the continuum ( $E = 0$ ) at  $\lambda^* \approx 1.4$ . The FSS *Ansatz* reduces the error by an order of magnitude for the same value of  $N = 100$ ,  $\lambda^{(100)} \approx 1.045$ .

### 5.2. Long-range potentials

For the two-electron Coulomb problem, that is a long-range two-body potential, the ground state is degenerate with the continuum with critical exponent  $\alpha = 1$  and has a normalizable eigenfunction at the critical point [45]. The critical point is the minimum value of the nuclear charge necessary to bind two electrons and is about 0.911 16.

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 [46–48]:

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

where  $\gamma$  and  $\delta$  are fixed parameters,  $r_{12}$  is the interelectronic distance and  $F_\ell(\theta_{12}, \mathbf{\Omega})$  is a suitable function of the angle between the positions  $\theta_{12}$  of the two electrons 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 [47, 48]. The complete wavefunction is then a linear combination of these terms multiplied by variational coefficients determined by matrix diagonalization.

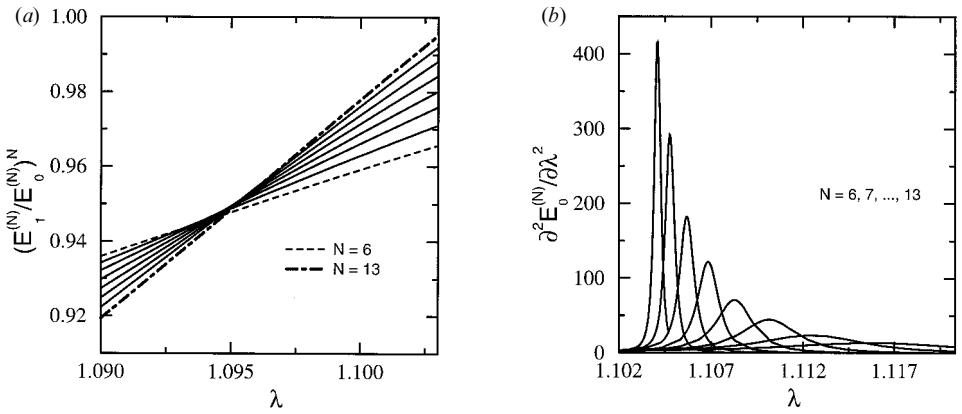


Figure 5. (a) The ratio of the ground-state energy to the second-lowest eigenvalue, for two-electron atoms, raised to a power  $N$  as a function of  $\lambda$  for several values of  $N$ . (b) Second derivative of the ground-state energy for the two-electron atoms as a function of  $\lambda$  for several values of  $N$ .

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  $\Theta$  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  $N \geq i + j + k$ , so the number of trial functions  $M(N)$  is

$$M(N) = \frac{1}{12}N^3 + \frac{5}{8}N^2 + \frac{17}{12}N + a_N, \quad (38)$$

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

The asymptotic behaviour (large  $N$ ) of the system is independent of the parameters of the trial functions. The values of the parameters were adjusted in order to get a faster convergence of the PR equation. We found numerically that  $\gamma = 2$  and  $\delta = 0.15$  are good choices for the ground state while  $\gamma = 0.5$  and  $\delta = 0.05$  are better for the triplet 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, one can look for its fixed point by taking the ratio of these two eigenvalues raised to a power  $N$  as a function of  $\lambda$ . Figure 5(a) shows the crossing points, which are the fixed points of the PR equation, for  $N = 6, 7, 8, \dots, 13$ . The values of the fixed points as functions of  $N$  can be extrapolated to the limit  $N \rightarrow \infty$  by using the Bulirsch and Stoer [38] algorithm, which is widely used for FSS extrapolation [11]. The extrapolated values of  $\lambda_c$  using the PR equation is  $\lambda_c = 1.0976 \pm 0.0004$ . This result is in excellent agreement with the best estimate of  $\lambda_c = 1.097\,660\,79$  [49]. By examining the behaviour of the ground-state energy as a function of  $\lambda$ , one notes that, when the value of  $N$  approaches the limit  $N \rightarrow \infty$ , the true ground state energy bends over sharply at  $\lambda_c$  to become degenerate with the lowest continuum at  $E_0 = -\frac{1}{2}$ . This behaviour 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. By virtue of this behaviour, we expect the first derivative of the energy with respect to  $\lambda$  to develop a step-like discontinuity at  $\lambda_c$  and the

second derivative to develop a delta-function-like behaviour as  $N$  becomes larger, as shown in figure 5(b).

The behaviour of the ground-state energy and its first and second derivatives resemble the behaviour 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 a critical point  $\lambda_c$ , which is the maximum value of  $\lambda$  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.

Having presented our results for the critical behaviour of the ground-state energy of the helium isoelectronic sequence, we may now consider other excited states, namely the  $2p^2\ ^3P$  state. We have performed a variational study of this level using the basis set defined above. As for the ground state, we obtained the lowest two eigenvalues which correspond to the block  $l = 1$ . The energy behaviour of this triplet state is very similar to that found for the ground state. The curves start to bend over sharply to a constant value as  $N$  becomes larger. The true excited state energy, in the limit  $N \rightarrow \infty$ , bends over sharply at  $\lambda_c^P$  to become degenerate with the lowest continuum at  $E_T^P = -\frac{1}{8}$ .

Taking the  $l = 1$  block as a transfer matrix of a pseudoclassical system, like the  $l = 0$  case, we can apply the PR equation to the present sector in order to obtain a sequence of pseudocritical  $\lambda$  as a function on  $N$ :  $\{\lambda_P^{(N,N')}\}$ . The extrapolated value of this sequence gives  $\lambda_c^P = 1.0058 \pm 0.0017$ . As far as we know the only estimate of  $\lambda_c$  for this triplet state is that given by Brändas and Goscinski [50]. By applying a Darboux function *Ansatz* [51, 52] to the  $E_n$  values of Midtdal [53] for  $n$  up to 27, they found that  $\lambda_c \approx 1.0048$ , which is in good agreement with our results.

Stillinger [54] discussed another family of long-range potentials that can be solved exactly. For the ground state of the potential  $V(r) = -3/32r^2 + b/8r^{1/2} - c/8r$ , he showed that there exists a normalizable eigenfunction at the critical point and the critical exponent is  $\alpha = 1$ . More recently, the FSS has been used to study the potential

$$V_\lambda(r) = -\frac{1}{r} + \frac{\lambda}{r^{1/2}}, \quad (39)$$

with results qualitatively very similar to the results of the two electron atoms [40]. We have found that the energy curves as a function of  $\lambda$  and bends over sharply at  $\lambda_c$  to become degenerate with the continuum [43].

## 6. Phase transitions and classifications of atoms

Using the FSS method, study of the analytical behaviour of the energy near the critical point shows 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’ while, for the open-shell system, the transition of the valence electron to the continuum is a ‘continuous phase transition’.

To see the main difference, we first briefly review the calculations for three electron atoms (see [14] for more details). The scaled Hamiltonian of the lithium-

like atoms, which can be written as

$$\mathcal{H}(\lambda) = \sum_{i=1}^3 \left( -\frac{1}{2} \nabla_i^2 - \frac{1}{r_i} \right) + \lambda \sum_{i < j=1}^3 \frac{1}{r_{ij}}, \quad (40)$$

where  $r_{ij}$  are the interelectron distances and  $\lambda$  is the inverse of the nuclear charge. As basis functions for this procedure we used the Hylleraas [47]-type functions as presented by Yan and Drake [55]

$$\Psi_{ijklmn}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \mathcal{C} \mathcal{A} \left\{ r_1^i r_2^j r_3^k r_{12}^l r_{23}^m r_{31}^n \exp[-\alpha(r_1 + r_2)] \exp[-\beta r_3] \chi_1 \right\} \quad (41)$$

where  $\alpha$  and  $\beta$  are fixed parameters,  $\chi_1$  is the spin function with spin angular moment  $\frac{1}{2}$  given by

$$\chi_1 = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3), \quad (42)$$

$\mathcal{C}$  is a normalization constant and  $\mathcal{A}$  is the usual three-particle antisymmetrizer operator [55]. We took  $\alpha = 0.9$  and  $\beta = 0.1$  in order to obtain accurate results near the critical charge  $Z \approx 2$ . All numerical evaluation of the necessary integrals needed to calculate the matrix elements has been made using an efficient algorithm recently developed by Drake and Yan [56]. The finite order of the basis set is allowed to be  $i + j + k + l + m + n \leq N$ . The maximum value of  $N$  was taken to be  $N = 8$ , which gives a  $1589 \times 1589$  Hamiltonian matrix [14].

The extrapolated value of the sequences  $\lambda^{(N)}$  for lithium-like atoms has been done by using the general algorithm of Bulirsch and Stoer [38]. From the PR method,  $\lambda_c$  was found to be  $0.48 \pm 0.03$ . In the neighbourhood of the critical charge, the ionization energy for lithium-like atoms,  $I = E_{\text{Li}} - E_{\text{He}}$ , goes smoothly to zero as a function of  $\lambda$  [14]. This behaviour is different from that of our previous results [9, 40] for the helium-like atoms where the ionization energy bends sharply to zero at the helium critical point  $\lambda_c^{(\text{He})} \approx 1.0976$ . The different behaviour of the energy as a function of the Hamiltonian parameter  $\lambda$  suggests an analogy with standard phase transitions in statistical mechanics, that the transition from a ground bound state to a continuum in the helium-like atoms resemble ‘first-order phase transitions’, while for lithium-like atoms the transition is continuous. To investigate this analogy we examined the first and second derivatives of the ionization energy as functions of  $\lambda$ .

By virtue of the behaviour of the energy curves, we expect the first derivative of the ionization energy with respect to  $\lambda$  to develop a step-like discontinuity at  $\lambda_c^{(\text{He})}$  for the helium-like atoms [9, 40] but to remain continuous for the lithium-like atoms. Figure 6(a) shows that the first derivative is continuous for lithium-like atoms as a function of  $\lambda$ . As expected, the second derivative will develop a sharp delta-function-like behaviour as  $N$  becomes larger for the helium-like atoms [9, 40] but it is much broader for the lithium-like atoms as shown in figure 6(b).

In previous studies, we showed that for the helium-like atoms the critical exponent for the energy  $E \approx (\lambda_c - \lambda)^\alpha$ ,  $\lambda \rightarrow \lambda_c^-$ , is equal to one:  $\alpha = 1$  [9, 40]. This result was in complete agreement with earlier theorem of Simon [36], which proved that  $H(\lambda_c)$  for two-electron atoms has a square integrable eigenfunction corresponding to a threshold bound state with zero ionization potential and an energy critical exponent  $\alpha = 1$ . For three-electron atoms, we obtained different results; the critical exponent was about two. Contrary to the helium case, where the Hamiltonian has a square integrable eigenfunction at  $\lambda^{(\text{He})} = \lambda_c^{(\text{He})}$ , the Hamiltonian for lithium-like atoms does not have a square integrable wavefunction at the bottom of the continuum.

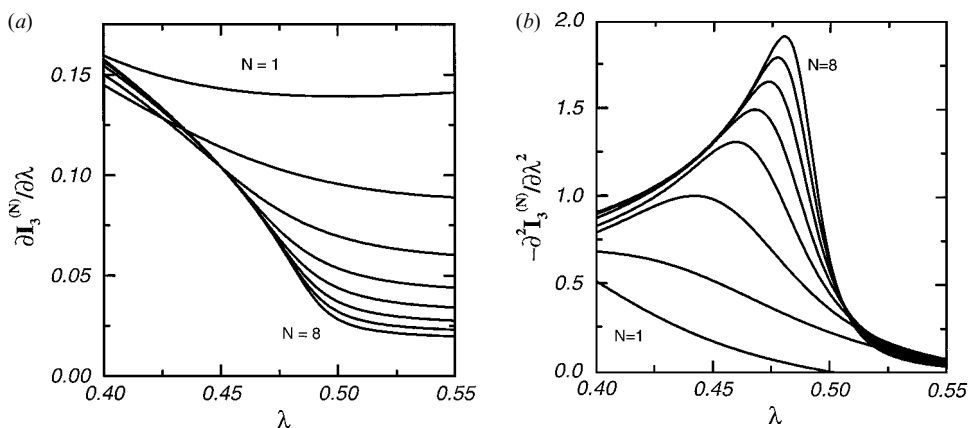


Figure 6. (a) First derivative of the ground state energy for the three-electron atoms as a function of  $\lambda$  for several values of  $N$ . (b) Second derivative of the ground state energy for the three-electron atoms as a function of  $\lambda$  for several values of  $N$ .

Results from the two- and three-electron atoms show that there is a fundamental difference in the behaviour of the energy as functions of  $\lambda$  for the closed-shell helium-like atoms and the open-shell lithium-like atoms. The transition in the former between a bound state and a continuum has all the characteristics of a first-order phase transition while the latter has the characteristics of a continuous phase transition.

## 7. Doubly charged negative atomic ions

Singly charged negative ions in the gas phase are of fundamental importance in atomic and molecular physics and have attracted considerable experimental and theoretical attention over the past few decades [57–61]. With the advancement of spectroscopic and theoretical methods, new atomic ions have been found to be stable such as  $\text{Ca}^-$  and  $\text{Sr}^-$  with small electron affinities [62, 63] (about 40 meV). However, the existence of free doubly charged atomic negative ions has remained a matter of some controversy [61]. In the 1960s and 1970s, there were several experiments which claimed the detection of doubly charged atomic ions, but most of these observations have been shown to be artefacts, and no evidence of atomic dianions was observed [64, 65]. Theoretically, Lieb [66] formulated an upper bound for the maximum number  $N_c$  of electrons, that can be bound to an atomic nucleus of charge  $Z$ :  $N_c \leq 2Z$ . This inequality gives the first proof that  $\text{H}^{2-}$  is not stable, which is in agreement with experiments [65] and many *ab initio* studies [59]. There are many *ab initio* and density functional calculations [58] of the electron affinities, the minimum energy required to detach from a negative ion its extra electron to form a neutral atom plus an electron at rest, of elements in the periodic table. However, there is no conclusive evidence that stable atomic dianions exist in the gas phase.

In this section, we introduce a simple model Hamiltonian which allows us to calculate the critical nuclear charges for almost all elements in the periodic table. Analysis of electron-electron correlations in a negative atomic ion shows that one of the electrons is held much farther away from the nucleus than the other electrons [67, 68]. For example, from the accurate wavefunction of the hydride ion  $\text{H}^-$ , we

can see that  $H^-$  is composed primarily of an electron bound weakly to the field of a polarized hydrogen atom [60].

This physical picture suggests that near the critical nuclear charge the weakly bound electron can be fairly represented by a one-particle model with an effective interaction potential. This model should approximate both the short-range potential of a negative ion core with  $Z = N - 1$  electrons and the partially screened long-range Coulomb potential for  $Z \neq N - 1$ . In atomic units and with the scaling transformation  $r \rightarrow Zr$ , where  $r$  is the radial distance of the weakly bound electron from the nucleus, the model potential can be represented as

$$V(r) = -\frac{1}{r} + \frac{\gamma}{r} [1 - \exp(-\delta r)] \quad (43)$$

where  $\gamma = (N-1)\lambda$ ,  $\lambda = 1/Z$  and the free parameter  $\delta$  is chosen to make the binding energy  $E$  in the potential equal to the ionization energy of an atom (or an ion) which is known from theory [69, 70] or experiments [58, 71]. The potential of interaction between the weakly bound electron and the ion core tends to  $-1/r$  at small  $r$  and to  $(-1 + \gamma)/r$  at large  $r$ . It is easy to see that the model potential (43) correctly reproduces such an effective potential at both small  $r$  and large  $r$ . The eigenvalues of the potential (43) were found by numerical integration of the Schrödinger equation. The eigenvalues can be easily calculated for any quantum numbers  $n$  and  $l$  and any parameters  $\gamma$  and  $\delta$ .

Results of fitting the parameter  $\delta$  to the well known accurate *ab initio* energies [69] of the isoelectronic series for elements with  $2 \leq N \leq 18$  show that  $\delta$  depends on  $\gamma$  almost linearly. The behaviour of the function  $\delta(\gamma)$  near  $\gamma = 1$ , which corresponds to  $Z = N - 1$ , can be fairly well approximated by a linear dependence of the form

$$\delta = \frac{\delta_0(\gamma - \gamma_1) - \delta_1(\gamma - \gamma_0)}{\gamma_0 - \gamma_1}, \quad (44)$$

where  $\gamma_0$ , and  $\delta_0$  are parameters that correspond to the neutral atom, and  $\gamma_1$  and  $\delta_1$  to the isoelectronic negative ion (if the negative ion does not exist, we used parameters that correspond to the positive ion). The ionization energy  $E_I$  is calculated by solving the Schrödinger equation with the potential (43) at  $\gamma = (N-1)\lambda$  and  $\delta$  determined by equation (44). In essence, our method consists of extrapolation of the binding energy from two data points  $\gamma = \gamma_0 = (N-1)/N$  (neutral atom) and  $\gamma = \gamma_1 = 1$  to the region of  $\gamma \sim 1$ . For example, let us consider the ground state and the excited state  $1s2s \ ^3S$  of helium isoelectronic ions. We reproduce the ionization energy curve as a function of  $Z$  using only the energies of helium and  $H^-$  as described above within an accuracy of  $5 \times 10^{-4}$  in atomic units in comparison with the exact calculations [13]. Since the  $1s2s \ ^3S$  state is unstable for  $Z = 1$ , we used the ionization energies of  $Li^+$  (instead of  $H^-$ ) and helium to perform the extrapolation. The accuracy of extrapolation for  $1s2s \ ^3S$  state is better than  $10^{-5}$ . Our goal is to use this model to estimate the critical charge, the minimum charge necessary to bind  $N$  electrons, to any atom. The critical charge can be found from the following equation:

$$E_I(Z_c) \equiv E(N, Z_c) - E(N-1, Z_c) = 0, \quad Z_c = \frac{1}{\lambda_c}, \quad (45)$$

where  $E_I$  is the extrapolated ionization energy. Results for the critical charges, shown in table 1, for atoms with  $2 \leq N \leq 18$  are in good agreement (mostly within an accuracy of 0.01) with both the *ab initio* multireference configuration interaction

Table 1. Critical nuclear charges for  $N$ -electron atoms

Atom	$N$	$nl$	$\delta_0$	$\delta_1$	$Z_c$	$Z_c^a$
He	2	1s	1.066	0.881	0.912	0.91
Be	4	2s	0.339	0.258	2.864	2.85
C	6	2p	0.255	0.218	4.961	4.95
N	7	2p	0.242	0.213	5.862	5.85
F	9	2p	0.239	0.215	7.876	7.87
Ne	10	2p	0.232	0.211	8.752	8.74
Mg	12	3s	0.162	0.130	10.880	10.86
Si	14	3p	0.128	0.112	12.925	12.93
P	15	3p	0.123	0.110	13.796	13.78
S	16	3p	0.124	0.111	14.900	14.89
Cl	17	3p	0.120	0.109	15.758	15.74
Ar	18	3p	0.117	0.108	16.629	16.60
Kr	36	4p	0.0704	0.0661	34.614	
Xe	54	5p	0.0466	0.0442	52.590	
Hg	80	6s	0.0359	0.0338	78.650	
Rn	86	6p	0.0333	0.0317	84.518	

<sup>a</sup> Critical charges from the *ab initio* multireference configuration interaction computations of Hogreve [72].

calculations of Hogreve [72] and the critical charges extracted by us from the figures of isoelectronic energies in [70].

Our computations of critical charges were extended to atoms up to  $N = 86$ . In table 1 are listed the configurations, the parameters  $\delta$  and critical charges for selected atoms [15]. Here, we used experimental ionization energies from atomic data tables [71]. Our goal here is 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  $S_e(N) \equiv N - Z_c(N) \geq 2$ . Figure 7 shows the strong correlation between the surcharge  $S_e(N)$  and the experimental electron affinity  $EA(N - 1)$ . 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 radon and can be related to the peak of electron with affinity of the element  $N = 85$ . Experimental results for negative ions of lanthanides remain unreliable. Since the electron affinities of lanthanides are relatively small, 0.5 eV or less [58, 73], we expect that the surcharges will be small (around one). The results for the surcharges clearly excluded the existence of any stable doubly negatively charged atomic ions in the gas phase and confirms the previous speculations 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 a singly charged negative ion because of the repulsive potential surrounding the isolated negative ion. This conclusion can be reached by examining the asymptotic form of the unscaled potential

$$V(r) = -\frac{Z - N + 1}{r}. \tag{46}$$

For the doubly charged negative ions,  $N = Z + 2$ , and this potential becomes repulsive.

Proceeding from the fact that free dianions do not exist in the gas phase, it is natural to ask under which conditions, if any, one could have stable dianions. One

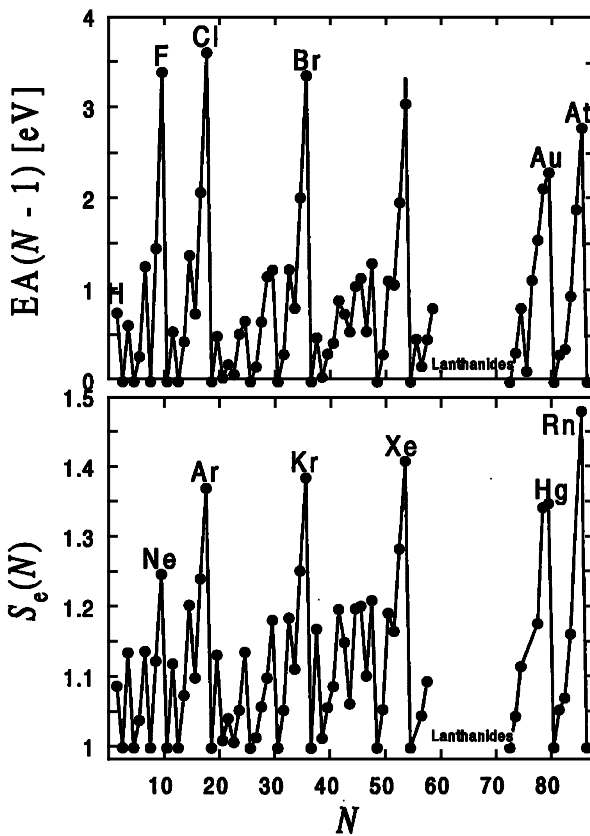


Figure 7. Experimental electron affinity,  $EA(N-1)$  compared with the calculated surcharge  $S_e(N) \equiv N - Z_c$  as functions of the number  $N$  of electrons.

possibility is to place these atoms in a strong magnetic field. In the presence of a constant magnetic field, the critical charge decreases since the atom becomes more stable. Results for the critical magnetic field  $B_c$ , the minimum field necessary to obtain the surcharge  $S_e = 2$ , for selected atoms have been listed in [15]. 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 au (1 au =  $2.35 \times 10^9$  G). However, dianions with an external s electron such as  $Ne^{2-}$ ,  $Ar^{2-}$  and  $Kr^{2-}$  do not exist at any magnetic field strength  $B$ . This can be attributed to the fact that, because of the different symmetries of s and p orbitals, the average  $\langle \rho^2 \rangle$  for a p electron will be smaller than that for an s electron and as a result the shift in the ionization energy will be larger in the presence of a magnetic field for an atom with a weakly bound p electron. Although it is not feasible to obtain such dianions in the laboratory, because of the strong magnetic field, they might be of considerable interest to models of magnetic white dwarf stellar atmospheres.

Our model Hamiltonian (43) is simple, captures the main physics of the loose electron near the critical charge, reproduces the correct asymptotic behaviour of the potential, gives very accurate numerical results for the critical charges in comparison with accurate *ab initio* calculations for atoms with  $2 \leq N \leq 18$  and is in full

agreement with the prediction of the statistical theory of the Thomas–Fermi–Von Weizsacker model of large atoms. In this theory, it was proved that  $N_c$ , the maximum number of electrons that can be bound to an atom of nuclear charge  $Z$ , cannot exceed  $Z$  by more than one [74].

Over the past few years, there has been an ongoing experimental and theoretical search for doubly charged negative molecular dianions [61]. In contrast with atoms, molecular systems can hold many extra electrons because the extra electrons can stay well separated [75]. However, such systems are challenging from both theoretical and experimental points of view. Our approach might be useful in predicting the stability of molecular dianions.

## 8. Discussion

In this review, we established an analogy between the mean-field theory of phase transitions and symmetry breaking of electronic structure configurations in the large- $D$  limit. In this context, symmetry-breaking solutions in both HF and exact solutions of  $N$ -electron atoms require new interpretations. The mapping of this problem to standard phase transitions allows us to treat the nuclear charge in an analogous fashion to the temperature in statistical mechanics.

Moreover, we have shown that the FSS method can be used indirectly to obtain critical parameters for quantum Hamiltonians by taking the lowest eigenvalues of a quantum Hamiltonian as leading eigenvalues of a transfer matrix of a classical pseudosystem. This approach was successfully used to obtain the critical charges for two- and three-electron atoms. However, we also presented a direct FSS approach to study the critical behaviour of quantum Hamiltonians without the need to make any explicit analogy to classical statistical mechanics. The critical parameters can be calculated by a systematic expansion in a finite basis set.

In this paper, we show that there are fundamental differences between short-range and long-range potentials. For the ground state of the Yukawa potential; the critical exponent  $\alpha = 2$ , the wavefunction is not normalizable at  $\lambda = \lambda_c$ , the energy curves go smoothly to zero as a function of  $\lambda$  and the second derivative develops a discontinuity in the neighbourhood of the critical point. This type of behaviour resembles a ‘continuous phase transition’. For the ground state of two-electron atoms; the critical exponent  $\alpha = 1$ , the wavefunction is normalizable at  $\lambda = \lambda_c$ , the energy curves bend over sharply at  $\lambda_c$  to become degenerate with the continuum and the first derivative develops a step-like discontinuity at  $\lambda_c$ . This resembles a ‘first-order phase transition’.

For the  $N$ -electron atoms, Morgan and co-workers [13] concluded that, although experiment has yet to find a stable doubly negative atomic ion, the critical charge obeys the following inequality:

$$N - 2 \leq Z_c \leq N - 1 \quad (47)$$

Our numerical results, using a simple one-dimensional potential, confirmed this inequality and show that, at most, only one electron can be added to a free atom in the gas phase. Research is under way to generalize this simple approach to molecular dianions.

Molecular systems are challenging from the critical phenomena point of view. In order to apply the FSS method, one needs to have a complete basis set. Modern quantum chemistry computations are generally carried out using only three types of basis set: Slater orbitals, Gaussian orbitals and plane waves, the last being reserved

primarily for extended systems in solid state. Each of these has their advantages and disadvantages. Evaluation of molecular integrals (e.g. four-centre integrals) are very difficult and time consuming with Slater basis functions. These integrals are relatively easy to evaluate with Gaussian basis functions. Research is still under way to combine the FSS method with the molecular Gaussian basis functions. Our initial results for simple one- and two-electron molecules indicate the feasibility of this approach.

This is the first review article about the analogy between symmetry breaking and phase transitions and critical phenomena for electronic structure problems in atomic and molecular physics. The field is still in its infancy and there are many open questions about the interpretations of the results. What exactly does correlation length mean for electronic structure of atoms and molecules? How do we compute the critical exponents and what do they mean? Why for the three-electron atoms and the screened Coulomb potential do the related classical pseudosystems display a continuous phase transition whereas for the two-electron atoms it displays a first-order transition? Do these quantum phase transitions really exist? There is a need to examine all these questions and the underlying structure of the critical parameters.

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### References

- [1] BINNEY, J. J., DOWRICK, N. J., FISHER, A. J., and NEWMAN, M. E. J., 1993, *The Theory of Critical Phenomena* (Oxford: Clarendon).
- [2] STANLEY, H. E., 1971, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press).
- [3] WIDOM, B., 1975, *Critical Phenomena in Fundamental Problems in Statistical Mechanics III*, edited by E. G. D. Cohen (New York: Elsevier).
- [4] SERRA, P., and KAIS, S., 1996, *Phys. Rev. Lett.* **77**, 466.
- [5] CHATTERJEE, A., 1990, *Phys. Rep.*, **186**, 249; WITTEN, E., 1980, *Phys. Today*, **33**, 38.
- [6] HERSCHBACH, D. R., AVERY, J., and GOSCINSKI, O., 1993, *Dimensional Scaling in Chemical Physics* (Dordrecht: Kluwer).
- [7] TSIPIS, C. A., POPOV, V. S., HERSCHBACH, D. R., and AVERY, J. S., 1996, *New Methods in Quantum Theory* (Dordrecht: Kluwer); GOODSON, D. Z., and HERSCHBACH, D. R., 1987, *Phys. Rev. Lett.*, **58**, 1628; DUDLEY HERSCHBACH Festschrift, 1993, *J. Phys. Chem.*, **97**; GERMANN, T. C., 1996, *J. Chem. Phys.*, **104**, 5100; HERSCHBACH, D. R., 1996, *Int. J. Quant. Chem.*, **57**, 295; KAIS S., and BLEIL, R., 1995, *J. Chem. Phys.* **102**, 7472.
- [8] LOESER, J. G., 1987, *J. Chem. Phys.*, **86**, 5635.
- [9] NEIROTTI, J. P., SERRA, P., and KAIS, S., 1997, *Phys. Rev. Lett.*, **79**, 3142.
- [10] FISHER, M. E., 1971, In *Critical Phenomena, Proceedings of the 51st Enrico Fermi Summer School*, Varenna, Italy, edited by M. S. Green (New York: Academic Press).
- [11] PRIVMAN, V. (editor), 1990, *Finite Size Scaling and Numerical Simulations of Statistical Systems* (Singapore: World Scientific).
- [12] NIGHTINGALE, M. P., 1976, *Physica A*, **83**, 561.
- [13] BAKER, J. D., FREUND, D. E., HILL, R. N., and MORGAN, J. D., 1990, *Phys. Rev. A*, **41**, 1247.
- [14] SERRA, P., NEIROTTI, J. P., and KAIS, S., 1998, *Phys. Rev. Lett.* **80**, 5293.

- [15] SEGEEV, A. V., and KAIS, S., 1999, *Int. J. Quant. Chem.*, **75**, 533.
- [16] KAIS, S., SUNG, S. M., and HERSCHBACH, D. R., 1994, *Int. J. Quant. Chem.*, **49**, 657.
- [17] FRANTZ, D. D., and HERSCHBACH, D. R., 1988, *Chem. Phys.*, **126**, 59; 1990, *J. Chem. Phys.*, **92**, 6688.
- [18] DUNN, M., GERMANN, T. C., GOODSON, D. Z., TRAYNOR, C. A., MORGAN III, J. D., WATSON, D. K., and HERSCHBACH, D. R., 1994, *J. Chem. Phys.*, **101**, 5987.
- [19] CABRERA, M., TAN, A. L., and LOESER, J. G., 1993, *J. Phys. Chem.*, **97**, 2467.
- [20] GOODSON, D. Z., and HERSCHBACH, D. R., 1987, *J. Chem. Phys.*, **86**, 4997; DOREN, D. J., and HERSCHBACH, D. R., 1988, *J. Phys. Chem.* **92**, 1816.
- [21] SERRA, P., and KAIS, S., 1997, *Phys. Rev. A* **55**, 238.
- [22] SERRA, P., and KAIS, S., 1996, *Chem. Phys. Lett.* **260**, 302.
- [23] SERRA, P., and KAIS, S., 1997, *J. Phys. A*, **30**, 1483.
- [24] BARBER, M. N., 1983, *Phase Transitions and Critical Phenomena* Vol. 8, edited by C. Domb and J. L. Lebowits (London: Academic Press).
- [25] CARDY, J. L., 1988, *Finite-Size Scaling* (New York: Elsevier).
- [26] THOMPSON, C. J., 1988, *Classical Statistical Mechanics* (Oxford: Clarendon).
- [27] GANTMACHER, F. R., 1959, *The Theory of Matrices* (New York: Chelsea).
- [28] NIGHTINGALE, M. P., 1979, *Meded. Koninklijke Ned. Akad. Wetenschappen*, Ser. B, **82**, 235.
- [29] BEALE, P. D., DUXBURY, P. M., and YEOMANS, J., 1985, *Phys. Rev. B* **31**, 7166.
- [30] DERRIDA, B., 1981, *J. Phys. A* **14**, L5; DERRIDA, B., and SALEUR, H., 1985, *J. Phys. A*, **18**, L1075.
- [31] SERRA, P., and STILCK, J. F., 1982, *Europhys. Lett.*, **17**, 423; 1994, *Phys. Rev. E*, **49**, 1336.
- [32] DERRIDA, B., and DE SEZE, L., 1982, *J. Phys. Paris*, **43**, 475.
- [33] REYNOLDS, P. J., STANLEY, H. E., and KLEIN, W., 1980, *Phys. Rev. B*, **21**, 1223.
- [34] GLUMAC, Z., and UZELAC, K., 1989, *J. Phys. A*, **22**, 4439.
- [35] PAULING, L., and WILSON, E. B., 1963, *Introduction to Quantum Mechanics* (New York: Dover Publications).
- [36] SIMON, B., 1977, *J. Functional Anal.* **25**, 338.
- [37] MERZBACHER, E., 1970, *Quantum Mechanics*, second edition (New York: Wiley).
- [38] BULIRSCH, R., and STOER, J., 1964, *Numer. Math.* **6**, 413.
- [39] HENKEL, M., *Finite Size Scaling and Numerical Simulations of Statistical Systems*, edited by V. Privman (Singapore: World Scientific) chapter VIII.
- [40] NEIROTTI, J. P., SERRA, P., and KAIS, S., 1998, *J. Chem. Phys.*, **108**, 2765.
- [41] KLAUS, M., and SIMON, B., 1980, *Ann. Phys. (NY)*, **130**, 251.
- [42] SERRA, P., NEIROTTI, J. P., and KAIS, S., 1998, *Phys. Rev. A*, **57**, R1481.
- [43] FLÜGGE, S., 1974, *Practical Quantum Mechanics* (Berlin: Springer).
- [44] SERRA, P., NEIROTTI, J. P., and KAIS, S., 1998, *J. Phys. Chem. A*, **102**, 9518.
- [45] HOFFMANN-OSTENHOF, M., HOFFMANN-OSTENHOF, T., and SIMON, B., 1983, *J. Phys. A*, **16**, 1125.
- [46] DRAKE, G. W. F., and YAN, Z.-C., 1994, *Chem. Phys. Lett.*, **229**, 489.
- [47] HYLLERAAS, E. A., 1928, *Z. Phys.*, **48**, 469.
- [48] BHATIA, A. K., and TEMKIN, A., 1964, *Rev. mod. Phys.*, **36**, 1050.
- [49] IVANOV, I. A., 1995, *Phys. Rev. A*, **51**, 1080.
- [50] BRĀNDAS, E., and GOSCINSKI, O., 1970, *Int. J. quant. Chem.*, **4**, 571.
- [51] BRĀNDAS, E., and GOSCINSKI, O., 1972, *Int. J. quant. Chem. Symp.*, **6**, 59.
- [52] ARTECA, G. A., FERNÁNDEZ, F. M., and ASTRO, E. A., 1986, *J. Chem. Phys.*, **84**, 1624.
- [53] MIDTDAL, J., 1965, *Phys. Rev.*, A, **138**, 1010.
- [54] STILLINGER, F. H., 1979, *J. Math. Phys.*, **20**, 1891.
- [55] YAN, Z., and DRAKE, G. W. F., 1995, *Phys. Rev. A*, **52**, 3711.
- [56] DRAKE, G. W. F., and YAN, Z., 1995, *Phys. Rev. A* **52**, 3681.
- [57] MASSEY, H. S., 1976, *Negative Ions*, third edition (Cambridge University Press).
- [58] HOTOP, H., and LINEBERGER, W. C., 1985, *J. Phys. Chem. Ref. Data*, **15**, 1.
- [59] BATES, D. R., 1990, *Adv. at. mol. opt. Phys.*, **27**, 1.
- [60] BERRY, R. S., 1969, *Chem. Rev.* **69**, 533.
- [61] SCHELLER, M. K., COMPTON, R. N., and CEDERBAUM, L. S., 1995, *Science* **270**, 1160.
- [62] PEGG, D. J., THOMPSON, J. S., COMPTON, R. N., and ALTON, G. D., 1987, *Phys. Rev. Lett.* **59**, 2267.

- [63] BERKOVITS, D., BOARETTO, E., GHELBERG, S., HEBER, O., and PAUL, M., 1995, *Phys. Rev. Lett.* **75**, 414.
- [64] SPENCE, D., CHUPKA, W. A., and STEVENS, C. M., 1982, *Phys. Rev. A*, **26**, 654.
- [65] CHANG, K. H., MCKEOWN, R. D., MILNER, R. G., and LABRENZ, J., 1987, *Phys. Rev. A*, **35**, 3949.
- [66] LIEB, E. H., 1984, *Phys. Rev. Lett.* **52**, 315.
- [67] KAIS, S., NEIROTTI, J. P., and SERRA, P., 1999, *Int. J. Mass Spectrometry*, **182–183**, 23.
- [68] RAU, A. R. P., 1996, *J. Astrophys. Ast.* **17**, 113.
- [69] CHAKRAVORTY, S. J., GWALTNEY, S.R., and DAVIDSON, E. R., 1993, *Phys. Rev. A*, **47**, 3649.
- [70] CHAKRAVORTY, S. J., and DAVIDSON, E. R., 1996, *J. phys. Chem.* **100**, 6167.
- [71] SUGAR, J., and CORLISS, C., 1985, *J. phys. Chem. Ref. Data* **14**, Suppl.; MOORE, C. E., 1971, *Natn. Stand. Ref. Dat. Ser., Natn. Bur. Stand. (US)*, **35**, Vols 1–3.
- [72] HOGREVE, H., 1998, *J. Phys. B*, **31**, L439.
- [73] NADEAU, M. J., GARWAN, M. A., ZHAO, X. L., and LITHERLAND, A. E., 1997, *Nucl. Instrum. Meth. B*, **123**, 521.
- [74] BENGURIA, R., and LIEB, E. H., 1985, *J. Phys. B*, **18**, 1045.
- [75] WANG, X. B., DING, C. F., and WANG, L. S., 1998, *Phys. Rev. Lett.* **81**, 3351.