Finite size scaling for critical conditions for stable dipole-bound anions

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Abstract

We present a finite-size scaling approach for the calculations of the critical parameters for binding an electron to an electric dipole field. This approach gives very accurate results for the critical parameters by using a systematic expansion in a finite basis set. The approach is general and could be used to obtain the critical conditions for stable dipole-bound dianions.

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1. Introduction

The finite-size scaling (FSS) approach has been used for studying the critical behavior of a quantum Hamiltonian $\mathscr{H}(\lambda_1, \ldots, \lambda_k)$ as a function of its set of parameters $\{\lambda_i\}$ [1–4]. In this context, critical means the values of $\{\lambda_i\}$ for which a bound state energy is non-analytic. In many cases, this critical point is the point where a bound state energy becomes absorbed or degenerate with a continuum [4].

In order to apply the FSS to quantum mechanics problems, let us consider the following Hamiltonian of the form [5]

$$\mathscr{H} = \mathscr{H}_0 + V_\lambda, \tag{1}$$

where $\mathscr{H}_0$ is λ-independent and V_λ is the λ-dependent term. We are interested in the study of how the different properties of the system change when the value of λ varies. Without loss of generality, we will assume that the Hamiltonian, Eq. (1), has a bound state E_λ for $\lambda > \lambda_c$ which becomes equal to zero at $\lambda = \lambda_c$.

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. For a given complete orthonormal λ-independent basis set $\{\Phi_n\}$, the ground state eigenfunction has the following expansion:

$$\Psi_\lambda = \sum_n a_n(\lambda)\Phi_n, \tag{2}$$

where n represents the adequate set of quantum numbers. In order to approximate the different quantities, we have to truncate the series, Eq. (2) at order N. Then the Hamiltonian is replaced by

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$M(N) \times M(N)$ matrix, with $M(N)$ being the number of elements in the truncated basis set at order N. In the FSS representation, we assumed that there exists a scaling function for the truncated magnitudes of any given operator $\mathcal{O}$ such that

$$\langle \mathcal{O} \rangle_\lambda^{(N)} \sim \langle \mathcal{O} \rangle_\lambda F_\mathcal{O}(N|\lambda - \lambda_c|^\nu) \tag{3}$$

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

Now, to obtain the critical parameters, we define the following function [5]:

$$\Delta_\mathcal{O}(\lambda; N, N') = \frac{\ln\left(\langle \mathcal{O} \rangle_\lambda^{(N)}/\langle \mathcal{O} \rangle_\lambda^{(N')}\right)}{\ln(N'/N)}. \tag{4}$$

If one takes the operator $\mathcal{O}$ to be the Hamiltonian one can obtain the critical λ_c from the following function [5]:

$$\Gamma(\lambda; N, N') = \frac{\Delta_\mathcal{H}(\lambda; N, N')}{\Delta_\mathcal{H}(\lambda; N, N') - \Delta_{\partial V_\lambda/\partial \lambda}(\lambda; N, N')}, \tag{5}$$

which is independent of the values of N and N' at the critical point $\lambda = \lambda_c$. Thus, for different values of N the curves of Γ as a function of λ will intersect at successions of pseudo-critical points $\lambda_c^{(N)}$. The successions of values of $\lambda_c^{(N)}$ can be used to obtain the extrapolated value of λ_c [4].

This general approach has been successfully applied to calculate the critical parameters for two-electron atoms [1], three-electron atoms [2], simple diatomic molecules [3], stability of three-body Coulomb systems [6] and crossover phenomena and resonances in quantum systems [7].

In this Letter, we applied the FSS approach to obtain the critical conditions for stable dipole-bound anions. Dipole-bound anions are unstable relative to autodetachment unless the dipole moment strength exceeds a certain critical value. This interesting problem has a long history with a number of methods having been used to obtain the critical value of the dipole moment [8–13]. Our goal in this Letter is to present the FSS as an alternative approach to obtain the critical conditions for stable dipole-bound anions and to provide a systematic approach to obtain critical parameters

for complex systems such as dipole-bound dianions [14–16].

2. One electron in an electric-dipole field

The Hamiltonian, in atomic units, for an electron in a two-center Coulomb potential with a charge $+Z$ at $\vec{r} = 0$ and a charge $-Z$ localized along the z-axis is given by

$$\mathcal{H}(Z; R; \vec{x}) = -\frac{1}{2}\nabla^2 - Z\left(\frac{1}{r} - \frac{1}{|\vec{r} - R\hat{k}|}\right), \tag{6}$$

where R is the distance between the fixed charges and $\hat{k}$ is a unitary vector in the z-direction.

After scaling the Hamiltonian has only one free parameter, the electric dipole moment $\mu = ZR$,

$$\mathcal{H}(Z; R; \vec{x}) = Z^2 \mathcal{H}(1; \mu; Z\vec{x}) = \frac{1}{R^2}\mathcal{H}(\mu; 1; \vec{x}/R). \tag{7}$$

Eq. (7) gives the relation between values of the energy calculated at fixed R and at fixed Z

$$\mu^2 E(Z = 1; R = \mu) = E(Z = \mu; R = 1). \tag{8}$$

Of course the two are equivalent but different results might appear depending on the approximate method used. For example, different values of the critical dipole moment μ_c, the minimum dipole moment that can bind an electron, for $Z = 1$, 2 and 3 were reported by Ugalde and co-workers [11] using configuration interaction calculations.

3. Basis-set and matrix elements

In order to apply the finite size scaling method one has to introduce an appropriate basis set. Since the potential has a cylindrical symmetry, the ground state wave function in spherical coordinates can be written as

$$\Psi_0(\vec{r}) = \Psi_0(r, \theta). \tag{9}$$

This ground-state wave function could be expanded in a complete spherical basis-set using

spherical harmonics with $m = 0$. We use a (non-orthogonal) Slater basis-set of the form

$$\Phi_{n,l}(\vec{r}) = \left[\frac{\alpha^{2n+3}}{(2n+2)!} \right]^{1/2} e^{-\alpha r/2} r^n Y_l^0(\theta, \phi);$$
$$n = 0, 1, \ldots; \quad l = 0, \ldots, n, \tag{10}$$

where α is a variational parameter used to optimize the numerical results. The normalization of different basis functions is given by

$$\langle n, l | n', l' \rangle = \frac{(n + n' + 2)!}{[(2n+2)!(2n'+2)!]^{1/2}} \delta_{l,l'}, \tag{11}$$

and the kinetic energy matrix elements are given by

$$\langle n, l | T | n', l' \rangle = \frac{\alpha^2 (n+n')!}{2[(2n+2)!(2n'+2)!]^{1/2}} \Big(l(l+1)$$
$$- \frac{1}{4}((n-n')^2 - (n+1) - (n'+1)) \Big) \delta_{l,l'}. \tag{12}$$

For the dipole potential matrix elements we obtain the following expression:

$$\langle n, l | \frac{1}{r} | n', l' \rangle = \frac{\alpha(n+n'+1)!}{[(2n+2)!\,(2n'+2)!]^{1/2}} \delta_{l,l'}. \tag{13}$$

For the last term in the Hamiltonian, Eq. (1), we use the well known expansion of the inverse distance in terms of Legendre polynomials as a constant times spherical harmonics with $m = 0$.

$$\frac{1}{|\vec{r} - \vec{r'}|} = \sum_{k=0}^{\infty} \sqrt{\frac{4\pi}{2k+1}} \frac{r_<^k}{r_>^{k+1}} Y_k^0(\theta, \phi);$$
$$r_< = \min(r, r'); \quad r_> = \max(r, r'). \tag{14}$$

After a straightforward calculation, we obtain

where $\Gamma(m, z)$ is the incomplete gamma function [17].

The bound state energy was calculated using the Ritz-variational method for non-orthogonal basis-set [18]. The Slater basis-set is truncated allowing a maximum value of n in Eq. (10) $n = 0, \ldots, N$, with the restriction over $l = 0, \ldots, n$, we obtain the size of the truncated Hamiltonian matrix to be $M(N) = (N+1)(N+2)/2$.

As expected, the best choice of α depends on the value of μ. For large values of μ, the ground-state is well localized and it is convenient to choose a large value of α. But near the critical value μ_c, the energy is close to the threshold and the wave function is different zero even for large values of r, therefore, it is better to choose a small value of α in order to get accurate results for the critical parameters. In order to show the importance of the parameter α and that the scaling relation Eq. (7) is valid only asymptotically for Ritz-variational solutions, we show in Fig. 1 the plot of $E_0(1; \mu)$ and the scaled energy $E_0(\mu; 1)/\mu^2$ calculated with the basis-set truncated at $N = 10$, that means the Hamiltonian is a 66×66 matrix. Although from the scaling relation, Eq. (7) both expressions of the energy must be equal, as in Eq. (8), in a truncated basis-set calculations they are different as shown in Fig. 1. Thus, different results might be obtained depending on the approximation method used in the calculations.

4. Finite size scaling calculations

At this point by identifying the parameter λ in Eq. (5) by the dipole moment μ we are ready to estimate its critical value. As discussed in the previous section, to study the critical region, where
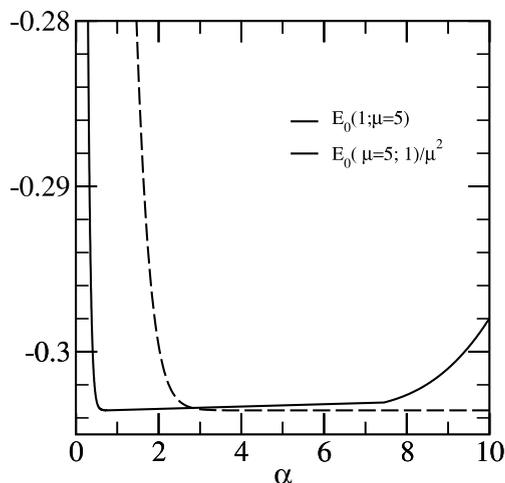
$$\left\langle n, l \left| \frac{1}{|\vec{r} - R\hat{k}|} \right| n', l' \right\rangle$$
$$= \alpha\sqrt{(2l+1)(2l'+1)} \sum_{k=|l-l'|}^{l+l'} \frac{(n+n'+2)! + (\alpha R)^{2k+1} \Gamma(n+n'-k+2; \alpha R) - \Gamma(n+n'+k+3; \alpha R)}{(\alpha R)^{k+1}[(2n+2)!(2n'+2)!]^{1/2}},$$

$$\tag{15}$$

Fig. 1. Scaled ground-state energy, as defined in Eq. (8) in the text, as a function of α of the electric dipole potential for a fixed value of $\mu = 5$.

Fig. 3. $\Gamma(\alpha = 0.01; \mu)$ as a function of μ for the ground state energy of the electric dipole potential for odd values of $n = 1, \ldots, 27$.

the value of the energy is very close to zero (the threshold value), we used a small value of α. We did several runs as shown in Fig. 1, and we choose $\alpha = 0.01$ for the finite size scaling calculations.

FSS calculations for spherically symmetric potentials show strong parity effects. We also find parity effect for the dipole potential, then Eq. (5) was used with $N' = N + 2$. In Fig. 2 we show the
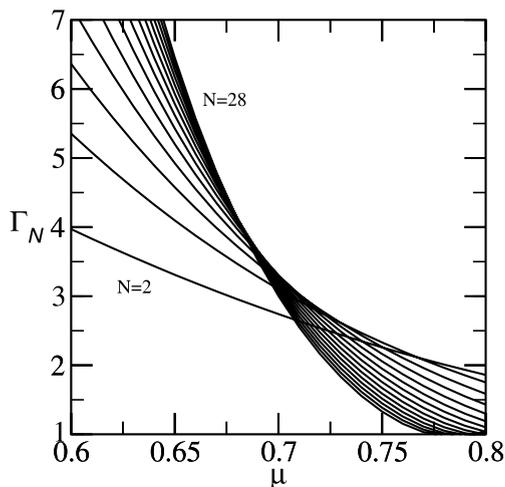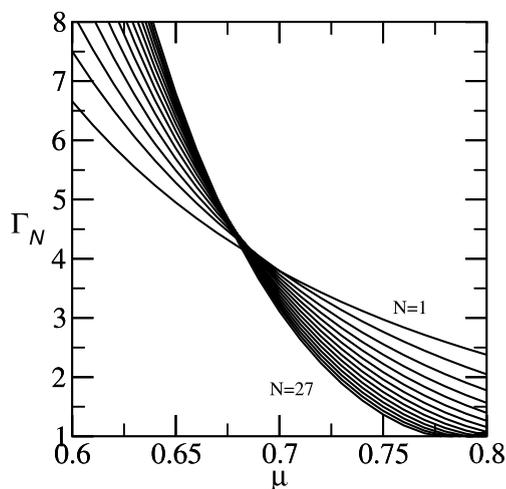
results of the FSS calculations for even values of $N = 2, \ldots, 28$ and in Fig. 3 for odd values of $N = 1, \ldots, 27$. Plotting Γ_N as a function of μ for different values of N gives a family of curves with an intersection at μ_c. Since the intersection between two consecutive curves depends on the size of the basis set N, in Fig. 4 we show the extrapolation curves for the pseudo-critical dipole moment $\mu_c^{(N)}(\alpha = 0.01)$ as a function of $1/N$ for even and odd values of N. The scaling was done with $E(\mu; 1)$

Fig. 2. $\Gamma(\alpha = 0.01; \mu)$ as a function of μ for the ground state energy of the electric dipole potential for even values of $N = 2, \ldots, 28$.
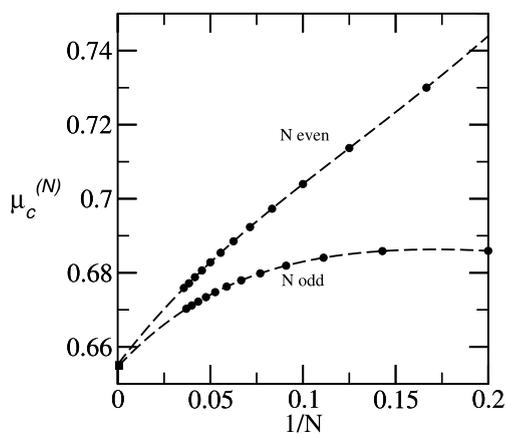

Fig. 4. $\mu_c^{(N)}(\alpha = 0.01)$ as a function of $1/N$ for the ground state energy of the electric dipole potential for even and odd values of $N = 5, \ldots, 28$. The extrapolated value $\mu_c \simeq 0.655$ a.u. is shown by a square.

and the extrapolated value is $\mu_c^{(ext)} \simeq 0.655$ a.u. This value of the critical dipole is in a good agreement with results obtained using other methods [8–10].

In summary, we have shown that the finite size scaling method can be used to estimate directly the critical parameters for binding an electron to an electric dipole field. Results show the method is accurate in predicting the critical dipole moment. The approach is simple and can be generalize to estimate the critical conditions for stable dipole-bound dianions. Research is underway in this direction and to estimate the relevant critical exponents.

Acknowledgements

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