PHYSICAL REVIEW A, VOLUME 64, 062502

Crossover phenomena and resonances in quantum systems

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(Received 22 January 2001; published 13 November 2001)

The finite-size scaling method is used to calculate the critical parameters of a two-parameter model Hamiltonian that exhibit resonances. We show the existence of a crossover phenomenon for the energy spectrum; the transition from a bound state to a continuum is a ''second-order phase transition'' in one region and a ''first-order phase transition'' in another region. As the parameters varied, the numerical value of the critical exponent of the energy levels changed from two to one. In the zone where the critical exponent equals one, the system has narrow resonances and they disappear when the exponent is two. The method has potential applicability in predicting stable and metastable atomic and molecular states. We also show that finite-size scaling methods are capable of detecting multicritical points.

DOI: 10.1103/PhysRevA.64.062502 PACS number(s): 31.15.−p

The finite-size scaling method (FSS) was formulated in statistical mechanics to extrapolate information obtained from a finite system to the thermodynamic limit [1,2]. In quantum mechanics, when using variation methods, one encounters the same finite-size problem in studying the critical behavior of a quantum Hamiltonian $\mathcal{H}(\lambda_1, \ldots, \lambda_k)$ 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 paper, a critical point λ_c is defined as the point where a bound-state energy becomes absorbed or degenerate with a continuum. In the variational calculations, 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 [3]. The problem of what happens when the continuum ''swallows'' a bound state has a long history with many important results and was reviewed in Ref. [3].

Recently, Neirotti, Serra, and Kais have developed the FSS method to calculate atomic and molecular critical parameters [4,5]. In particular, FSS calculations for two and three electron atoms gave very accurate results for the critical nuclear charges [6,7]. These results have shown that the analytical behavior of the energy as a function of the nuclear charge for lithiumlike atoms is completely different from that of heliumlike atoms. Analogy with standard phase transitions show that for helium, the transition from a bound state to a continuum is ''first-order,'' while lithium exhibits a ''second-order phase transition.'' For the helium sequence, the question of whether or not the radius of convergence, of the $1/Z$ expansion for the energy, is the same as the variational critical energy was discussed by several authors [8–10]. The coincidence between the critical point and the radius of convergence was conjectured by Reinhardt using arguments based on dilatation analyticity [11] and later rigorously confirmed, analytically and numerically, by Baker *et al.* [12]. Our results for the helium sequence using the finite-size scaling method were in complete agreement with the Reinhardt analysis [3,6].

The nature of the resonances states, narrow or broad, is crucially dependent on the behavior of the corresponding bound eigenvalue in the neighborhood of a threshold. If there is a true bound state at the threshold, then the Hellman-Feynman theorem implies that the eigenvalue hits the continuum linearly in $(\lambda-\lambda_c)$ [13], i.e., in a ''first-order phase transition,'' and the corresponding continuum state will develop a sharp $\mathrm{Im}(E) \ll \mathrm{Re}(E)$ resonance. However, if there is no bound state at the threshold, then the eigenvalue merges into the continuum quadratically in $(\lambda-\lambda_c)$ [13], i.e., in a ''second-order phase transition.'' This behavior occurs in many atomic systems. For example, for three electron atoms, we have shown that the transition from the ground state to the continuum is a second-order phase transition with a critical nuclear charge $Z_c \simeq 2$[7]. This finding confirmed the experimental and theoretical results that doubly negative hydrogen, $Z=1<Z_c$, does not exist in the ground state. However, the closed shell He atom exhibits a ''first-order phase transition.'' In particular, the excited state energy of the He$(2p^2)$ ^3P hits the continuum linearly with $Z_c \simeq 0.994$, this result predicts the formation of a resonance state for $\mathrm{H}^{-2}(2p^3)$ $^4S^0$. This system, H^{-2} has been a matter of controversial debate in the literature of whether or not it does exhibit resonances. Recently, Sommerfeld *et al.*, using large-scale calculations in the framework of the complex-rotated Hamiltonian, have shown that $(2p^3)$ $^4S^0$ is a resonance state with a long lifetime [14]. For ten electron atoms, the transition is of first-order nature and the critical nuclear charge was found to be $Z_c \simeq 8.74$ [15], the isoelectronic series includes Ne, F^-, and O^{2-}. The F^- ion has a stable bound state, $Z=9>Z_c$, and the doubly negative ion O^{--}, $Z=8<Z_c$, has a sharp resonance corresponding to the ground state [15].

The transition from a bound state to a resonance state has been discussed by Taylor in his book, *Scattering Theory* [16]. Since the resonances (i.e., complex poles of the scattering amplitude) are associated with complex eigenvalues of the non-Hermitian Hamiltonian, we will discuss here briefly the transition from a bound state to a resonance state using the non-Hermitian formalism of quantum mechanics (see, for example, Ref. [17]). In the solution of the time-independent Schröedinger equation, one should specify the boundary conditions. Let us assume that by imposing the boundary condition of $\Psi(x)\to 0$ as $|x|\to\infty$ a closed form expression for the nth eigenvalue is obtained, $E_n(J)$, where J is a potential parameter. Not all eigenvalues are necessarily associated with bound states. For example, in the case of Morse potential, only the first $n\leqslant N$ states are associated with bound states, whereas all other real and negative (i.e., below threshold) eigenvalues are associated with virtual states. Virtual states are associated with exponential divergent asymptotes, $\Psi(x)\to\exp(+kx)$ where $k>0$. However, by imposing the boundary conditions as mentioned above, one does not determine the contour of integration and it may be considered as $x=f(x')$, such that $x\to -x$ when $x'\to\infty$. In Ref. [17], three different examples are given where a bound state becomes a resonance state (associated with a complex eigenvalue of the Hamiltonian) as a potential parameter (denoted here by J) is varied. The resonances are associated with exponential divergent asymptotes, $\Psi(x)\to\exp(+ikx)$ where $\mathrm{Re}(k)>0$ and $\mathrm{Im}(k)<0$, which become square integrable when $x=f(x')$ such that $x\to x'\exp(-i\phi)$ as $x'\to\infty$, where $\phi>\arctan[-\mathrm{Im}(k)/\mathrm{Re}(k)]$.

From the three models presented in Ref. [17], one can see that a bound state becomes a resonance state when $E(J)$ has a singularity nearest J_c [where $E_n(J_c)=0$] which is a branch point at $J=J_b$ with fractional exponent $\alpha=1/2$. Byers Brown pointed out that this singularity may happen at the complex J plane and the fractional exponent can be in general $\alpha=k/m$. He explained that also the conjugate $J=J_b^*$ must also be a branch point since the two points are connected by a branch cut. His analysis for a complex branch point with an arbitrary exponent has never been published, but one can find a description of his method in Ref. [18] and in Ref. [19]. Moiseyev and Freidland [19] associated the branch point at $J=J_b$ with the Puisean expansion in $(J-J_b)^{1/m}$, where m is the number of the eigenfunctions that are coalesced. The coalesence of n number of eigenfunctions at $J=J_b$ leads to an incomplete spectrum of the Hamiltonian and to the generation of a defective (i.e, self-orthogonal) eigenfunction. The behavior of $E(J)$ around the branch points are given by [19]

$$E_n(J)=\sum_{k=0}^{\infty}\gamma_{n,k}(J-J_b)^{k/m}. \tag{1}$$

For our studied case, which will be described below, we will show that only the narrow resonances and only within the framework of the finite matrix representation of the Hamiltonian, the bound-resonance transition happens at $J_b=J_c$ when

$$E_n(J)=-|\gamma_{n,2}|(J-J_c)-|\gamma_{n,3}|(J-J_c)^{3/2}, \tag{2}$$

where $\gamma_{n,k};k=2,3$ get real values. It is clear that in this special case for $J\geqslant J_c$ the nth energy level is associated with a bound state. However, complex eigenvalues associated with resonance states are obtained when J gets values that are smaller than J_c. Note that around $J=J_c$, one gets that $\mathrm{Re}(E_n)\sim\gamma_{n,1}(J-J_c)$, and therefore, the fractional exponent that is characteristic for the bound-resonance transition would not be obtained by a straightforward application of the FSS method to our studied case.

As we will show in this paper, when the number of the basis functions that are used to represent our model Hamiltonian is increased, all resonances, including the most narrow one, are not obtained by a such bound-resonance transition mechanisms. They are obtained, however, due to a virtual-resonance transition, where the virtual states are associated with complex eigenvalues (with real parts embeded below the threshold energy; i.e., the real parts are negative when the threshold energy is equal to zero). We emphasize, here, the fact that the eigenvalues associated with these types of virtual states are complex since the virtual states that are associated with bound-virtual transitions are associated with real (and negative) eigenvalues. The bound-virtual state transition happen when $E_n(J)$ does have a Taylor expansion in $J-J_c$. As we will show here, when the potential barriers in our model Hamiltonian are sufficiently small such a transition occurs when

$$E_n(J)=-|\gamma_{n,4}|(J-J_c)^2. \tag{3}$$

However, it may happen (as in our studied case) that as J is varied, a virtual state associated with $\Psi(x)\to\exp(+kx)$ where $k>0$, becomes a virtual state that is associated with $\Psi(x)\to\exp(+kx)$ where $\mathrm{Re}(k)>0$ and $\mathrm{Im}(k)<0$. As we will show, the resonances in such a case are obtained when this type of virtual state (associated with complex wave vector ik) becomes a resonance state as J is varied. Such virtual-resonance transition is associated with a branch point with exponent one half,

$$E_n(J)=\gamma_{n,1}(J-J_c)^{1/2} \tag{4}$$

or with a branch point,

$$E_n(J)=\gamma_{n,2}(J-Jc)-\gamma_{n,k}(J-J_c)^{1/k}, \tag{5}$$

where the value of k depends on the value of n (in our calculations $k=1$ or $k=5$).

To illustrate the appearance of resonances as a potential parameter is varied, let us consider the following one-dimensional Hamiltonian:

$$\mathcal{H}(a,J)=\frac{p^2}{2}+\left(\frac{x^2}{2}-J\right)e^{-ax^2}, \tag{6}$$

where a and J are free parameters. The potential in Eq. (6) exhibits predissociating resonances analogous to those found in diatomic molecules [20,21], and was used as a model potential to check the accuracy of different methods for the calculations of resonances [22,23].

We studied the critical behavior of the eigenfunctions and resonances of Hamiltonian Eq. (6) using the finite-size scaling method [5]. As a basis function for the finite-size scaling procedure, we used the orthonormalized eigenfunctions of the harmonic oscillator where mass equals one and frequency equals a,

$$\Psi_n(a;x)=\left(\frac{a}{\pi}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}e^{-(ax^2/2)}H_n(\sqrt{a}x), \tag{7}$$

where $H_n(x)$ are the Hermite polynomials of order n [24].

In order to obtain the matrix elements of the Hamiltonian Eq. (6) we need to calculate the kinetic-energy terms

$$\begin{aligned}T_{m,n}&\equiv<m\left|\frac{p^2}{2}\right|n>\\&=\frac{a}{2}\left[\left(n+\frac{1}{2}\right)\delta_{m,n}-\frac{\sqrt{(n+1)(n+2)}}{2}\delta_{m-2,n}\right.\\&\qquad\left.-\frac{\sqrt{(n-1)n}}{2}\delta_{m+2,n}\right]\end{aligned} \tag{8}$$

and the potential terms [25]

$$e_{m,n}\equiv\langle m|e^{-ax^2}|n\rangle=(-1)^{n+(n+m/2)}\frac{\Gamma\left(\frac{m+n+1}{2}\right)}{\sqrt{2\pi m!n!}},$$

$$m+n\ \ \text{even}=0,\qquad m+n\ \ \text{odd}. \tag{9}$$

The other matrix elements, $\langle m|x^k e^{-ax^2}|n\rangle$ for any value of k, may be evaluated using the recurrence relations between Hermite polynomials [24].

By diagonalizing the Hamiltonian in the above basis set, we obtained the eigenstates as a function of both parameters a and J. Now we are in a position to calculate the critical behavior of the system using finite-size scaling method [5]. In this context, critical means the values of a and J for which a bound-state energy becomes absorbed or degenerate with a continuum. We define $J_c^{(n)}(a)$ as the value of J for which the n-state energy becomes equal to zero (the threshold energy is set at zero),

$$J_c^{(n)}(a)\equiv\inf_{\{J\}}\{E_n(a,J)<0\} \tag{10}$$

and the related critical exponent for the energy α_n is given by

$$E_n(a,J)\underset{J\to J_c^{(n)+}}{\sim}(J-J_c^{(n)})^{\alpha_n}. \tag{11}$$

The critical line $J_c^{(n)}(a)$ and the critical exponent α_n were calculated using Eqs. (16) and (17) of Ref. [5]

$$\Gamma_\alpha^{(n)}(a,J;N,N')=\frac{\Delta\mathcal{H}^{(n)}(a,J;N,N')}{\Delta\mathcal{H}^{(n)}(a,J;N,N')-\Delta^{(n)}_{\partial\mathcal{H}/\partial J}(a,J;N,N')}, \tag{12}$$

where for any operator $\mathcal{O}$ at order N, the function $\Delta_{\mathcal{O}}$ is given by

$$\Delta_{\mathcal{O}}(\lambda;N,N')=\frac{\ln(\langle\mathcal{O}\rangle_\lambda^{(N)}/\langle\mathcal{O}\rangle_\lambda^{(N')})}{\ln(N'/N)}. \tag{13}$$

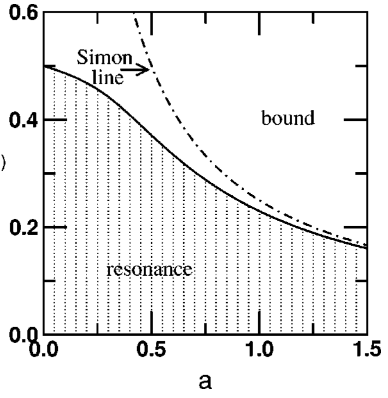

FIG. 1. Phase diagram for the ground-state energy, the critical J as a function of a, for $N=300$. The solid line separates the bound-state energies from the resonance energies. The Simon line is shown by the dashed line.

At the critical point $J=J_c^{(n)}(a)$ Eq. (12) is independent of the values of N and N' and gives the critical exponent α_n,

$$\alpha_n=\Gamma_\alpha^{(n)}(a,J_c^{(n)}(a);N,N'). \tag{14}$$

Figures 1 and 2 show the "phase diagrams" $J^{(n)}$ as a function of a for the ground-state $n=0$, and the excited-even state $n=2$. In both figures, the critical line separates the resonance region from the bound region. As we will show later, the transition from bound to resonance states go through virtual states. There are no bound states with positive energy for $a>0$, but there is at least one bound state for $J\geqslant J^*(a)\equiv 1/4a$ [26]. This result shows that the solid line in Fig. 1 does not crosses the curve $J^*=1/4a$ (the Simon line). Numerical results show that $J_c(a)$ goes asymptotically to $J^*(a)$ when $a\to\infty$. For fixed a, the ground-state $E_0(J,a)$ is concave, nonincreasing and continuous as a function of J, and it is decreasing for $J\geqslant 1/4a$ [27].

In the limit $a=0$, the Hamiltonian Eq. (6) reduces to the Hamiltonian of a harmonic oscillator where frequency equals one plus a constant J. Then the ground state is $E_0=1/2-J$ and therefore, the "critical" value of the parameter is $J_c(a=0)=1/2$. Of course, for $a=0$ there is no "true" critical parameters, because the system has an infinite number of

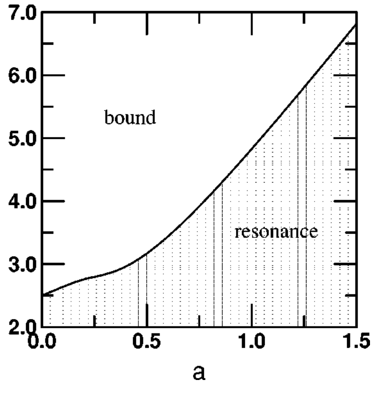

FIG. 2. Phase diagram for the even excited-state energy, the critical J as a function of a, for $N=300$. The solid line separates the bound-state energies from the resonance energies.

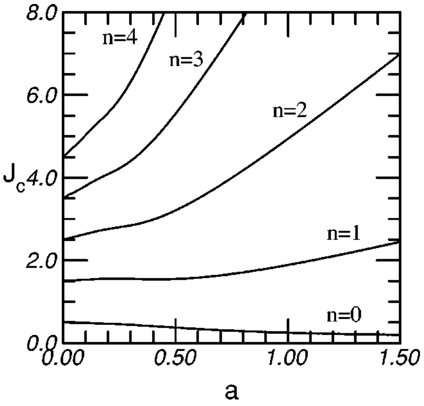

FIG. 3. Phase diagram for several energy states, the critical J as a function of a, for $N=300$.

bound states for all values of J. But $J=1/2$ corresponds to the value of J where the ground-state energy is equal to zero in agreement with the definition Eq. (10). For all values of $a>0$, there is no bound state with positive energy and the phase curve goes continuously to the point $(a=0,J=1/2)$ when $a\rightarrow 0$. Simple variational bounds show that the slope of the critical line $J_c(a)$ at $a=0$ is smaller than -1/8 (numerical results give a slope value near -0.14). In Fig. 3, the critical J_c is shown as a function of a for several states, $n=0,1,2,3$ and $n=4$. From a theorem proved by Klaus and Simon [13] valid for the Hamiltonian Eq. (6) we know that the critical exponent for the energy is $\alpha_n=2\ \forall n,a>0$, where n labels isolated bound states.

In Fig. 4 the critical exponent α_0 is shown as a function of a. A crossover phenomenon appears for this exponent. For large values of a, we obtain $\alpha_0 \simeq 2$,

$$E_0(a,J) \underset{J\rightarrow J_c^{(0)+}}{\sim} (J-J_c^{(0)})^2, \quad a \text{ fixed.} \tag{15}$$

But for small values of a, we have $\alpha_0 \simeq 1$

$$E_0(a,J) \underset{a\sim 0}{\sim} (J-J_c^{(0)}). \tag{16}$$

As a matter of fact, that sharp transition from $\alpha_0=2$ to $\alpha_0=1$ at $a\sim 0.2$ in Fig. 4 and at $a\sim 0.1$ in Fig. 5, results from the truncation of the Hamiltonian matrix. As the size of the basis set that is used to represent the Hamiltonian is increased, this transition occurs at $a\rightarrow 0$. Namely, the crossover phenomenon disappear as the size of the basis set is increased. As we will show later in Fig. 6 when $\alpha_0=2$ bound states become virtual states as J is reduced.

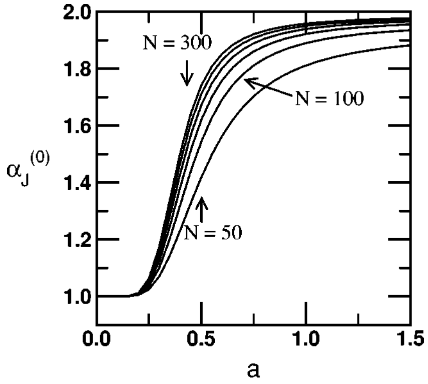

FIG. 4. The critical exponent for the ground state as a function of a for different values of $N=50,100,\ldots,300$.

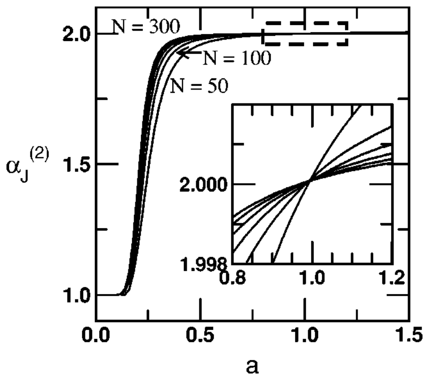

FIG. 5. The critical exponent for the even excited state as a function of a for different values of $N=50,100,\ldots,300$. Note the appearance of a special point at about $a=1$.

Figure 5 show the same behavior of α_2 as a function of a. For large values of a, the exponent is $\alpha_2=2$, but for small values of a, the exponent is one. The crossover region is related to the characteristic length of the finite basis set. The larger the number of functions, the larger the region with $\alpha_0^{(N)}\sim 2$. This fact is characteristic of this kind of scaling phenomena. For small values of a, the behavior of the system is linear except in a small neighborhood of the critical point.

For a *true* change in the "phase transition" (second order to first order), a scaling relation appears and the curves with different N should cross at approximately the same point. This point is called a multicritical point in theory of phase transition [2].

An additional crossing point appears for α_2 as shown in Fig. 5. As discussed before, this special point is a kind of

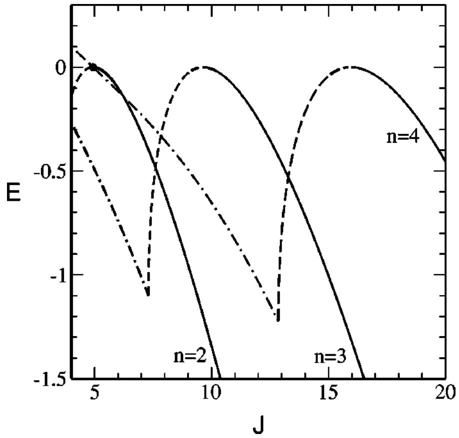

FIG. 6. Energies for the states, $n=2$, $n=3$, and $n=4$ (continuous line), and virtual state energies (dashed lines) and the real part of the complex energy for $n=3$ and $n=4$ (dot-dashed line) calculated using Eqs. (18),(19) with $a=a_c=1.027$, $x_0=6$. The multicritical point (●) is located at $(a,J)\sim(1.027,4.932)$.

multicritical point, but with no change in the value of the critical exponent $\alpha_2=2$. Even when we are using real square-integrable functions. It is necessary to study virtual and resonances states to explain this crossing point. Because complex rotating methods cannot give the virtual states, we use a numerical integration of the Schrödinger equation.

In order to obtain virtual and resonances states, we have to find eigenfunctions of Hamiltonian Eq. 6, which grow up exponentially when $|x|\rightarrow\infty$. Using the fact that the potential goes to zero very fast, we may obtain accurate results for Siegert states [28]. $V(x)$ is assumed to be zero for $|x|>x_0$,

$$V(x)=\begin{cases} \left(\frac{x^2}{2}-J\right)e^{-ax^2}, & |x|<x_0 \\ 0, & |x|>x_0. \end{cases} \qquad (17)$$

Following Meyer and Walter [29], instead of the Hamiltonian defined in Eq. (6) we solved the non-Hermitian eigenvalue problem

$$\left[-\frac{1}{2}\frac{d^2}{dx^2}+V(x)\right]\Psi_s(x)=p^2\Psi_s(x). \qquad (18)$$

With the energy-dependent boundary conditions at $x=0,x_0$:

$$\left.\frac{d\Psi_s}{dx}\right|_{x=0}=0;\quad \left.\frac{d\Psi_s}{dx}\right|_{x=x_0}=ik\Psi_s(x_0), \qquad (19)$$

where $k=\sqrt{2E}$ and the energy is determinate by the condition

$$p=k. \qquad (20)$$

Eigenfunction expansions as used in Ref. [29] are not accurate near the critical point. Instead of that,, we developed a shooting-point method in order to make a direct numerical integration of Eq. (18) with the condition (20). Real energies (bound and virtual) were founded by bisection methods and for complex energies was necessary to combine the Newton-Raphson and grid methods.

As we show in Fig. 6, the "multicritical" point is related to the crossing of the bound state $n=2$ line with the resonance $n=4$ at the critical $\mathrm{Re}(E)=0$ energy. In Fig. 6, we show also the results for $n=3$. The dashed lines in Fig. 6 describe virtual states. The cusp behavior is a reflection of a transition through a branch point with an exponent of one half from a virtual state associated with a real eigenvalue to a virtual state that is associated with *complex* eigenvalue. In Fig. 7, we show the trajectory in the [Im(E)-Re(E)] plan of the $n=4$ solution as the parameter J is varied. Up to $J=16$ (from above), the $n=4$ solution is associated with a bound state (i.e., real negative eigenvalue) and moves toward the $E=0$ direction. At $J\sim16$ and $E=0$, the bound state becomes a virtual state. However, since it is associated with a real eigenvalue, we cannot see in this plot the reflection of the J-trajectory solutions towards negative real eigenvalues. At $J\sim13$, the virtual state penetrates into the complex energy plane via a branch point with exponent of one half. This penetration is clearly shown in Fig. 7. As J is increased below the $J=13$ value, the complex virtual state moves in the complex energy plane and at $J\sim5$, the real part of eigenvalue of this virtual state becomes positive and it becomes a resonance state that is labeled in Fig. 7 by a solid line in the complex energy plane. This resonance state becomes square integrable by scaling its asymptote by a complex factor $\exp(i\phi/2)$. For illustration reasons, the rotating continua at $\phi=0.4$ and at $\phi=\pi/2$ are shown in Fig. 7.

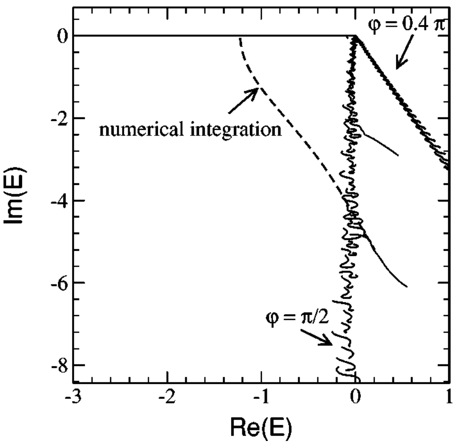

FIG. 7. Trajectories for a $N=500$ complex rotated expansion with $\phi=2\pi/5$ and $\phi=\pi/2$. The state $n=4$ calculated with direct integration with Siegert condition is also shown (dashed line).

For this model Hamiltonian, we expect the formation of sharp resonances for small values of a where the transition seems like a "first order" and their disappearance for large values of a where the transition is "second order." In order to confirm these predictions, we calculate the resonance energies by the complex-rotation method [17]. In this method the coordinate x of the Hamiltonian was rotated into the complex plane, that is $H(x)\rightarrow H(xe^{i\phi/2})$, thus the wave functions of both the bound and resonance states are represented by square integrable functions and may be expanded in standard L^2 basis functions. Figure 8 show the resonance energies, the imaginary part $\mathrm{Im}(E)=-\Gamma/2$, where Γ is the

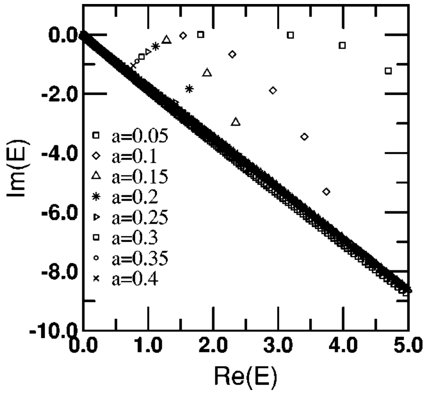

FIG. 8. Resonance energies for different eigenvalues along the $n=0$-critical line for different values of a at order $N=300$ and rotational angle $\phi=\pi/3$.

inverse of lifetime and the position $\mathrm{Re}\,E$, along the critical line for different values of the parameter a. For small values of a, the resonance is sharp, $\mathrm{Im}(E) \ll \mathrm{Re}(E)$, as predicted and they disappear for large values of a.

We may summarize our results by saying that with the help of the FSS method that was originally developed for the studies of critical phenomena in statistical mechanics, we have calculated the branch points characteristic parameters of the energy spectrum of a model Hamiltonian, as a parameter in the potential is varied. We have shown that for a model potential that has been served as a test case for resonance theories and computational algorithms, the transition of a bound state to a resonance state is via two types of virtual states. Three transitions occur. The first one is of a bound/virtual(real-eigenvalue) transition. The second one is virtual(real-eigenvalue)/virtual(complex-eigenvalue) transition, and the third one leads to the appearance of a resonance state. We have shown that within the framework of the finite basis-set approach, the narrow resonances are obtained via one direct bound/resonance-state transition mechanism.

ACKNOWLEDGMENTS

We would like to acknowledge the financial support of the Office of Naval Research (ONR) and the National Science Foundation (NSF). One of us (P.S.) thanks G. Raggio for useful discussions and CONICET, SECYTUNC, and CONICOR for partial financial support. The US-Israel binational Foundation (BSF), The Israel Science Foundation (ISF), and the Foundation for Promotion of Research at Technion are acknowledged for their partial support.

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