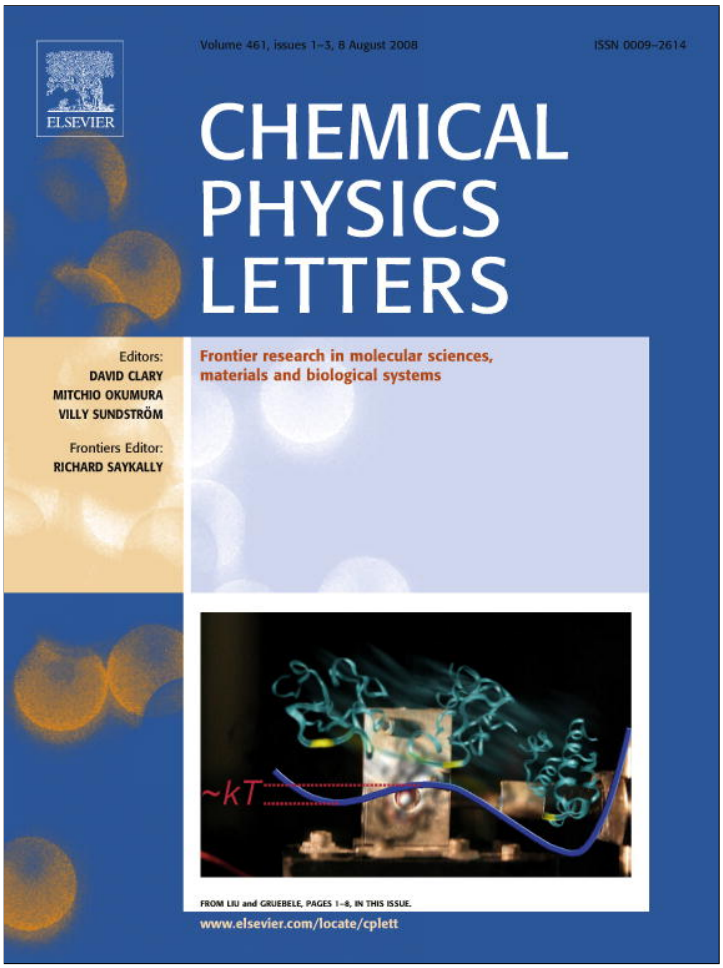

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Dimensional scaling for stability of two particles in a dipole field

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ABSTRACT

We present dimensional scaling calculations for the critical parameters needed to bind one and two-electrons to a finite linear dipole field and the stability diagram for the hydrogen–antihydrogen like molecules. We find that calculations at the large-D limit are much simpler that $D = 3$, yet yield similar results for the critical parameters and the stability diagrams.

1. Introduction

The study of stability of bound states for molecular systems as a function of physical parameters is a subject of great interest in the fields of molecular physics and quantum chemistry. Experimental and theoretical search of small stable multiple charged anions is an active research field [1,2]. Recently, it was demonstrated computationally the existence of dipole-bound dianions of different molecules [2–4] and the stability of atomic anions induced by superintense, high-frequency laser fields [5].

Although at the present time we are able to perform accurate calculations for many body systems, some near threshold properties and critical behavior of small molecules are still not fully understood and a subject of current interest [6]. Froelich et al. [7] have found that when colliding at low speed, hydrogen and antihydrogen, they have a tendency to recombine into protonium (proton plus antiproton, Pn) and positronium (electron plus positron, Ps) before the particles and antiparticles annihilate. Both Pn and Ps are highly unstable but are slightly longer lived than they would be in the absence of the other pairing. In this Letter, we are going to center the discussion on the stability of two attractive quantum systems: the dipole-bound dianion and the hydrogen–antihydrogen like quasi-molecules.

In order to study the behavior of atomic and molecular systems near critical points we frequently need model calculations which are simple but still capture the main physics of the problem. In this context, a critical point is defined as the point where a bound state becomes absorbed or degenerated with the continuum. It has been shown that in certain cases quantitative and qualitative predictions for $D = 3$ results can be obtained from $D \neq 3$ calculations. The most famous example is the renormalization group approach to critical phenomena [8]. In the case of electronic structure, dimensional scaling method provides such a model to calculate the critical parameters and stability diagrams [9]. In this model we take the dimensionality $D \to \infty$ with the number of electrons N and the nuclear charges Z fixed [10,11]. One should note that the large-D limit is a semi-classical approximation to $D = 3$ but different from the conventional WKB approximation [12]. When we apply dimensional scaling to electronic structure, the limit $D \to \infty$ reduces to a semi-classical electrostatic problem in which the electrons are assumed to have fixed positions relative to the nuclei and to each other in the scaled D-space [13]. This configuration corresponds to the minimum of an effective potential which includes Coulomb interactions and centrifugal terms originated from the D-dependent kinetic energy part.

In previous works, we have investigated the stability conditions for the dipole-bound anion [14], the dipole-bound dianion [15] and the hydrogen–antihydrogen like quasi-molecules [16] at $D = 3$ using ab initio and finite size scaling calculations. The main focus of this work is to perform the large-D limit calculations for the critical conditions of these systems and compare the obtained results with the $D = 3$ calculations.

This Letter is organized as follows. In Section 2 we give a brief description of the two-particle systems in the large-D limit. As an important limit case, we discuss in Section 3 the one-electron system. In Section 4 we study the two-electron system, comparing the 'exact' and the Hartree–Fock approximation at the large-D limit. In Section 5 we present the stability diagram of the hydrogen–antihydrogen quasi-molecule ($Z - \overline{Z}$) at the large D-limit followed by a conclusion section.

2. Two particles in a dipole field at the large D-limit

We consider two particles in the field of a finite dipole. The finite dipole consists of two Coulomb centers of charges $\pm Z$ located along the z-axis at $\pm R/2$. Two interesting problems can be modeled: The two-electron case, that describes the attachment of two-electrons to a polar molecule [15,17,18], and the hydrogen–antihydrogen like quasi-molecules $Z - \overline{Z}$ case, the Coulomb centers represent

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a nucleus and an anti-nucleus, and the light particles represent an electron and a positron [16,19–21]. These particles have opposite charges, thus the two-particle interaction is attractive. This fact will have important consequences at the large-D limit.

Note that, even with different symmetries, both systems have the one particle-dipole as one particle limit and both have cylindrical symmetry. Taking this last observation into account we can write the ground state function in the following form:

$$\Psi_0(\vec{x}_1,\vec{x}_2) = \Psi_0(\rho_1, z_1, \rho_2, z_2, \cos(\varphi_{12})), \tag{1}$$

where φ_{12} is the dihedral angle between the particle positions. We then scale coordinates by f^2 and energy by $1/f^2$, with $f = (D-1)/2$, and transform the wave function Ψ by

$$\Psi(\vec{x}_1,\vec{x}_2) = \frac{1}{\sqrt{\mathscr{J}}}\Phi(\vec{x}_1,\vec{x}_2), \tag{2}$$

where $\mathscr{J} = (\rho_1\rho_2)^{D-2}(\sin(\varphi_{12}))^{D-3}$ is the Jacobian in D-dimensional cylindrical coordinates. The effective D-dimensional Hamiltonian for the wave function Φ is given in Ref. [22]. This transformation has the advantage of making the large-D limit Hamiltonian explicitly dependent on all variables that appear in the wave-function and the kinetic energy term is not a simple sum of the two individual kinetic energies.

Therefore, the effective Hamiltonian can not be written as a sum of two individual Hamiltonians, not even for the non-interacting case. We will return to this important point later. After this transformation, the effective scaled Hamiltonian takes the form [13,22]

$$\mathscr{H}_\infty = \frac{1}{2\sin^2(\varphi_{12})}\left(\frac{1}{\rho_1^2}+\frac{1}{\rho_2^2}\right) + V_1(\lambda_1;\rho_1,z_1) + V_2(\lambda_1;\rho_2,z_2) + \lambda_2 W(r_{12}) \tag{3}$$

where V_i is the one-particle dipole potential, W is the Coulomb repulsion (attraction) between electrons (between electron and positron), $\lambda_1 = ZR$ is the dipole moment and $\lambda_2 = R$.

At the large-D limit, particles are localized and the ground state energy is given by

$$E_0(\lambda_1,\lambda_2) = \min_{\{\rho_1,z_1,\rho_2,z_2,\varphi_{12}\}} \mathscr{H}_\infty(\lambda_1,\lambda_2;\rho_1,z_1,\rho_2,z_2,\varphi_{12}) \tag{4}$$

Thus, the problem of evaluate the ground state energy is reduced to finding the global minimum of the effective Hamiltonian $\mathscr{H}_\infty$.

3. One-electron dipole

In this section, we study the near-threshold behavior of one-electron in the presence of a finite dipole. Clearly, this is a simple system and it was studied at $D = 3$ by many authors. Analytical and numerical calculations showed that within the Born–Oppenheimer approximation, molecules with dipole moments greater than $\mu_c = 1.625D$ (0.63931 a.u.) can bind an extra electron to form dipole-bound anions [14,18,23–28]. For the one-electron dipole, the scaled Hamiltonian at the large D-limit is given by [29]

$$\mathscr{H} = \frac{1}{2\rho^2} - \lambda_1\left(\frac{1}{|\vec{r}-\hat{k}/2|} - \frac{1}{|\vec{r}+\hat{k}/2|}\right). \tag{5}$$

In this case, is straightforward to show that Eq. (4) is analytically solvable. The critical value of $\lambda_1 = ZR = \mu$, the minimum dipole moment that can bind an electron, is given by

$$\lambda_1^c = \frac{3\sqrt{3}}{4} = 1.2990381\ldots. \tag{6}$$

As we mentioned before, the critical value for $D = 3$ is $\mu_c^{(3)} = 0.63931\ldots$ [25]. The large D-limit fails to give a good value for the critical dipole moment. For $D = 3$ the energy of the one-electron dipole decays exponentially to zero for $\lambda_1 \to \lambda_1^c$ [30], and the electron becomes highly delocalized. This fact implies that a semi-classical limit such as the large-D, where the electron is localized, cannot give good results. Moreover, it is straightforward to show that the ground state energy at the large-D limit goes quadratically to zero at the critical point instead of exponentially at $D = 3$. However, away from the threshold region, the large-D limit results are in excellent agreement with accurate ground state variational calculations [14] at $D = 3$ as shown in Fig. 1.

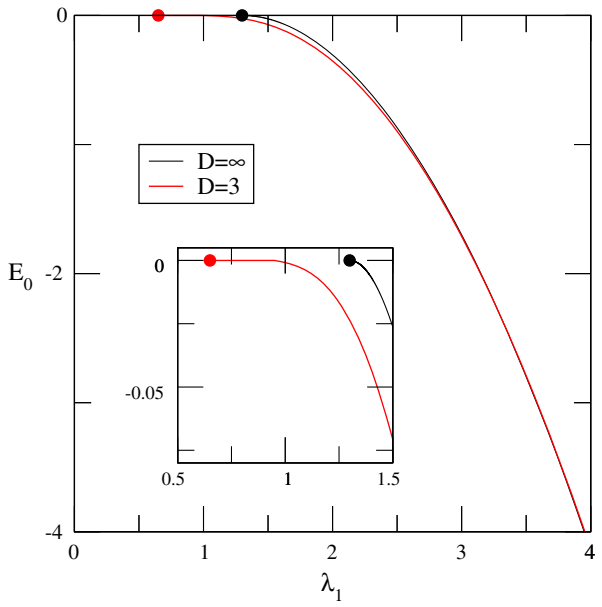

Fig. 1. Ground state energy for an electron in a dipole field for $D = 3$ and $D = \infty$, the exact critical dipole moments are shown by dots. The insert shows the near-threshold region.

4. Two-electron dipole

The possibility of binding two-electrons to a finite dipole has attracted the attention of many authors in the last two decades [4,18,15]. Recently, 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 [15]. When finite size scaling calculations are employed in order to study the two-electron dipole, one is faced with the complexity of the matrix element calculations and the high computational cost for increasing the size of the basis set. However, the large-D limit provides a simple and fast alternative to obtain the stability diagram for such a non-trivial problem. In the large D-limit, the Hamiltonian for two-electrons in a dipole field is given by

$$\mathscr{H} = \frac{1}{2\sin^2\varphi_{12}}\left(\frac{1}{\rho_1^2}+\frac{1}{\rho_2^2}\right) - \lambda_1\left(\frac{1}{|\vec{r_1}-\hat{k}/2|} - \frac{1}{|\vec{r_1}+\hat{k}/2|} + \frac{1}{|\vec{r_2}-\hat{k}/2|} - \frac{1}{|\vec{r_2}+\hat{k}/2|}\right) + \frac{\lambda_2}{r_{12}}, \tag{7}$$

where $r_{12} = \sqrt{\rho_1^2+\rho_2^2-2\rho_1\rho_2\cos\varphi_{12}+(z_1-z_2)^2}$. This Hamiltonian can be further simplified by using the Hartree–Fock (HF) approximation [31,32] as it was done at $D = 3$. Many atomic and molecular systems were solved using the Hartree–Fock approximation at the

large-D limit [33–36]. If we consider Hartree–Fock approximation to the energy, then its large-D limit will be given by the minimum of Eq. (7), in which the variable ϕ_{12} is fixed at 90° [32]. Recently, Svidzinsky, Scully and Herschbach (SSH) [36] transform the wave function in the form

$$\Psi(\vec{x}_1,\vec{x}_2) = (\rho_1\rho_2)^{D-2}\Phi(\vec{x}_1,\vec{x}_2), \tag{8}$$

this gives the following large-D limit Hamiltonian

$$\mathscr{H}^{\mathrm{SSH}} = \frac{1}{2}\left(\frac{1}{\rho_1^2}+\frac{1}{\rho_2^2}\right) - \lambda_1\left(\frac{1}{|\vec{r}_1-\hat{k}/2|}-\frac{1}{|\vec{r}_1+\hat{k}/2|}+\frac{1}{|\vec{r}_2-\hat{k}/2|}-\frac{1}{|\vec{r}_2+\hat{k}/2|}\right)+\frac{\lambda_2}{r_{12}}. \tag{9}$$

Note that the difference between these two Hamiltonians is that the factor $\sin^{-2}\varphi_{12}$ in the kinetic energy of Hamiltonian Eq. (7) is absent in the SSH version. As a consequence of this, the total kinetic energy is the sum of the two individual kinetic energies. In Fig. 2, we show the results for the ionization energy for the two-electron dipole at $D = 3$ and at the large-D limit. As shown in Fig. 2, for $\lambda_2 = 1$ the exact ionization energy at the large-D limit is larger than the $D = 3$ energy while the SSH energy gives a lower value. In our case, the values obtained for the coordinates $(\rho_1,z_1;\rho_2,z_2)$ are almost the same in both cases, but the dihedral angle φ_{12} goes from values close to $\pi/2$ for the exact solution to values close to π for SSH. On the other hand, the constraint $\phi_{12} = \pi/2$ follows from the fact that in HF approximation the expectation value of $(\vec{\rho}_1,\vec{\rho}_2)$ is zero. Because of this constraint, HF approximation always overestimates the energy as seen in Fig. 2.

In Fig. 3 we compare the ground state stability diagram of the two-electron dipole obtained at the large-D limit with the exact finite size scaling calculations [15]. As seen in Fig. 3, the large-D limit calculations, both SSH and exact, give very good approximations to the exact stability diagram, with three distinct regions: zero-electron, one-electron and two-electron binding to a dipole field.

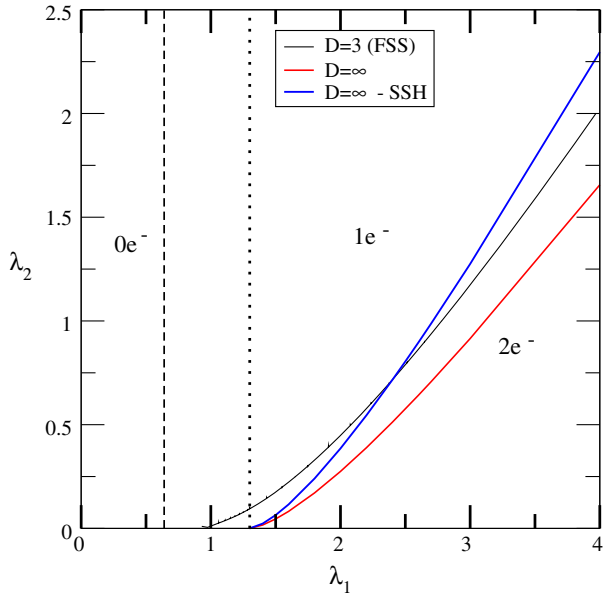

Fig. 3. Ground state stability diagram for two-electrons in a dipole field for $D = 3$ obtained with finite size scaling and $D = \infty$ exact and in the SSH approximation (see Eq. (9) in the text). The dashed line represents the ionization line for the one-electron system at $D = 3$, and the dotted line at $D = \infty$.

5. Hydrogen–antihydrogen like quasi-molecule

The behavior and properties of antimatter have been the subject of research for many decades [37,38]. In this section we are interested in the study of the hydrogen–antihydrogen like quasi-molecules at the large-D limit. In this case the positive and negative Coulomb centers represent a nucleus and an anti-nucleus respectively. There exist two important differences between this system and the two-electron dipole studied in Section 4, the particle–antiparticle symmetry in the lepton-hadron terms, and the attractive character of the interleptonic potential. The Hamiltonian of the

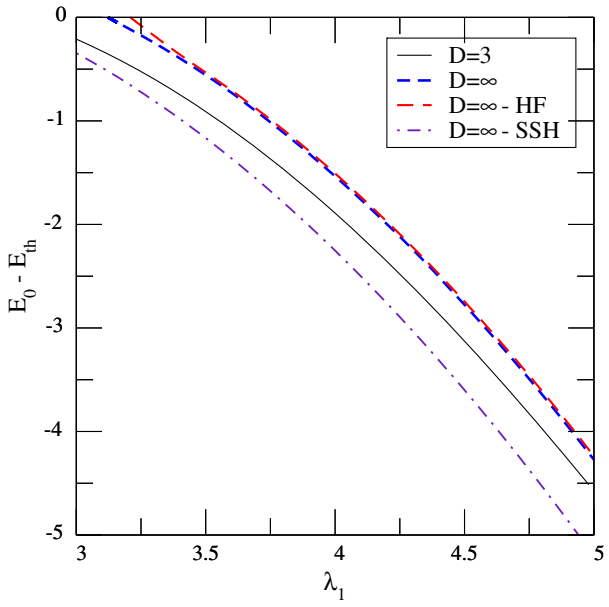

Fig. 2. Ionization energies for the two-electron dipole for $D = 3$ and showing the exact large-D limit, large-D limit HF and large-D limit SSH energies for $\lambda_2 = 1$.

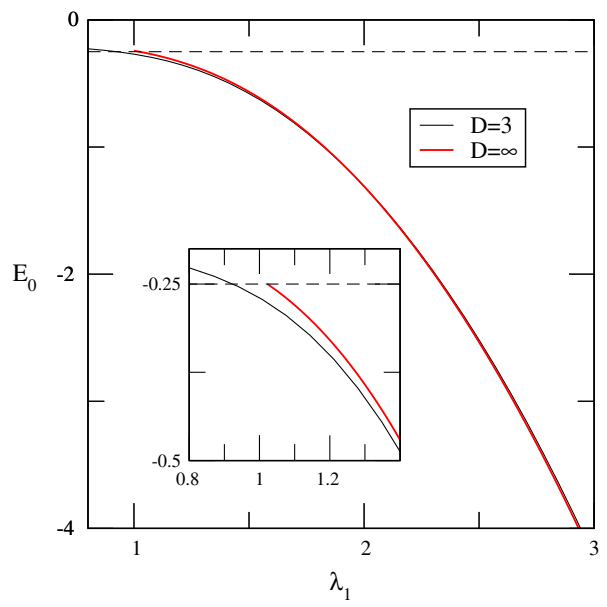

Fig. 4. Ground state energies for the $Z-\bar{Z}$ for $D = 3$ and $D = \infty$. The calculations were made for $\lambda_2 = 1$. The insert shows the near-threshold region.

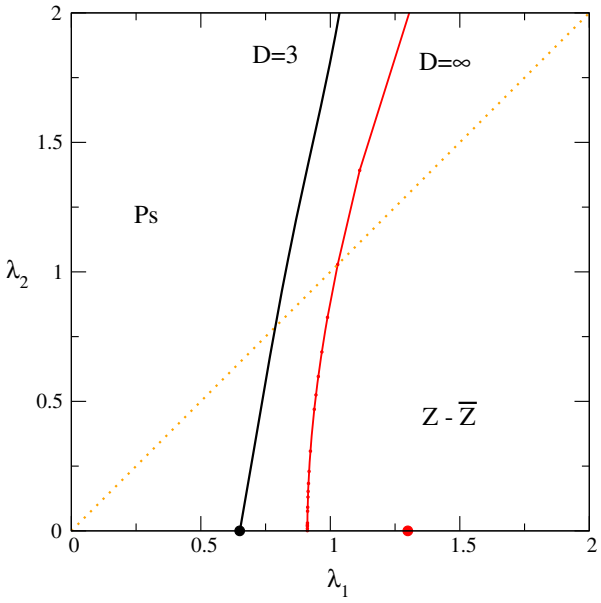

Fig. 5. Ground state stability diagram for the $Z-\bar{Z}$ for $D=3$ and $D=\infty$. The black and the red points represent the ionization point for the one-electron dipole at $D=3$ and $D=\infty$ respectively. The dotted curve represent the $H-\bar{H}$ case ($Z=1$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

hydrogen–antihydrogen like quasi-molecule, at the large-D limit takes the form

$$\mathscr{H} = \frac{1}{2\sin^2\varphi_{12}}\left(\frac{1}{\rho_1^2}+\frac{1}{\rho_2^2}\right) - \lambda_1\left(\frac{1}{|\vec{r}_1-\hat{k}/2|}-\frac{1}{|\vec{r}_1+\hat{k}/2|}-\frac{1}{|\vec{r}_2-\hat{k}/2|}+\frac{1}{|\vec{r}_2+\hat{k}/2|}\right)-\frac{\lambda_2}{r_{12}}. \tag{10}$$

Here, the interparticle potential and the factor $\sin^{-2}\varphi_{12}$ in the kinetic energy is essential to obtain a stable solution at this limit. Thus, the SSH approximation at the large-D limit does not apply since the attraction between leptons always gives a minimum with energy equal to $-\infty$. For the exact large-D limit Hamiltonian, the kinetic energy does not diverge, given a solution which is in good agreement with the $D=3$ calculations except in the threshold region. This can be observed for $\lambda_2=1$ in Fig. 4. In Fig. 5 we compare the large-D limit stability diagram with the exact calculations [16] for one-electron, one-positron, atom–antiatom systems. Again, the simple large-D limit gives a good prediction for the stability of different regions as one varies the parameters λ_1 and λ_2.

6. Conclusions

We present dimensional scaling calculations for the ground state energy and critical parameters for binding one and two-electrons to a finite dipole and the stability diagram for hydrogen–antihydrogen like molecules. For the two-electron dipole and the hydrogen–antihydrogen like molecules cases presented in this work it is clear that the large-D limit provides a rather good description of the problem. It is easy to implement, merely minimizing an effective potential at the scaled large-D limit. The results can be improved systematically by including higher order terms in the $1/D$-expansion.

Recently, we have shown that dimensional scaling, combined with the high-frequency Floquet theory, provides useful means to evaluate the stability of gas phase atomic anions in a superintense laser field [5]. At the large-dimension limit in a suitably scaled space, electrons become localized along the polarization direction of the laser field. We find that calculations at large-D are much simpler than $D=3$, yet yield similar results for the field strengths needed to bind an extra one or two-electrons to H and He atoms. The problems discussed in this Letter can be related to stability in external field. Once again, the simple large-D analysis provides a simple alternative way to analyze stability of different systems.

Acknowledgments

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