

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

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We present finite-size scaling calculations of the critical parameters for binding an electron to a finite linear quadrupole field. This approach gives very accurate results for the critical parameters by using a systematic expansion in a finite basis set. The model Hamiltonian consists of a charge Q located at the origin of the coordinates and k charges $-Q/k$ located at distances \vec{R}_i , $i=1,\dots,k$. After proper scaling of distances and energies, the rescaled Hamiltonian depends only on one free parameter $q=QR$. Two different linear charge configurations with $q>0$ and $q<0$ are studied using basis sets in both spherical and prolate spheroidal coordinates. For the case with $q>0$, the finite size scaling calculations give an extrapolated critical value of $q_c=1.469\,70\pm 0.000\,05$ a.u. by using a basis set with prolate spheroidal coordinates. For the quadrupole case with $q<0$, we obtained an extrapolated critical value of $|q_c|=3.982\,51\pm 0.000\,01$ a.u. for stable quadrupole bound anions. The corresponding critical exponent for the ground state energy $\alpha=1.9964\pm 0.0005$, with $E\sim(q-q_c)^\alpha$. © 2004 American Institute of Physics. [DOI: 10.1063/1.1695552]

I. INTRODUCTION

Recently there has been increasing interest in multipole-bound negative ions. 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 Teller¹ have shown that, within the context of the Born–Oppenheimer approximation, molecules with dipole moments greater than $\mu_c=1.625$ D can bind an electron to form dipole-bound anions.^{1–8} The ground-state energy of the system tends to zero exponentially as the dipole moment reaches its critical value.^{9,10} However, subsequent experimental and computational studies taking into account corrections to the Born–Oppenheimer approximation gives a more realistic estimate of $\mu_c=2.5$ D (Refs. 11–18).

By analogy with the binding of an extra electron by a strong dipole field, it is natural to examine the possibility of electron binding by molecules with significant quadrupole moments and vanishing dipole moments. The search for quadrupole-bound anions has attracted both theorists^{19–24} and experimentalists.^{25–29} One of the first studies of potentially quadrupole-bound anions was performed by Jordan and Liebman.¹⁹ They considered attachment of an extra electron to a $(\text{BeO})_2$ dimer and concluded by using a Hartree–Fock level of theory that the extra electron is bound in the $(\text{BeO})_2^-$ anion primarily by the quadrupole field of the neutral dimer. Later Gutowski and Skurski calculated at the coupled-cluster level of theory with single, double, and noniterative triple

excitations the global minimum on the potential energy surface of $(\text{BeO})_2^-$ and showed that it corresponds to a rhombic D_{2h} structure, which may be considered as a quadrupole-bound anion.²² This system was reexamined by Gutsev, Jena, and Bartlett using coupled-cluster singles and doubles with perturbation triples method.²³ They have found that the binding energy of the extra electron in the $(\text{BeO})_2^-$ anion to be about 0.9 eV which is larger than the Hartree–Fock value of 0.65 eV (Ref. 19).

Recently Gutsev *et al.*²³ used coupled-cluster singles and doubles with perturbation triples method to search for quadrupole-bound anions. They reported the structure and properties of K_nCl_m^- and K_nCl_m^- ($n, m=0-2$). The KCl_2 was found to have an electron affinity of 4.2 eV and is stable toward dissociation by 26 kcal/mol. The $(\text{KCl})_2$ dimer has a rhombic ground state with a large electric quadrupole moment. Rhombic and linear configurations of the $(\text{KCl})_2^-$ anion correspond to stationary states that are nearly degenerate in total energy. The rhombic anion has a single, weakly bound state that could be a quadrupole-bound state.²³

Prasad *et al.*²¹ have evaluated the critical values of the quadrupole moment required for linear symmetric MX_2 systems to have a bound anion state. Recently Pupyshev and Ermilov²⁴ determined numerically, using a linear combination of atomic orbital and finite-difference approximation, the critical charge values which ensure the existence of bound state for one electron in the quadrupole and octupole fields.

In this paper, we present finite-size scaling calculations of the critical parameters for binding an electron to a finite quadrupole field. This approach gives very accurate results for the critical parameters by using a systematic expansion in

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a finite basis set. In Sec. II, we briefly review the finite-size scaling (FSS) method in quantum mechanics. In Sec. III, we present rigorous bounds for stable quadrupole-bound anions. In Sec. IV the FSS calculations for the critical parameters for stable quadrupole-bound anion in two linear charge configurations are presented in both spherical and prolate spheroidal coordinates. Finally conclusions are given in Sec. V.

II. FINITE-SIZE SCALING METHOD

The finite-size scaling approach has been developed for studying the critical behavior of a given quantum Hamiltonian $\mathcal{H}(\lambda_1, \dots, \lambda_k)$ as a function of its set of parameters $\{\lambda_{ij}\}$ (Refs. 30 and 31). In this context, ‘‘critical’’ means the values of $\{\lambda_{ij}\}$ 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.³²

In order to apply the FSS method to quantum mechanics problems, let us consider a Hamiltonian of the form³¹

$$\mathcal{H} = \mathcal{H}_0 + V_\lambda, \quad (1)$$

where \mathcal{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 $\lambda = \lambda_c$. The asymptotic behavior of E_λ near λ_c defines the critical exponent α :

$$E_\lambda \underset{\lambda \rightarrow \lambda_c^+}{\sim} (\lambda - \lambda_c)^\alpha. \quad (2)$$

In this approach, *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 expansion

$$\Psi_\lambda = \sum_n a_n(\lambda) \Phi_n, \quad (3)$$

where n represents an adequate set of quantum numbers. In order to approximate the different quantities, we have to truncate the series, Eq. (3), at order N . Then the Hamiltonian is replaced by an $M(N) \times M(N)$ matrix, with $M(N)$ being the number of elements in the truncated basis set at order N . In the FSS representation, we assume the existence of a scaling function for the truncated magnitude of any given operator \mathcal{O} such that

$$\langle \mathcal{O} \rangle_\lambda^{(N)} \sim \langle \mathcal{O} \rangle_\lambda F_{\mathcal{O}}(N|\lambda - \lambda_c|^\nu), \quad (4)$$

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 function

$$\Delta_{\mathcal{O}}(\lambda; N, N') = \frac{\ln(\langle \mathcal{O} \rangle_\lambda^{(N)} / \langle \mathcal{O} \rangle_\lambda^{(N')})}{\ln(N'/N)}. \quad (5)$$

If one takes the operator $\mathcal{O} = \mathcal{H}$, then $\langle \mathcal{H} \rangle_\lambda^{(N)} = E_\lambda^{(N)}$ is the usual linear-variational approximation to the ground-state

energy E_λ . From $\mathcal{O} = \partial \mathcal{H} / \partial \lambda$ we obtain a second equation, which together with Eq. (5) is used to define the function

$$\Gamma(\lambda; N, N') = \frac{\Delta_{\mathcal{H}}(\lambda; N, N')}{\Delta_{\mathcal{H}}(\lambda; N, N') - \Delta_{\partial \mathcal{H}_\lambda / \partial \lambda}(\lambda; N, N')}, \quad (6)$$

which is independent of the values of N and N' at the critical point $\lambda = \lambda_c$. The particular value of Γ at $\lambda = \lambda_c$ is the critical exponent α for the ground-state energy as defined in Eq. (2) (Ref. 31):

$$\alpha = \Gamma(\lambda = \lambda_c; N, N'). \quad (7)$$

Actually Eqs. (6) and (7) are asymptotic expressions. For three different values of N, N', N'' (we choose $N' = N - 2$ and $N'' = N + 2$) the curves of $\Gamma(\lambda, N)$ as a function of λ will intersect at successions of pseudocritical points $\lambda_c^{(N)}$,

$$\Gamma(\lambda = \lambda_c^{(N)}; N - 2) = \Gamma(\lambda = \lambda_c^{(N)}; N), \quad (8)$$

giving also a set of pseudocritical exponents:

$$\alpha^{(N)} = \Gamma(\lambda_c^{(N)}; N). \quad (9)$$

The successions of values of $\lambda_c^{(N)}$ and $\alpha^{(N)}$ can be used to obtain the extrapolated value of λ_c and α (Ref. 32).

This general approach has been successfully applied to calculate the critical parameters for two-electron atoms,³⁰ three-electron atoms,³³ simple diatomic molecules,³⁴ stability of three-body Coulomb systems,³⁵ and crossover phenomena and resonances in quantum systems.³⁶

III. ONE ELECTRON IN AN ELECTRIC-QUADRUPOLE FIELD

In this section, we will present some general results for an electron in the presence of a quadrupole potential.

We will analyze the case of k Coulomb centers with the quadrupole as the first nonvanishing multipole moment. A short comment about point quadrupole potentials is included at the end of the section.

The model system consists of a charge Q at the origin of coordinates and k charges $-Q/k$ located at \vec{R}_i , $i = 1, \dots, k$, where the position vectors \vec{R}_i are chosen with the constraint that the first nonzero multipole be the quadrupole moment for $k > 1$. Note that for the dipole system we have a symmetry in $Q \rightarrow -Q$; therefore, the energy is an even function of the dipole moment. For the case of a quadrupole potential this symmetry does not apply; thus, the cases $Q > 0$ and $Q < 0$ have different critical charges.

The Hamiltonian for an electron in this quadrupole field is given by

$$\mathcal{H}_{quad} = -\frac{1}{2} \nabla^2 - \frac{Q}{r} + \frac{Q}{k} \sum_{i=1}^k \frac{1}{|\vec{r} - \vec{R}_i|}, \quad k \geq 2. \quad (10)$$

For $k = 1$ Hamiltonian, Eq. (10), represents an electron in a dipole field.

It was shown by Hunziker and G nter³⁷ that there exists $Q^* > 0$ such that for $|Q| < Q^*$ the Hamiltonian, Eq. (10), has no bound states.

For the case of k charges equidistant from the central charge $|\vec{R}_i|=R$, $i=1,\dots,k$, the Hamiltonian could be scaled in both Q or R variables:

$$\begin{aligned}\mathcal{H}_{quad}(Q,R,\vec{r}) &= Q^2\mathcal{H}_{quad}(1,QR,Q\vec{r}) \\ &= \frac{1}{R^2}\mathcal{H}_{quad}(QR,1,\vec{r}/R).\end{aligned}\quad (11)$$

Therefore, it actually has only one free parameter. After scaling distances and energies, the rescaled Hamiltonian in the new variable $q=QR$ takes the form

$$\mathcal{H}_{quad} = -\frac{1}{2}\nabla^2 - \frac{q}{r} + \frac{q}{k} \sum_{i=1}^k \frac{1}{|\vec{r}-\hat{r}_i|}, \quad (12)$$

where \hat{r}_i is a unit vector in the direction of the charge i .

It is straightforward to show, using variational arguments, that the Hamiltonian, Eq. (12), can support at least one bound state for large values of $|q|$. Using a simple exponential trial wave function located at the positive charges, the contribution of the negative charges will be exponentially small for large values of $|q|$. Therefore, the expectation value of the Hamiltonian, Eq. (12), is less than zero for large enough values of $|q|$, and at least one bound state exists. Note that these results holds for both cases $q>0$ and $q<0$. Therefore there is a critical value q_c for binding an electron in a quadrupole potential.

In particular, for $q>0$ we also have an upper bound for the critical charge q_c . From simple variational arguments for $q>0$, the following inequality holds:

$$q_c^{(k=1)} = q_c^{(dipole)} \leq q_c^{(k=2)} \leq q_c^{(k)} < q_c^{(\infty)}, \quad (13)$$

where $q_c^{(k)}$ is the critical parameter of the Hamiltonian, Eq. (12), $q_c^{(1)}$ corresponds to the critical value of the dipole, and $q_c^{(\infty)}$ is calculated by taking the limit $k\rightarrow\infty$ for a fixed value of q , which corresponds to a charge q at the center of a uniform charged sphere of radius $R=1$ and charge $-q$. At this limit, the potential becomes

$$V(r) = \begin{cases} -\frac{q}{r} + q & \text{if } r < 1, \\ 0 & \text{if } r > 1. \end{cases} \quad (14)$$

The Schrödinger equation for this potential is exactly solvable in terms of continued fractions. Thus one can obtain the critical parameter $q_c^{(\infty)}$ with an arbitrary precision. Therefore we have rigorous lower and upper bounds for the critical parameter corresponding to $2 \leq k < \infty$:

$$q_c^{(dipole)} = 1.278\dots \leq q_c^{(k)} < q_c^{(\infty)} = 1.547\dots \quad (15)$$

For $q<0$, the case with $k=1$ is the dipole potential, so the lower bound is the same $q_c^{(dipole)} = 1.278$. However, there is no upper bound $q_c^{(\infty)}$ since for $k\rightarrow\infty$ there is no bound states for any value of q .

In the next section, we will present numerical calculations using finite-size scaling for the case $k=2$. The model Hamiltonian for this system consists of a charge q at the origin and two charges $-q/2$ at $z = \pm 1$:

$$\mathcal{H}(q) = -\frac{1}{2}\nabla^2 - \frac{q}{r} + \frac{q}{2} \left\{ \frac{1}{|\vec{r}-\hat{z}|} + \frac{1}{|\vec{r}+\hat{z}|} \right\}. \quad (16)$$

For the above Hamiltonian, Eq. (16), we have the symmetries

$$[\mathcal{H}(q), L_z] = 0 \quad \text{and} \quad [\mathcal{H}(q), \Pi_z] = 0, \quad (17)$$

where L_z is the angular momentum along the z axis and Π_z is the inversion operator, $\Pi_z\Phi(x,y,z) = \Phi(x,y,-z)$. Therefore the ground-state wave function is an even function of the coordinate z and does not depend on the azimuthal angle.

Hunziker and Günter have discussed some known binding and nonbinding criteria for a charged particle moving in the field of a neutral system of N fixed-point charges.³⁷ For our particular case, Hamiltonian, Eq. (16), we can prove the following:

Lemma $\exists q_c > 0$ such that for $|q| < q_c$ the Hamiltonian, Eq. (16), has no bound states. *Proof* Let E_{quad} and $\Psi_0(\vec{r})$ be the ground-state energy and wave function of the finite quadrupole Hamiltonian, Eq. (16), respectively, and define

$$V_{\pm} = \frac{1}{|\vec{r} \pm \hat{z}|} - \frac{1}{r}. \quad (18)$$

Since from condition, Eq. (17), the ground state $\Psi_0(\vec{r})$ must be an even function of the coordinate z :

$$\langle \Psi_0 | V_+ | \Psi_0 \rangle = \langle \Psi_0 | V_- | \Psi_0 \rangle. \quad (19)$$

The dipole Hamiltonian can be written in terms of both V_{\pm} :

$$\mathcal{H}_{dip} = -\frac{1}{2}\nabla^2 + qV_{\pm}. \quad (20)$$

Using the variational principle we obtain

$$\langle \Psi_0 | \mathcal{H}_{dip} | \Psi_0 \rangle \geq E_{dip}, \quad (21)$$

where E_{dip} is the exact ground-state energy of the Hamiltonian, Eq. (20). In addition we can write

$$\langle \Psi_0 | \mathcal{H}_{dip} | \Psi_0 \rangle = \langle \Psi_0 | T | \Psi_0 \rangle + q \langle \Psi_0 | V_{\pm} | \Psi_0 \rangle, \quad (22)$$

where T is the kinetic energy operator. Using the symmetry relation (19) we find that

$$\begin{aligned}\langle \Psi_0 | \mathcal{H}_{dip} | \Psi_0 \rangle &= \langle \Psi_0 | T + \frac{q}{2}V_+ + \frac{q}{2}V_- | \Psi_0 \rangle \\ &= \langle \Psi_0 | \mathcal{H}(q) | \Psi_0 \rangle = E_{quad}(q).\end{aligned}\quad (23)$$

From Eqs. (21) and (23) we obtain

$$E_{quad}(q) \geq E_{dip}(q). \quad (24)$$

It is rigorously known that the finite dipole Hamiltonian, Eq. (20), does not support bound states for $q < q_c^{dipole} = 1.278630$, which is the critical value of q for the point dipole potential.² Thus Eq. (24) ensures that there exists a value q_c , $|q_c| \geq q_c^{dipole}$, such that the finite quadrupole Hamiltonian, Eq. (16), has no bound states. Note that because $E_{dip}(q) = E_{dip}(-q)$, the proof is valid for both cases $q>0$ and $q<0$.

For the case of an electron in a point-quadrupole potential, the Hamiltonian is given by

$$\mathcal{H}_{point} = -\frac{1}{2}\nabla^2 - \frac{QP_2(\cos(\theta))}{r^3}, \quad (25)$$

where $P_2(\cos(\theta))$ is the standard Legendre polynomial of degree 2 and we take $Q > 0$.

It is known that this Hamiltonian, Eq. (25), does not admit *physical* solutions. The Hamiltonian is not bounded from below and the square integrable eigenfunctions with negative energies, which are arbitrarily large in absolute values, exist for any value of Q (Refs. 38 and 39). Therefore, to describe the binding of an electron to a molecule with the quadrupole moment as a dominant term we have to exclude the divergence at $r=0$.

There is no unique way to exclude this divergence. One possibility, as we have done in this study, is to replace the point quadrupole by a finite one. In this case, the quadrupole moment is dominant at large distances but the outer multipole series expansion has infinite terms. There are no divergences faster than r^{-1} and the Hamiltonian is bounded from below. A minimum value of the energy (ground state), if it exists, is finite and the corresponding square-integrable wave function does not present the “fall to the center” problem.³⁸

Another possible way to avoid this divergence is to include a cutoff radius r_c and consider a pure quadrupole potential for $r > r_c$ and a hard core repulsion for $r < r_c$ (Ref. 22):

$$V_1(\vec{r}) = \begin{cases} +\infty, & r < r_c, \\ -\frac{QP_2(\cos(\theta))}{r^3}, & r > r_c. \end{cases} \quad (26)$$

A similar qualitative result could be obtained with the potential

$$V_2(\vec{r}) = \begin{cases} -\frac{QP_2(\cos(\theta))}{r_c^3}, & r < r_c, \\ -\frac{QP_2(\cos(\theta))}{r^3}, & r > r_c. \end{cases} \quad (27)$$

Since $V_2(\vec{r}) \leq V_1(\vec{r}) \forall \vec{r}$, it is straightforward to prove, applying the variational principle, that if V_2 does not support a bound state, then V_1 does not either. Thus the existence of a critical value $Q_c^{(2)}$ of Q for V_2 ensures that a critical value $Q_c^{(1)}$ of Q for V_1 also exists with $Q_c^{(2)} \leq Q_c^{(1)}$. We may apply again the variational principle in order to prove that $V_2(\vec{r})$ does not support a bound state if the central potential of the form

$$V(r) = \begin{cases} -\frac{Q}{r_c^3}, & r < r_c, \\ -\frac{Q}{r^3}, & r > r_c, \end{cases} \quad (28)$$

does not have bound states. Using the Calogero inequality for the maximum number of S -waves bound states of an attractive central potential^{40,41} one can show that a critical value $Q_c \geq \pi^2 r_c / 36$ exists for this potential and therefore also exists for both potentials V_1 and V_2 .

IV. FINITE-SIZE SCALING CALCULATIONS

Now, we are in a position to apply the FSS calculations for the Hamiltonian, Eq. (16), for both cases $q > 0$ and $q < 0$. All FSS equations presented in Sec. II are valid with $\lambda = |q|$.

For the case $q > 0$ we expect the Slater basis set in spherical coordinates to be adequate. A complete basis set for the ground-state calculations is given by

$$\Phi_{n,l}(\vec{r}) = \left[\frac{4\pi\beta^{2n+3}}{(4l+1)(2n+2)!} \right]^{1/2} e^{-\beta r/2} r^n P_{2l}(\theta), \quad (29)$$

$$n = 0, 1, \dots, \quad l = 0, 1, \dots, [n/2],$$

where β is a variational parameter used to optimize the numerical results and $P_{2l}(\theta)$ is the Legendre polynomial of order $2l$.

For $q < 0$ the ground-state wave function is zero at the origin of the coordinates. Thus, it is natural to work with prolate spheroidal coordinates (ξ, η, φ) (Ref. 39) defined as

$$\xi = r_1 + r_2, \quad \eta = r_1 - r_2, \quad \phi = \tan^{-1}(y/x), \quad (30)$$

where

$$r_1 = \sqrt{x^2 + y^2 + (z-1)^2}, \quad r_2 = \sqrt{x^2 + y^2 + (z+1)^2}. \quad (31)$$

ξ goes from 1 to ∞ , η goes from -1 to 1 , and the azimuthal angle φ varies from 0 to 2π .

In these coordinates the scaled Hamiltonian takes the form

$$\mathcal{H} = -\frac{1}{2}\nabla^2 + \frac{4q\eta}{\xi^2 - \eta^2}. \quad (32)$$

The symmetries, Eq. (17), imply that the ground-state wave function does not depend on φ and is an even function of η . Therefore, we choose the basis set

$$\Phi_{n,l}(\xi, \eta) = C_{n,l} e^{-\beta\xi} \xi^n P_{2l}(\eta), \quad n = 0, 1, \dots, \quad (33)$$

$$l = 0, 1, \dots, [n/2],$$

where β , as in the Slater basis set, is a free parameter used to optimize numerical results.

For numerical calculation, the basis set is truncated at a maximum value N which determines the size $M(N)$ of the truncated Hamiltonian matrix:

$$M(N) = \begin{cases} \frac{N^2 + 4N + 3}{4} & \text{for odd } N, \\ \left(\frac{N+2}{2}\right)^2 & \text{for even } N. \end{cases}$$

Then, we calculate the ground-state energy using the Ritz-variational method for a nonorthogonal basis set. The matrix elements for both cases are given in the Appendix.

FSS calculations for both spherical and cylindrical potentials show strong parity effects.³² For this reason we choose $N' = N + 2$ in all cases. In the following subsections, we present the FSS results for the linear quadrupole Hamiltonian, Eq. (16), for both cases $q > 0$ and $q < 0$.

Note that the particular choice of the scaled Hamiltonian, Eq. (16), with R has a technical reason: the trun-

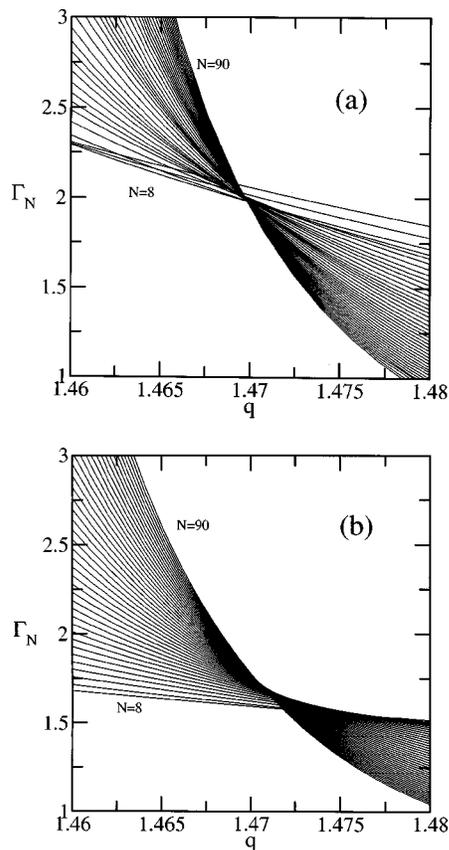


FIG. 1. $\Gamma(q, N)$ as a function of q for the ground-state energy of the electric quadrupole ($q > 0$) potential for even values of N (a) in spherical coordinates and (b) in the prolate spheroidal basis set.

calculated Hamiltonian matrix is a linear function of q . Therefore, the expensive calculations of the matrix elements (about 10 days of CPU time in a dual 2.6-MHz PC) have to be done only one time. In order to obtain the limit of a point quadrupole potential, one should take the limit $R \rightarrow 0, q \rightarrow \infty$, with $qR^2 = \text{const}$, in the Hamiltonian, Eq. (10). Since we scaled the Hamiltonian with R , this limit is not easy to study numerically. In order to apply the finite-size scaling method one has to choose an alternative scaling in Eq. (11) in order to write the Hamiltonian as a function of R and calculate the matrix elements for each value of R .

A. Linear charge configuration with $q > 0$

In Fig. 1(a) we show $\Gamma(q, N)$, as defined in Eq. (6), as a function of q for even values of N using the Slater basis set, Eq. (29), in spherical coordinates. Figure 1(b) shows $\Gamma(q, N)$ as a function of q using prolate spheroidal coordinates, Eq. (33). Curves obtained using odd values of N are qualitatively identical and they are not shown in the figures.

We show in Fig. 2 the pseudocritical $q_c^{(N)}$, defined in Eq. (8), as a function of $1/N$ for even values of N for both basis sets. In the case of spherical basis set, the extrapolated value is $q_c^{(ext)} = 1.4696 \pm 0.0005$. Using prolate spheroidal coordinates the extrapolated value is $q_c^{(ext)} = 1.4697 \pm 0.0001$.

To obtain the critical exponent for the energy, we plot in Fig. 3 the values $\alpha^{(N)}$, as defined by Eq. (9), as a function of

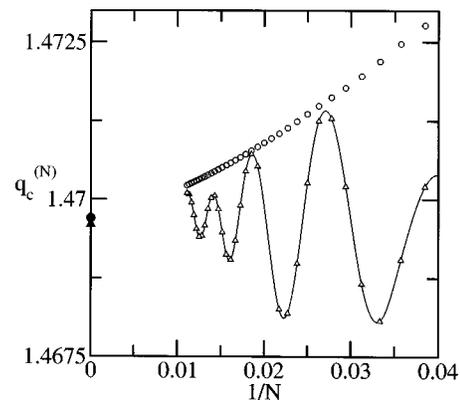


FIG. 2. $q_c^{(N)}$ as a function of $1/N$ for the ground-state energy of the electric quadrupole ($q > 0$) for even values of $N = 26, \dots, 90$. Results for the two basis sets are shown. The solid points show the extrapolated critical parameters. $q_c^{(ext)} = 1.4696 \pm 0.0005$ (triangles) for spherical coordinates and $q_c^{(ext)} = 1.4697 \pm 0.0001$ (circles) for prolate spheroidal coordinates.

$1/N$ for even values of N . With the spherical basis set we obtained an extrapolated value of the critical exponent $\alpha^{(ext)} = 1.98 \pm 0.03$ and $\alpha^{(ext)} = 1.84 \pm 0.04$ using the elliptical basis set.

We can see in Figs. 2 and 3 that the behavior of the finite-size calculations has a strong dependence on the basis sets. In the case of the Slater basis set there exists a non-monotonic behavior that makes the asymptotic studies difficult. It is a known result⁴² that spherically symmetric potentials that go to infinity as $1/r^3$ have a critical exponent $\alpha = 2$. If we examine our numerical results, it is reasonable to assume that our system has the same critical exponent.

In order to support this assumption we can examine the data collapse for the FSS results. The data-collapse ansatz⁴³ establishes that when scaling laws, Eqs. (2) and (4), are valid, then near the critical point q_c all curves $E_\lambda^{(N)} N^{\alpha/\nu}$ plotted against $(q - q_c) N^{1/\nu}$ must collapse onto a single universal curve.

Assuming that our model has the same critical exponents $\nu = 1$ and $\alpha = 2$ for the Hamiltonian with a spherical poten-

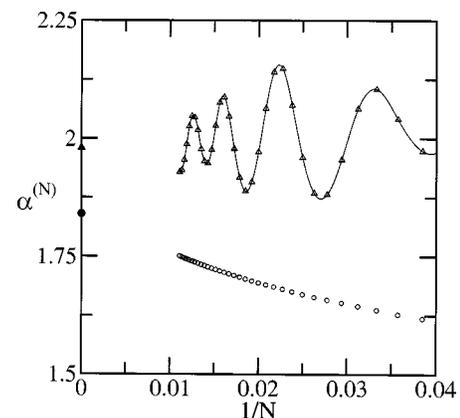


FIG. 3. $\alpha^{(N)}$ as a function of $1/N$ for the ground-state energy of the electric quadrupole ($q > 0$) for even values of $N = 26, \dots, 90$. The results for both basis sets are shown. The solid points show the extrapolated critical exponents. $\alpha^{(ext)} = 1.98 \pm 0.03$ (triangles) for spherical coordinates and $\alpha^{(ext)} = 1.84 \pm 0.04$ (circles) for prolate spheroidal coordinates.

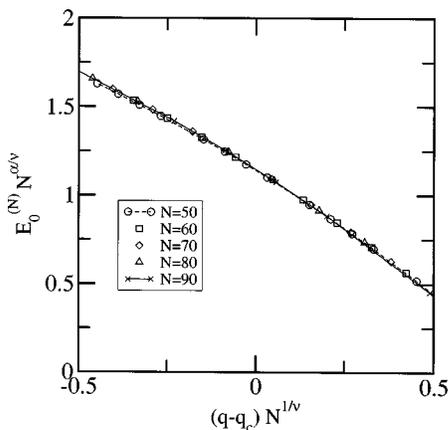


FIG. 4. Data-collapse curves for the ground-state energy of the quadrupole $q > 0$ with $\alpha = 2$, $\nu = 1$ and $q_c = 1.470$ for spherical coordinates.

tial that goes to infinity as $1/r^3$, we can use the data collapse to estimate q_c . In order to obtain the value of q_c , we plot $E_\lambda^{(N)} N^{\alpha/\nu}$ as a function of $(q - q_c) N^{1/\nu}$ for different values of N , leaving q_c as a free parameter. Using values of energies as a function of q calculated in spherical coordinates, by minimizing the distance between the two curves we can obtain an approximate value for the critical parameter. Figure 4 shows the estimated $q_c = 1.470$ which is in a complete agreement with the previous extrapolated value $q_c^{(ext)} = 1.4696$.

B. Linear charge configuration with $q < 0$

Here, we repeat the above FSS calculations for the quadrupole case with $q < 0$. FSS calculations cannot be performed using the Slater basis set in spherical coordinates since the exact ground-state wave function vanishes at $\vec{r} = 0$. So we cannot obtain accurate near-threshold values of the energy and its derivative even for very large values of N . However, the basis set, Eq. (33), defined in prolate spheroidal coordinates, seems to be a natural choice to approximate the ground-state wave function.

Figure 5 shows the intersection of $|q_c^{(N)}|$ as a function of

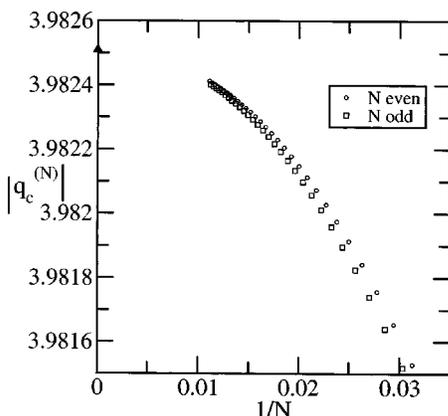


FIG. 5. $|q_c^{(N)}|$ as a function of $1/N$ for the ground-state energy of the electric quadrupole ($q < 0$) for even and odd values of $N = 34, \dots, 90$ and for the prolate spheroidal basis set. The solid point shows the extrapolated critical parameter. $|q_c^{(ext)}| = 3.98251 \pm 0.00005$ (triangles).

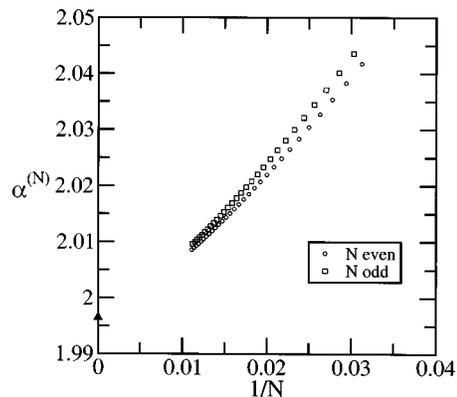


FIG. 6. $\alpha^{(N)}$ as a function of $1/N$ for the ground-state energy of the electric quadrupole ($q < 0$) for even and odd values of $N = 34, \dots, 90$. Results obtained with the prolate spheroidal basis set. The solid point show the extrapolated critical exponent. $\alpha^{(ext)} = 1.9964 \pm 0.0005$ (triangles).

$1/N$ using prolate spheroidal coordinates. We obtained the extrapolated value $|q_c^{(ext)}| = 3.98251 \pm 0.00001$. We also present in Fig. 6 the values of the pseudocritical exponent $\alpha^{(N)}$ as a function of $1/N$. The extrapolated value is $\alpha^{(ext)} = 1.9964 \pm 0.0005$.

Even the FSS method, Eq. (6), does not give accurate results for critical parameters using the Slater basis set in spherical coordinates. We test the data-collapse ansatz with the energies calculated in this basis set. As before, we assume that $\alpha = 2$ and $\nu = 1$, and minimizing the distance between $E_0^{(50)}$ and $E_0^{(90)}$, we obtained by data collapse an approximated critical parameter $|q_c| \approx 3.9777$, which is in good agreement with the above-extrapolated value $|q_c|^{(ext)} = 3.98251$. The data-collapse results are shown in Fig. 7.

V. CONCLUSIONS

We have presented finite-size scaling calculations of the critical parameters for the stability of an electron bound by a quadrupole field. Moreover, we have shown that there is a strong dependence on the basis set in performing FSS calculations. For the case $q > 0$, we assume that spherical coordi-

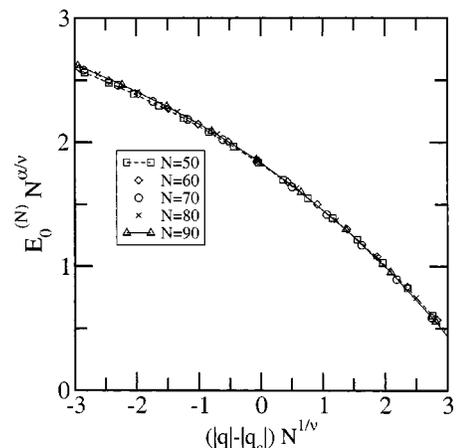


FIG. 7. Data collapse for the ground-state energy of the quadrupole ($q < 0$) with $\alpha = 2$, $\nu = 1$ and $q_c = 3.97675$ for spherical coordinates.

nates are more suitable than prolate spheroidal coordinates. Although the results with this choice were very accurate, the oscillating behavior of the FSS calculations introduces noise in the asymptotic analysis. However, for $q < 0$, the results are better with prolate spheroidal coordinates. The extrapolated values obtained for q_c using finite-size scaling calculations are in good agreement with the results of Pupyshev and Ermilov obtained by other methods.²⁴

In addition, the FSS method permits the calculation of the critical exponents. Our numerical results are in good agreement with the one obtained for rotationally invariant Hamiltonians with potentials having the same asymptotic properties at $r \rightarrow \infty$. This finding is supported by the data-collapse ansatz as shown in Figs. 4 and 7.

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APPENDIX: MATRIX ELEMENTS FOR THE QUADRUPOLE-FIELD HAMILTONIAN

In this appendix we include the matrix elements for the quadrupole-field Hamiltonian in both spherical and prolate spheroidal coordinates. Since the problem has cylindrical symmetry and we need an expansion for the ground-state wave function, we have to use complete basis sets for Σ states. In both coordinates this means that the calculations

are independent of the azimuthal angle. Because of the special symmetries as shown in Eq. (17), we consider only Legendre polynomials of even degree in θ in spherical coordinates and in η in prolate spheroidal coordinates.⁴⁴

1. Basis set and matrix elements in spherical coordinates

The overlap integral is given by

$$\langle m, n | m', n' \rangle = \frac{(m+m'+2)!}{[(2m+2)!(2m'+2)!]^{1/2}} \delta_{n, n'}, \quad (\text{A1})$$

the kinetic energy matrix elements take the form

$$\begin{aligned} \langle m, n | T | m', n' \rangle &= \frac{\beta^2 (m+m')!}{2[(2m+2)!(2m'+2)!]^{1/2}} \\ &\times \left(2n(2n+1) - \frac{1}{4}[(m-m')^2 - (m+1) \right. \\ &\left. - (m'+1)] \right) \delta_{n, n'}, \end{aligned} \quad (\text{A2})$$

and finally the potential energy matrix elements are given by

$$\langle m, n | \frac{1}{r} | m', n' \rangle = \frac{\beta(m+m'+1)!}{[(2m+2)!(2m'+2)!]^{1/2}} \delta_{n, n'} \quad (\text{A3})$$

and

$$\begin{aligned} \langle m, n | \frac{1}{|\vec{r} \pm \hat{k}|} | m', n' \rangle &= \beta \sqrt{\frac{(4n+1)(4n'+1)}{(2m+2)!(2m'+2)!}} \sum_{k_{par}=2|n-n'|}^{k_{par}=2|n+n'|} \frac{\gamma_{nn'k}^2}{2n+2n'+k+1} \\ &\times \frac{(m+m'+k+2)! + \beta^{2k+1} \Gamma(m+m'-k+2, \beta) - \Gamma(m+m'+k+3, \beta)}{\beta^{k+1}}, \end{aligned} \quad (\text{A4})$$

where β is a variational parameter used to optimize the numerical results:

$$\gamma_{nn'k} = \frac{\tau(n+n'+k)}{\tau(n+n'-k)\tau(n-n'+k)\tau(-n+n'+k)} \quad (\text{A5})$$

and

$$\tau(n) = \frac{n!}{\sqrt{(2n)!}}. \quad (\text{A6})$$

2. Basis set and matrix elements in prolate spheroidal coordinates

In prolate spheroidal coordinates (ξ, η, φ) defined by Eqs. (30) and (31) we use a nonorthogonal basis set for Σ states.

The normalization constant is defined by the normalization condition $\langle m, n | m, n \rangle = 1$

$$\begin{aligned} C_{m,n} &= \left\{ \frac{2}{(4n+1)} \left[\alpha_{2(m+1)}(2\beta) \right. \right. \\ &\left. \left. - \frac{(8n^2+4n-1)\alpha_{2m}(2\beta)}{(4n-1)(4n+3)} \right] \right\}^{-1/2} \end{aligned} \quad (\text{A7})$$

and $\alpha_k(x)$ is an exponential integral related to the incomplete gamma function⁴⁵

$$\alpha_k(x) = \int_1^\infty e^{-xt} t^k dt = \frac{\Gamma(k+1, x)}{x^{k+1}}. \quad (\text{A8})$$

Then the overlap integral is given by

$$\begin{aligned} \langle m, n | m', n' \rangle = & \frac{2}{4n+1} C_{m,n} C_{m',n'} \left\{ \left[\alpha_{m+m'+2}(2\beta) \right. \right. \\ & - \left. \frac{(8n^2+4n-1)\alpha_{m+m'}(2\beta)}{(4n-1)(4n+3)} \right] \delta_{n,n'} \\ & - \frac{2(n+1)(2n+1)\alpha_{m+m'}(2\beta)}{(4n+3)(4n+5)} \delta_{n',n+1} \\ & \left. - \frac{2n(2n-1)\alpha_{m+m'}(2\beta)}{(4n-3)(4n-1)} \delta_{n',n-1} \right\}, \end{aligned} \quad (\text{A9})$$

and the kinetic energy has the form

$$\begin{aligned} \langle m, n | T | m', n' \rangle \\ = C_{m,n} C_{m',n'} \frac{4\delta_{n,n'}}{4n+1} \{ -\beta^2 \alpha_{m+m'+2}(2\beta) + 2\beta(m'+1) \\ \times \alpha_{m+m'+1}(2\beta) + [\beta^2 - m'^2 - m' + 2n(2n+1)] \\ \times \alpha_{m+m'}(2\beta) - 2\beta m' \alpha_{m+m'-1}(2\beta) \\ + m'(m'+1) \alpha_{m+m'-2}(2\beta) \}. \end{aligned} \quad (\text{A10})$$

Finally, the terms in the potential corresponding to two equal sign charges, located at $(0,0,\pm 1)$ in scaled units, take the form

$$\begin{aligned} \langle m, n | \frac{1}{|\vec{r}-\hat{k}|} + \frac{1}{|\vec{r}+\hat{k}|} | m', n' \rangle \\ = \langle m, n | \frac{8\xi}{\xi^2 - \eta^2} | m', n' \rangle \\ = \frac{8}{4n+1} C_{m,n} C_{m',n'} \alpha_{m+m'+1}(2\beta) \delta_{n,n'}. \end{aligned} \quad (\text{A11})$$

For the matrix elements of potential $1/r$ we used the standard expansion of $1/|\vec{r}-\vec{r}'|$ in Legendre functions in prolate spheroidal coordinates³⁹ with $\vec{r}'=0$:

$$\frac{1}{r} = 2 \sum_{k=0}^{\infty} \frac{(-1)^k (4k+1)(2k-1)!!}{2^k k!} P_{2k}(\eta) Q_{2k}(\xi), \quad (\text{A12})$$

where $P_n(x)$ and $Q_n(x)$ are the Legendre polynomials and Legendre associated functions of the second kind, respectively.⁴⁵ Therefore we need the integrals

$$U_{m,n}^k(x) = \int_1^{\infty} e^{-x\xi} \xi^k Q_m(\xi) P_n(\xi) d\xi. \quad (\text{A13})$$

These integrals can be calculated by applying a recursive formula beginning with $U_{0,0}^k$ which has an analytical expression.⁴⁶ Since recursive processes are numerically unstable, we calculate these matrix elements with a multiprecision FORTRAN 90 code⁴⁷ with 100 digits testing 32 correct digits for the value of the matrix elements in order to use them in standard real(16) FORTRAN codes.

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