Critical conditions for stable dipole-bound dianions

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We present finite size scaling calculations of the critical parameters for binding two electrons to a finite linear dipole field. This approach gives very accurate results for the critical parameters by using a systematic expansion in a finite basis set. A complete ground state stability diagram for the dipole-bound dianion is obtained using accurate variational and finite size scaling calculations. We also study the near threshold behavior of the ground state energy by calculating its critical exponent. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2822285]

I. INTRODUCTION

Recently, there has been increasing interest in multipole-bound negative ions.[1,2] Negative ions play an important role in stellar and terrestrial atmospheres as well as in laboratory and cosmic plasmas.[3,4] For the case of dipole-bound negative ions, the outer electron is weakly bound by the dipole moment of a neutral molecule in a diffuse orbital localized at the positive end of the dipole. Fermi and Teller,[5] have shown that, within the context of the Born-Oppenheimer approximation, molecules with dipole moments greater than $\mu_c = 1.625$ D (0.655 a.u.) can bind an electron to form dipole-bound anions.[5–12] The ground state energy of the system tends to zero exponentially as the dipole moment reaches its critical value.[13,14] However, subsequent experimental and computational studies taking into account corrections to the Born-Oppenheimer approximation give a more realistic estimate of $\mu_c = 2.5$ D.[15–22]

Skurski *et al.*[23] have examined the problem of the binding of two electrons in a dipole field of a neutral molecule. They have demonstrated computationally the existence of dipole-bound dianions of different molecules.[24] Silanes *et al.*[25] performed a full configuration interaction calculations for two electrons moving in the field of a fixed finite dipole in order to determine the conditions for stability relative to one electron detachment.

In this paper, we present variational and finite size scaling calculations of the critical parameters for binding two electrons to a finite dipole field. This approach gives very accurate results for the critical parameters by using a systematic expansion in a finite basis set. The paper is organized as follows. In Sec. II, we briefly review the finite size scaling and variational methods in quantum mechanics. The model is presented in Sec. III. In Sec. IV, we give the numerical results for the two electron dipole. We present a complete ground state stability diagram and we show how is the behavior of the energy near the critical parameters. Finally, the conclusions are given in Sec. V.

II. NEAR THRESHOLD CALCULATIONS IN QUANTUM MECHANICS

We are interested in the critical behavior of a given quantum Hamiltonian $\mathcal{H}(\lambda_1, \ldots, \lambda_k)$ as a function of its set of parameters $\{\lambda_i\}$.[26,27] In this context, critical means the values of $\{\lambda_i\}$ for which a bound state energy is nonanalytic. In many cases, this critical point is the point where a bound state energy becomes absorbed or degenerate with a continuum.[28] Let us consider the following Hamiltonian of the form

$$\mathcal{H} = \mathcal{H}_0 + V(\lambda_1, \lambda_2, \ldots, \lambda_k), \tag{1}$$

where $\mathcal{H}_0$ is λ-independent and V is the λ-dependent term. In atomic and molecular physics, the parameters λ_i could be the nuclear charges, internuclear distances, multipolar moments, etc. We are interested in the study of how the different properties of the system change when the value of λ_i varies. In this work, we vary one of the parameters λ_i keeping the rest $\lambda_{j\neq i}$ constant. Without loss of generality, we will assume that the Hamiltonian [Eq. (1)] has a bound state $E(\lambda_1, \lambda_2, \ldots, \lambda_k)$ for $\lambda_i > \lambda_i^c \forall i$, which becomes equal to the threshold energy at $\lambda_i = \lambda_i^c$. The asymptotic behavior of $E(\lambda_1, \lambda_2, \ldots, \lambda_k)$ near λ_i^c defines the critical exponent α_i. The critical exponent characterizes the near threshold behavior of the energy; therefore, we expect different values for α if the system has many possible thresholds. In our case, in the Born-Oppenheimer approximation, the two electron system has a unique threshold corresponding to a simple ionization, then $\alpha_i = \alpha$, $i = 1, \ldots, k$,

$$E(\lambda_1, \lambda_2, \ldots, \lambda_k) - \mathcal{E}_{\text{th}} \underset{\lambda_i \to \lambda_i^{c+}}{\sim} (\lambda_i - \lambda_i^c)^{\alpha}, \qquad \lambda_j = \text{const} \quad \text{for } j \neq i, \tag{2}$$

where $\mathcal{E}_{\text{th}}$ is the threshold energy which is a function of a subset of the parameters $\{\lambda_1, \lambda_2, \ldots, \lambda_k\}$.

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In order to perform numerical calculations, we choose a λ-independent basis set $\{\Phi_n\}$; the ground state eigenfunction has the following expansion:

$$\Psi_{\{\lambda_i\}} = \sum_n a_n(\lambda_1, \lambda_2, \ldots, \lambda_k)\Phi_n, \tag{3}$$

where n represents an adequate set of quantum numbers. In order to approximate the different quantities, we have to truncate the series [Eq. (3)]. The truncation is made, giving the maximum value N that can take one or more quantum numbers (usually, the principal quantum number), and we call it truncation at order N. Then, calculations are done in a subspace of dimension $M(N)$, where $M(N)$ is the actual number of basis functions. Then, the Hamiltonian is now represented by an $M \times M$ Hermitian matrix [see below, Eqs. (20) and (21) for the two electron dipole case]. Using the Ritz variational method,[29,30] we can evaluate an upper bound of the ground state energy of the quantum Hamiltonian (1). We solve the generalized eigenvalue problem,

$$\det(H - \Lambda S) = 0, \tag{4}$$

where Λ is an eigenvalue, and the matrix elements are given by

$$H_{ij} = \langle \Phi_i | \mathcal{H} | \Phi_j \rangle, \quad S_{ij} = \langle \Phi_i | \Phi_j \rangle. \tag{5}$$

The lowest eigenvalue of Eq. (4) is a variational upper bound to the ground state energy $E_0^{(N)}(\lambda_1, \lambda_2, \ldots, \lambda_k)$ and the elements of the correspondent eigenvector determines the coefficients $a_n^{(N)}(\lambda_1, \lambda_2, \ldots, \lambda_k)$ needed for the evaluation of the ground state wave function $\Psi_{0\{\lambda_i\}}^{(N)}$. We can evaluate critical parameters $\{\lambda_i^c\}$ extrapolating the values obtained from the conditions

$$[E_0^{(N)}(\lambda_1, \lambda_2, \ldots, \lambda_k) - \mathcal{E}_{\text{th}}]|_{\lambda_i = \lambda_i^{c(N)}} = 0, \tag{6}$$

but this method does not provide critical exponents. At this point, we can obtain a ground state stability diagram in the k-dimensional space.

Finite size scaling (FSS) provides an alternative approach to evaluate critical parameters and critical exponents. This method has been developed for studying critical conditions in quantum mechanics.[26,27] In this approach, *finite size* corresponds to the number of elements in a basis set used to expand the exact wave function of a given Hamiltonian. From here, in order to simplify notation, we are going to make explicit just the parameter λ_i that we vary, all the other parameters are fixed $\lambda_j > \lambda_j^c \forall j \neq i$. In particular, to obtain the critical exponent α for the energy, we define the following functions:[27]

$$\Delta_{\mathcal{H}}(\lambda_i; N, N') = \frac{\ln(I_{\lambda_i}^{(N)}/I_{\lambda_i}^{(N')})}{\ln(N'/N)}, \tag{7a}$$

$$\Delta_{\partial\mathcal{H}/\partial\lambda_i}(\lambda_i; N, N') = \frac{\ln((\partial I_{\lambda_i}^{(N)}/\partial\lambda_i)/(\partial I_{\lambda_i}^{(N')}/\partial\lambda_i))}{\ln(N'/N)}, \tag{7b}$$

where I_{λ_i} is the ionization energy, $I_{\lambda_i} \equiv E_0 - \mathcal{E}_{\text{th}}$. From Eq. (7), we define the function

$$\Gamma(\lambda_i; N, N') = \frac{\Delta_{\mathcal{H}}(\lambda_i; N, N')}{\Delta_{\mathcal{H}}(\lambda_i; N, N') - \Delta_{\partial\mathcal{H}/\partial\lambda_i}(\lambda_i; N, N')}, \tag{8}$$

which is independent of the values of N and N' at the critical point $\lambda_i = \lambda_i^c$. The particular value of Γ at $\lambda_i = \lambda_i^c$ is the critical exponent α for the ground state energy, as defined in Eq. (2),[27]

$$\alpha = \Gamma(\lambda_i = \lambda_i^c; N, N'). \tag{9}$$

Actually Eqs. (8) and (9) are asymptotic expressions. For three different values of N, N', and N'' (we choose $N' = N-1$ and $N'' = N+1$), the curves of $\Gamma(\lambda_i, N)$ as a function of λ_i will intersect at successions of pseudocritical points $\lambda_i^{c(N)}$,

$$\Gamma(\lambda_i = \lambda_i^{c(N)}; N-1, N) = \Gamma(\lambda_i = \lambda_i^{c(N)}; N, N+1), \tag{10}$$

giving also a set of pseudocritical exponents,

$$\alpha^{(N)} = \Gamma(\lambda_i^{c(N)}; N). \tag{11}$$

The successions of values of $\lambda_i^{c(N)}$ and $\alpha^{(N)}$ can be used to obtain the extrapolated values of λ_i^c and α.[28,31]

This general approach has been successfully applied to calculate the critical parameters for two electron atoms,[26] three electron atoms,[32] simple diatomic molecules,[33,34] one electron dipole,[12] one electron quadrupole,[35] stability of three-body Coulomb systems,[36] criticality of atomic Shannon information entropy,[37] and crossover phenomena and resonances in quantum systems.[38]

III. TWO ELECTRONS IN AN ELECTRIC-DIPOLE FIELD

The Hamiltonian for two electrons in a dipole field in the Born-Oppenheimer approximation in a.u. is given by

$$\mathcal{H} = \sum_{i=1}^{2} \left[-\frac{1}{2}\nabla_i^2 - Q\left(\frac{1}{|\mathbf{r}_i - \mathbf{R}/2|} - \frac{1}{|\mathbf{r}_i + \mathbf{R}/2|} \right) \right] + \frac{1}{r_{12}}, \tag{12}$$

where the nuclei with charges Q and $-Q$ ($Q > 0$) are located in the z axis at $R/2$ and $-R/2$, respectively, and r_{12} is the interelectronic distance. The Hamiltonian could be scaled in both Q and R variables. Scaling in R,

$$\mathcal{H}(Q, R, \mathbf{r}) = \frac{1}{R^2}\mathcal{H}_s(\lambda_1, \lambda_2, \mathbf{r}/R), \tag{13}$$

where $\lambda_1 = QR$, $\lambda_2 = R$, and

$$\mathcal{H}_s = \sum_{i=1}^{2} \left[-\frac{1}{2}\nabla_i^2 - \lambda_1\left(\frac{1}{|\mathbf{r}_i - \hat{k}/2|} - \frac{1}{|\mathbf{r}_i + \hat{k}/2|} \right) \right] + \frac{\lambda_2}{r_{12}}. \tag{14}$$

It is useful for the study of the critical conditions to identify the threshold, in this case, the one electron dipole. For this purpose, Hamiltonian (14) can be written as

$$\mathcal{H}_s = h(\lambda_1, \mathbf{r}_1) + h(\lambda_1, \mathbf{r}_2) + \frac{\lambda_2}{r_{12}}, \tag{15}$$

where h is the one electron dipole Hamiltonian,

$$h(\lambda_1,\mathbf{r}) = -\tfrac{1}{2}\nabla^2 - \lambda_1\left(\frac{1}{|\mathbf{r}-\hat{k}/2|} - \frac{1}{|\mathbf{r}+\hat{k}/2|}\right). \tag{16}$$

Critical conditions for one electron in an electric-dipole field have been studied in previous works.[5–7,12] For values of the electric-dipole moment lower than $\lambda_1=\mu_c\simeq 0.655$,[12] this system cannot bind an electron. The ground state energy of the one electron dipole tends to zero exponentially as the dipole moment reaches its critical value μ_c. For such system, $\alpha=\infty$ and there is no square integrable wave function at the threshold.[39]

The aim of this work is to make a complete analysis of the near threshold behavior for the two electron dipole [Eq. (14)]. It is possible to show that for $\lambda_1>\mu_c$, there exists $\lambda_2^c(\lambda_1)>0$ such that for $\lambda_2<\lambda_2^c$, the system binds two electrons.[40] In order to be consistent with Sec. II, we should define $\lambda_2=1/R$, but this is not necessary because this is an arbitrary choice and it is physically more adequate than $\lambda_2=R$. We want to obtain the ground state stability diagram in the space of the Hamiltonian parameters λ_i. At the moment we know where the system is stable with one electron. In the next section, we will calculate the values of the parameters which make the system stable with two additional electrons.

IV. FINITE SIZE SCALING AND VARIATIONAL CALCULATIONS

In order to apply finite size scaling and variational methods, we have to introduce appropriate basis sets. The Schrodinger equation for the two electron dipole is

$$\mathcal{H}_s(\lambda_1,\lambda_2)\Psi_0(\mathbf{r}_1,\mathbf{r}_2,\lambda_1,\lambda_2) = E_0(\lambda_1,\lambda_2)\Psi_0(\mathbf{r}_1,\mathbf{r}_2,\lambda_1,\lambda_2), \tag{17}$$

where $\mathcal{H}_s$ is defined in Eq. (14) and from Sec. II, our trial function takes the form

$$\Psi(\mathbf{r}_1,\mathbf{r}_2;\lambda_1,\lambda_2) = \sum_n a_n(\lambda_1,\lambda_2)\Phi_n(\mathbf{r}_1,\mathbf{r}_2). \tag{18}$$

The basis set $\{\Phi_n\}$ consists of functions of the type

$$\Phi_n = Ce^{-\beta(\xi_1+\xi_2)}(\xi_1^{p_n}\eta_1^{q_n}\xi_2^{r_n}\eta_2^{s_n} + \xi_1^{r_n}\eta_1^{s_n}\xi_2^{p_n}\eta_2^{q_n})r_{12}^{m_n}, \tag{19}$$

where C is the normalization constant, (ξ,η,ϕ) (Ref. 31) are the usual prolate spheroidal coordinates, ϕ is the azimuthal angle, $\xi=(r_a+r_b)$, $\eta=(r_a-r_b)$, r_a and r_b are the distances to the centers, and β is a variational parameter. Powers are integer numbers with $p_n,q_n,r_n,s_n,m_n\geqslant 0$. This basis set has been used since the pioneering work of James and Coolidge.[41]

For the numerical calculation, the basis set is truncated at order N by the condition

$$p_n+q_n+r_n+s_n+m_n \leqslant N, \tag{20}$$

obtaining for the number of basis functions,

$$M(N) = \begin{cases} \dfrac{1}{240}(N+2)(N+3)(N+4)(10+N(N+6)), & N \text{ is even} \\ \dfrac{1}{240}(N+1)(N+3)(N+5)(13+N(N+6)), & N \text{ is odd.} \end{cases} \tag{21}$$

The integrals needed for the evaluation of the matrix elements [Eq. (5)] required for the evaluation of the ground state energy and any other expectation value were solved in a previous work[42] and used successfully in the study of the stability of two electron diatomic molecules.[34] In our previous work,[42] we have developed an efficient method to evaluate these integrals. All the integrals needed for the evaluation of the matrix elements are obtained as analytic recursion expressions. In order to obtain accurate results, we used multiprecision FORTRAN,[43] an extension of standard FORTRAN 90 that allows us to work with an arbitrary number of significant figures. Once the matrix elements are obtained, the eigenvalue problem is solved using a standard double precision FORTRAN code.

The threshold energy corresponds to the ground state energy of the one electron Hamiltonian,

$$h(\lambda_1)\phi_0(\mathbf{r},\lambda_1) = \mathcal{E}_0(\lambda_1)\phi_0(\mathbf{r},\lambda_1), \tag{22}$$

where h is defined in Eq. (16). The critical conditions for Eq. (22) were studied in Ref. 12 using Slater-type functions.

At this point, we are ready to estimate the critical parameters λ_1^c and λ_2^c using the results of Sec. II. In order to evaluate the ground state energy and the required expectation values, we start with a variational optimization of the wave function parameter β. The optimal value β is different for each region of the Hamiltonian parameters λ_1 and λ_2. In this work, all the numerical calculations were done using $\beta=1.0$, 0.9, 0.4, 0.2, and 0.15.

In Fig. 1, we show the FSS calculations for a fixed value of λ_2 ($\lambda_2=1.0$) using Eq. (8). These numerical calculations were done for $N\leqslant 9$, which means that we used up to 1036 basis functions. As mentioned in Sec. II, the curves Γ_N intersects for different values of N, giving us the values of the

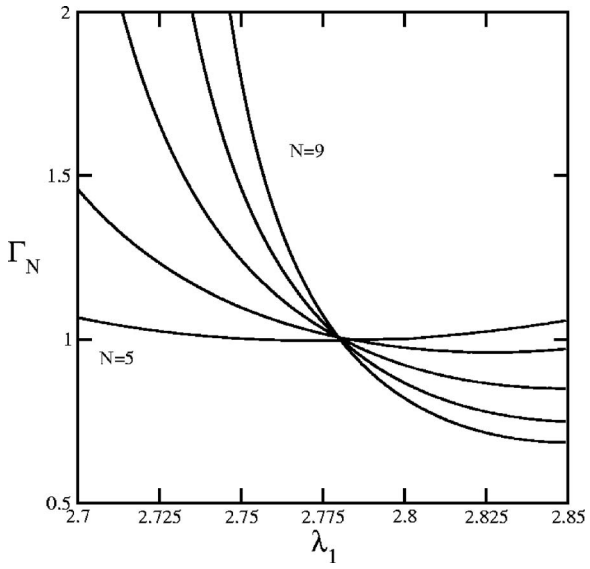

FIG. 1. $\Gamma(\lambda_1,\lambda_2,N-1,N)$ as a function of λ_1 for the ground state energy of the two-electron dipole for different values of N, $\beta=0.9$ and $\lambda_2=1.0$.

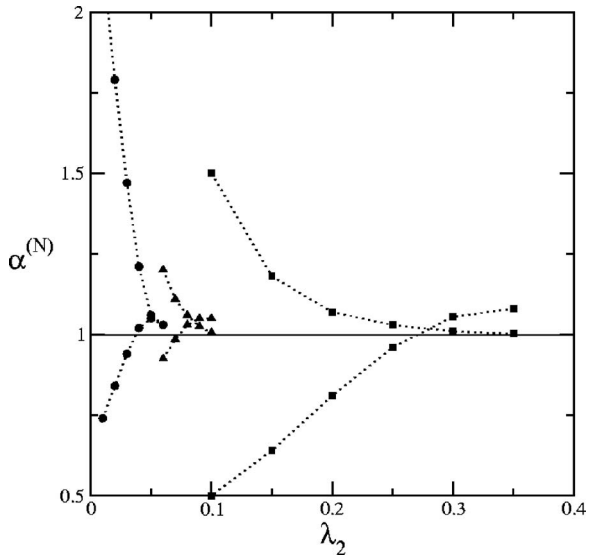

FIG. 3. Different solutions of Eq. (8) for $\beta=0.15$ (circle), 0.20 (triangle), and 0.40 (square).

critical exponent $\alpha=1.0044\pm0.0002$ and the critical parameter $\lambda_1^{c(\mathrm{FSS})}=2.7794\pm0.0001$. The critical parameter can be calculated using just the variational method and Eq. (6); for $\lambda_2=1.0$, we obtain $\lambda_1^{c(\mathrm{Var})}=2.7801\pm0.0001$. We repeat this procedure for different values of λ_2, obtaining the critical or the ionization line $\lambda_1^c(\lambda_2)$. With these results and the known results for the one electron dipole,[5–12] we construct, in Fig. 2, the complete ground state stability diagram. It is clear that the three different regions exist in this figure. The first one (from the left) is the region where the system cannot attach an electron. In the middle, we have the one electron dipole as a stable configuration. These regions are separated by a single ionization line; at this line, there is no square integrable wave function and the ground state energy goes exponentially to the threshold energy. The last region is where the system can bind two electrons and is separated from the one electron region by a single ionization line. Our calculations show that for $\lambda_2>\lambda_2^*\geqslant 0$, the critical exponent for the energy is $\alpha=1$ and then, the two electron wave function is square integrable at the threshold.[39] It is easy to show that for $\lambda_2=0$ (non interacting electrons), we have $\lambda_1^c=\mu_c$, $\alpha=\infty$ and then, we are in the presence of a double ionization. We could not determine numerically if there exist $\lambda_2^*>0$ such that the critical exponent is $\alpha\neq 1$. If this occurs we could have a double ionization line. All the calculations for the two electron system were done with $N\leqslant 8$ (671 functions) and various variational parameters β.

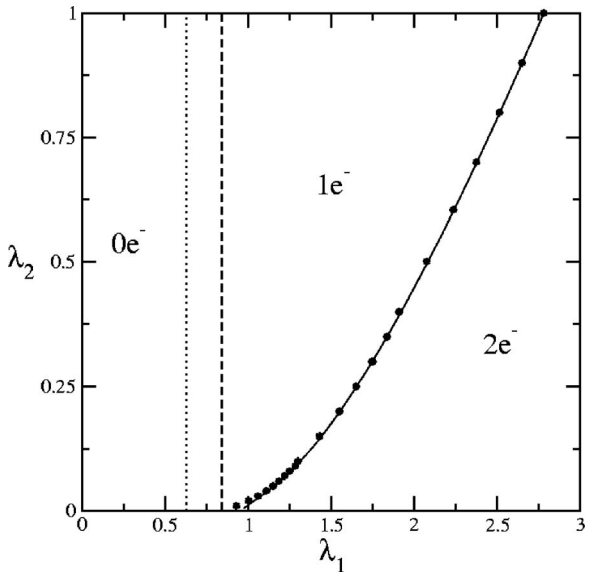

FIG. 2. Ground state stability diagram of the two-electron dipole for $N=8$ and $\beta=0.9$, 0.4, 0.2, and 0.15. The full black line represents the variational single ionization line and the stars are the FSS calculations of this line. The dotted and dashed lines are the exact and variational ionization lines for the one electron dipole, respectively.

It is interesting to note that Eq. (8) has two solutions for some Hamiltonian parameters for each value of N. This identical phenomenon has been observed in our previous studies.[44] In Fig. 3, we show the two critical exponents obtained using these two solutions. For values of λ_2 where the variational parameter β works better, both solutions are closer. We must remember that Eq. (8) is an asymptotic expression, and for $N\to\infty$, both solutions must converge to the same value. It is clear from Fig. 3 that numerical calculations are much more difficult as the parameter λ_2 decreased. This occurs because for λ_2 small, the threshold of the two electron system is closer to the threshold of the one electron system where the critical exponent is $\alpha=\infty$.

In order to show the locations of the two electrons relative to the dipole axis and to each other, we plot in Fig. 4 the average square distance on the dipole axis $\langle z^2\rangle$ as a function of λ_1 for different values of $\lambda_2=0.1$, 0.5, and 1.0 and different variational parameter $\beta=0.2$, 0.4, and 0.9. Note the jump in the distance as one crosses the transition line and loses one electron. This same behavior occurs for the distance between the two electrons $\langle r_{12}\rangle$, as shown in Fig. 5. As we move from the stable region with two electrons at large values of λ_1 to the one electron stable dipole, the electron-electron distance increases, indicating the transition from dipole-bound dian-

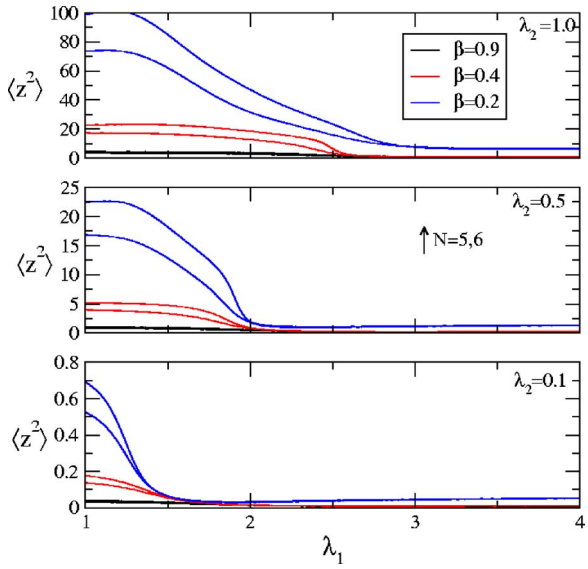

FIG. 4. (Color online) The average square distance on the dipole axis $\langle z^2 \rangle$ as a function of λ_1 for different values of λ_2=0.1, 0.5, and 1.0 and different variational parameter β=0.2, 0.4, and 0.9.

ions to dipole-bound anions. This first-order jump in the distance is consistent with the energy exponent of α=1.

V. CONCLUSIONS

The problem of binding excess electrons to polar molecules and their clusters has long fascinated researchers. In this paper, we have presented finite size scaling and variational calculations of the critical parameters for stability of two electrons bound by a dipole field. We have shown a complete analysis of the ground state stability diagram for the dipole-bound dianions in the Born-Oppenheimer approximation. Our developed method for the evaluation of two center two electron integrals[34,42] gives us enough accuracy to perform FSS calculations in a wide region of the Hamiltonian parameters. We performed a detailed study of the ground state stability of this system and obtained the stability diagram and the critical exponents.

Jordan and Wang[45] have discussed the shortcoming of the finite dipole model which gives electron binding energies much larger than those determined experimentally for real molecules with the same dipole moment. This is because of the neglect of repulsive interactions of the excess electrons with electrons of the neutral molecule. This can be overcome by incorporating into the Hamiltonian a repulsive term describing the interaction of the excess electrons with the distribution of charges of the neutral molecule. Work is currently underway to modify the Hamiltonian to include the effects of valence and core electrons and to calculate its critical parameters.

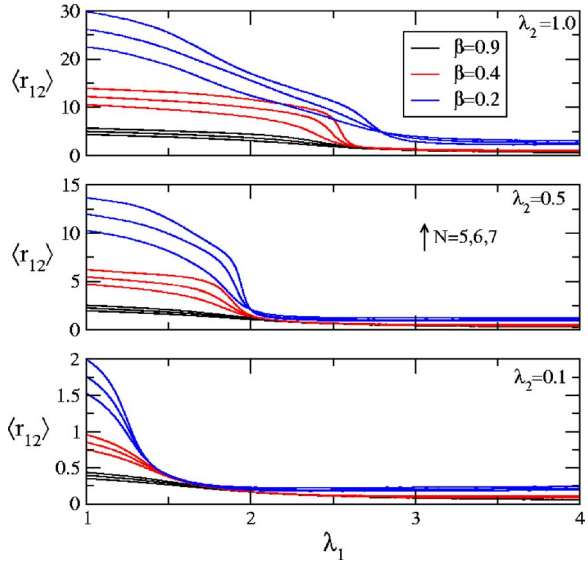

FIG. 5. (Color online) The average distance between the two electrons $\langle r_{12} \rangle$ as a function of λ_1 for different values of λ_2=0.1, 0.5, and 1.0 and different variational parameter β=0.2, 0.4, and 0.9.

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