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Phase transitions and the stability of atomic and molecular ions

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Abstract

Quantum phase transitions at absolute zero temperature can take place as some parameter in the Hamiltonian of the system is varied. For such transitions, crossing the phase boundary means that the quantum ground state changes in some fundamental way. 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 here a method to calculate the critical nuclear charge for which an atom can bind an extra electron to form a stable negative ion. The estimate of the critical nuclear charge will be used to explain and predict the stability of atomic negative ions. The method can be generalized to predict the stability of molecular negative ions. A detailed calculation for the critical parameters for two center molecular ions is also included. (Int J Mass Spectrom 182/183 (1999) 23–29) © 1999 Elsevier Science B.V.

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1. Introduction

Negative ions are of fundamental importance in atomic and molecular physics. With the advancement of spectroscopic and theoretical methods new ions have been found to be stable with small electron affinities. Recently, Pegg et al. [1] used photoelectron detachment spectroscopy to show that the Ca^- ion is stable with an electron affinity of 0.043 ± 0.007 eV. This result is unexpected because in the past it has been generally believed that negative ions of all alkaline earths group elements are unstable. The Periodic Table of the negative atomic ions is still only beginning to be understood and there is no systematic way to describe them. 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 dimensional scaling method and the large dimensional limit model of electronic structure configurations [2].

Dimensional scaling method has become a common technique for simplifying complicated problems in three-dimensional space. In this method one takes the dimension of space, D, as a variable, solves the problem at some dimension $D \neq 3$, where the physics becomes much simpler, and then uses perturbation theory or other techniques to obtain an approximate result for $D = 3$ [3]. For electronic structure of the

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Dedicated to the memory of Professor Ben Freiser.

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N-electron atoms, the pseudoclassical $D \rightarrow \infty$ limit is simple and gives unique geometrical configurations [4]. 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 establish 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 the N-electron atoms [5], 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 complete mapping can be represented with the following analogies [2]: (i) nuclear charge ↔ temperature, (ii) external electric field ↔ ordering field, (iii) ground state energy ↔ free energy, (iv) asymmetry parameter ↔ order parameter, and (v) stability limit point (critical charge, Z_c) ↔ critical point (critical temperature, T_c). Using this scheme, we can define and calculate the critical exponents (α, β, δ, and γ) for the symmetry breaking of electronic structure configurations [2].

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 behavior 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 [6]. By searching for a fixed point of the phenomenological renormalization equation, the critical charge is found $Z_c \simeq 0.911$, which is in complete agreement with previous calculations [7]. 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 $Z_c \simeq 2$, which explains why He^- is an unstable ion [8].

In the next section we will briefly review the finite size scaling method and the results for two and three electron atoms. In Sec. 3 we will estimate the critical charges for negative ions form Be up to Ar. Sec. 4 generalizes the atomic calculations of the critical parameters to small molecular systems. Finally, we give the conclusions and discuss the possibility of describing the negative ions of the elements in a systematic way.

2. Finite size scaling method

The finite size scaling method was formulated in statistical mechanics to extrapolate information obtained from a finite system to the thermodynamic limit [9,10]. In quantum mechanics, when using variation methods, one encounters the same finite size problem in studying the critical behavior of a quantum Hamiltonian $\mathcal{H}(\lambda_1, \cdots, \lambda_k)$ 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 nonanalytic. In this study, a critical point is defined as the point where a bound state energy becomes absorbed or degenerate with a continuum. In this case, the finite size corresponds to the number of elements in a complete basis set used to expand the exact wave function of a given Hamiltonian.

To carry out the calculations for the critical parameters $\{\lambda_i\}$, one should proceed with the following scheme [6,11]: (i) choose a convenient orthonormal basis set and calculate the matrix elements of the Hamiltonian, (ii) calculate the two leading eigenvalues of the finite Hamiltonian (of order N) matrix and their corresponding correlation length of the classical pseudosystem

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

(iii) use the phenomenological renormalization equation to obtain a sequence of pseudocritical parameters $\lambda^{(N)}$

$$\frac{\xi_N(\lambda^{(N,N')})}{N} = \frac{\xi_{N'}(\lambda^{(N,N')})}{N'} \tag{2}$$

where N is the order of the Hamiltonian matrix and $N' = N - 1$, except when there are parity effects, then one has to take $N' = N - 2$, and finally (iv) extrapolate the values of the sequences to obtain the critical parameters in the limit $N \to \infty$.

The finite size scaling (FSS) procedure was carried out for the two and three electron atoms with very accurate results for the critical nuclear charges. Results show that the analytical behavior of the energy as a function of the nuclear charge for lithium is completely different from that of helium. The first derivative of the ionization energy with respect to the nuclear charge develops a steplike discontinuity at $Z_c^{\mathrm{He}} \simeq 0.91$ for the heliumlike atoms but remains continuous for the lithiumlike atoms at $Z_c^{\mathrm{Li}} \simeq 2$. Analogy with standard phase transitions show that for helium, the transition from a bound state to a continuum is “first order” [12], while lithium exhibits a “second order phase transition” [8].

3. *N*-Electron atoms

For the N-electron atoms, there are well known inequalities for the minimum charge Z_c necessary to bind N electrons [7]. Lieb [13] has proved that N_c, the number of negative particles that can be bound to an atom of nuclear charge Z, satisfies $N_c < 2Z + 1$. Currently, as far as we know, there is no numerical estimates of the critical nuclear charges except for two [7] and three electron atoms [8] and Herrick and Stillinger’s estimates of Z_c for the neon isoelectronic sequence, $Z_c \simeq 8.77$ [14]. Now our previous analysis can be generalized to include the general N-electron atoms. Especially, the first 18 atoms, where very accurate ground state energies, $E(N, Z)$, as a function of both the number of electrons, N, and the nuclear charge, Z, are available [15]. The search for the critical nuclear charge as a function of the number of electrons will be performed using the following equation

Table 1
Approximate critical charges for N-electron atoms

Number of electrons, N	Critical charge, Z_c	Number of electrons, N	Critical charge, Z_c
2	0.91	11	10.21
3	2.08	12	10.96
4	2.87	13	12.14
5	4.10	14	12.98
6	4.98	15	13.82
7	5.87	16	14.93
8	7.03	17	15.80
9	7.89	18	16.63
10	8.76		

$$E(N, Z_c) = E(N - 1, Z_c) \tag{3}$$

The solution of this equation, $Z_c(N)$, means the minimum charge necessary to bind N electrons. For neutral atoms, with $N = Z$, the nonrelativistic ground state energies can be simply written as

$$E(N, Z) = Z^2 \sum_{i=0} C_i(N)\left(\frac{1}{Z}\right)^i \tag{4}$$

The leading coefficients C_0 and C_1 are known exactly [15], the rest of the expansion coefficients where determined by numerically fitting to the reported accurate energies [16]. In this study, we approximated the energies with seventh order polynomials.

The results of Z_c as a function of N are given in Table 1 and shown in Fig. 1. Above the stability line of $Z = N - 1$, there are five unstable atomic ions, He^-, Be^-, N^-, Ne^-, Mg^-, which means that the Z_c is less than or equal $Z = N - 1$ and these atoms cannot bind an extra electron. For the rest of the atoms up to Cl, the value of Z_c is below the line $Z = N - 1$, and all atoms can bind an extra electron to form stable negative ions. These results are in complete agreement with the experimentally recommended electron affinities [17], which is the measure of the ability of an atom to bind an additional electron.

4. Two center molecular ions

For molecular systems, the analogy between symmetry breaking and phase transitions has already been

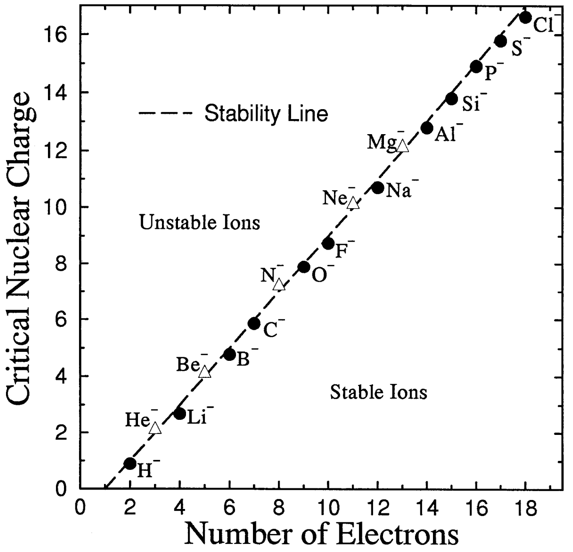

Fig. 1. Critical charges for N-electron atoms, Z_c, as a function of the number of electrons N.

established at the large-D limit [18]. 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 one can perform the following mapping [2]: (i) inverse nuclear distance $(1/R)$ ↔ temperature T, (ii) difference between the nuclear charges Δ ↔ ordering field h, (iii) ground state energy $E_\infty(R, \Delta)$ ↔ free energy $f(T, h)$, (iv) asymmetry parameter $\psi \equiv -(\partial E_\infty(R, \Delta)/\partial\Delta)$ ↔ order parameter $m \equiv -(\partial f(T, h)/\partial h)$, and (v) stability limit point $(R_c, \Delta = 0)$ ↔ critical point $(T_c, h = 0)$.

The hydrogen molecular ion exhibits a critical point with mean field critical exponents [2]. For the Hartree–Fock hydrogen molecule at the large-D limit symmetry breaking of the electronic structure configurations was also described as standard phase transitions which characterized by a bicritical point. This procedure was generalized to mean field phase diagrams for one-electron molecules [18].

Now let us carry out the analysis of stability of molecular systems at the physical space, $D = 3$. As an example we present detailed calculations for the simplest molecular systems, the one electron two-center Coulomb systems. For this system, the nuclei A and B are located on the z axis at $z_A = -R/2$ and $z_B = +R/2$ with nuclear charges, Z_a and Z_b, respectively; the electron is located at (ρ, z), where ρ is the distance from the z axis.

In the Born-Oppenheimer approximation, the ground state energy is then parametrically dependent upon the internuclear distance R and the difference between the nuclear charges. To investigate the analytical behavior of the energy as a function of both parameters, we used the variational method.

The Hamiltonian of the system can be written in atomic units as:

$$\mathcal{H}(R, Z_a, Z_b) = -\frac{1}{2}\nabla^2 - \frac{Z_a}{r_a} - \frac{Z_b}{r_b} + \frac{Z_aZ_b}{R} \qquad (5)$$

where r_a, r_b are the electron-nuclear distances. Under the transformation $r \rightarrow r/R$ the eigenvalues of the Hamiltonian transform as $E \rightarrow ER^2$ and the Hamiltonian (5) in prolate spheroidal coordinates takes the form

$$\begin{aligned}\mathcal{H}(R, Z_a, Z_b) = -\frac{2}{\lambda^2-\mu^2}\Bigg\{&\frac{\partial}{\partial\lambda}(\lambda^2-1)\frac{\partial}{\partial\lambda}\\ &+\frac{\partial}{\partial\mu}(1-\mu^2)\frac{\partial}{\partial\mu}\\ &+R[(Z_a+Z_b)\lambda\\ &+(Z_a-Z_b)\mu]\Bigg\} + Z_aZ_bR \qquad (6)\end{aligned}$$

and the Jacobian of the transformation is given by

$$\mathcal{J} = \tfrac{1}{8}(\lambda^2-\mu^2) \qquad (7)$$

To carry out the variational calculations, we used the following complete basis set

$$\Phi_{l,m}(\lambda, \mu) = \exp\left(-\frac{\lambda-1}{2}\right)L_m(\lambda-1)\,P_l(\mu) \qquad (8)$$

where P_l is the Lagrange polynomial of degree l and L_m is the Laguerre polynomial of degree m and order 0 [19].

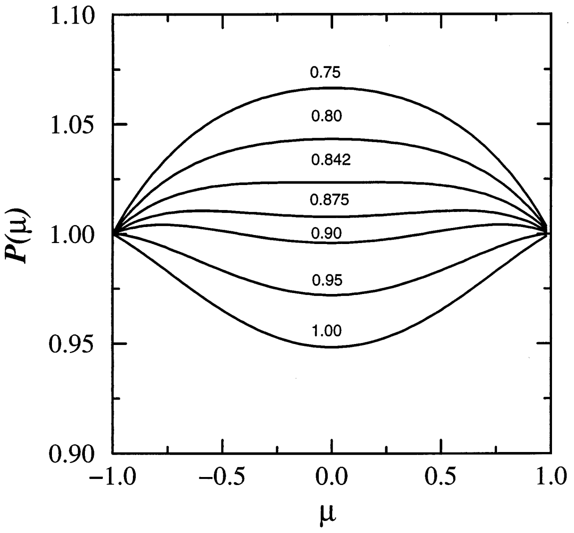

Fig. 2. The probability density $P(\mu;\, R)$ as a function of μ for several values of R.

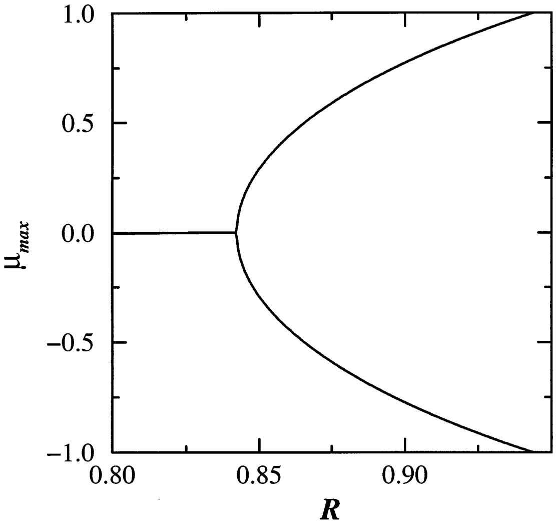

Fig. 3. Position of the probability maxima $\mu_{\max}$ as a function of R. It is shown here the fork shaped region at which the double maxima regime starts to develop.

If we fixed $Z_a = Z_b = 1$ in (6), one recovers the Hamiltonian of the H_2^+ molecular ion. There is no nonanalytical behavior of the ground state energy as a function of the parameter R in the present approximation. This behavior can be understood by taking into account that electron tunneling between the two centers has an exponential decay in the internuclear distance. This means that tunneling is there even for large distances and the ground state energy curve does not cut the hydrogen threshold at finite R [20,21].

In order to study the behavior of the ground state wave function as R is varied, let us define the following probability density function:

$$P(\mu;\, R) = \int_1^\infty d\lambda\ \mathcal{J}(\lambda,\, \mu)|\Psi_0(\lambda,\, \mu;\, R)|^2 \tag{9}$$

where Ψ_0 is the ground state wave function. This function represents the probability density of finding the electron at μ when the distance between the two centers is fixed at R. In Fig. 2 we plot the probability density P as a function of μ for different values of R. It is easy to see that at small and large values of R the curves have different behavior. For small R, the curves show just one maximum at $\mu = 0$, which means that the electron has high probability to be found in the plane $(x,\, y,\, 0)$, perpendicular to the z axis. For large R the curves have two maxima, which means that it has a minimum in the symmetry plane and the electron has the same probability to be found near one or the other center. Fig. 3 shows the position of the maxima $\mu_{\max}$ as a function of R. There is a fork shaped region, $0.8420(5) \leq R \leq 0.9432(5)$ in which the transition from one maxima to two takes place.

If we fix $Z_a = 1$ and $Z_b = Z > 1$ the system suffers a drastic change. The symmetry of the system is already broken because the difference between the two charges $\Delta Z = Z - 1$ plays the role of an external field [2].

The energy curves E_0/Z^2 as a function R can be classified into two classes: (i) below a certain value of the nuclear charge $Z^* = 1.271\ 156\ 7(5)$ the energy curve has a minimum and the ion is stable and (ii) above Z^* the curve has no minimum and the ion is not stable. The transition between these two regimes is analytical, though the behavior of the system is rather different. We expect that all curves below Z^* might develop a long range barrier and then metastable states exist with a long mean lifetime. At the Z^* the system exhibits an inflection point with $R^* =$

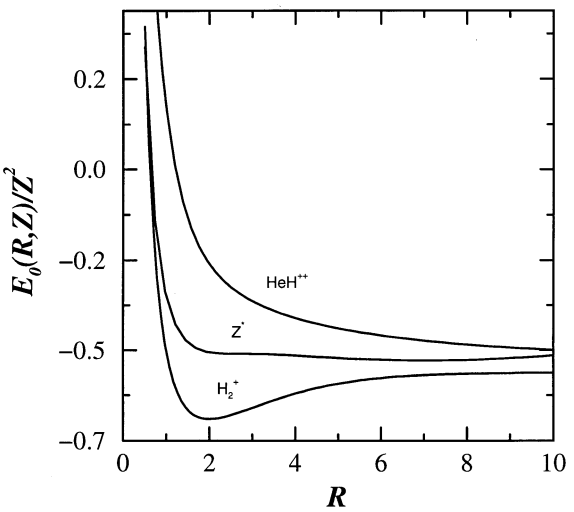

Fig. 4. Ground state energy in units of the hydrogen threshold energy, as a function of the internuclear distance R for several values of the nuclear charge Z.

2.715 320 6(5). The energy curve at this point has a cubic behavior as a function of R and linear as a function of Z. The behavior of the energy curves for large R is asymptotically the same, all of them approach the hydrogen atom threshold form above. In Fig. 4 we plot the energy curves for the cases H_2^+, Z^*, and HeH^{++}. In this figure one can see that the ion HeH^{++} is not stable, the ground state energy curve is repulsive, in agreement with previous results [22].

5. Discussions

The FSS method of searching for Z_c for a given atom, Eq. (2) is general and can be extended to the whole Periodic Table of elements if one is provided with a convenient basis set. In this article for atoms larger than Be we used the already existing ground state energies as a function of both the number of electrons and the nuclear charge. These calculations for the critical nuclear charges were in good agreement with the exact FSS results for He and Li atoms. Although we examined in this article only the first 18 atoms using the nonrelativistic ground state energies, this approach can be generalized to include the heavy elements as well. However, for heavy atoms, one has to include the relativistic effects. The search for the critical charges using Eq. (3) is limited to obtain an approximate critical charge and does not give information about the analytical behavior of the energies near the critical charge nor does it give the critical exponents. For molecular systems, the energy for H_2^+ is an analytical function of R, but one should expect a nonanalytical behavior for larger molecular systems, for which the electron–electron interaction becomes very important. The advantages of this approach for molecular systems is that once you calculate the critical geometry you can predict which molecular system will be stable.

This approach to explain the stability of atomic negative ions as a kind of "quantum phase transition" [23] generate a number of open questions which should be addressed: (i) what is the order of such "phase transitions"? (ii) what are the critical exponents? do all elements belong to the same or different universality classes? (iii) how to compute critical parameters for molecular systems? and finally (iv) what is the relevant correlation length and what its physical meaning? In principle, the phenomenological renormalization equations in the finite-size scaling approach might address these questions. In practice, the complexity of large systems and the lack of complete basis sets to obtain accurate critical parameters invites developing new approximations within the finite-size scaling approach.

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