Calculation of the Density of Resonance States Using the Stabilization Method

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The stabilization method is used to calculate the density of resonance states and when applied to isolated resonances yields a most simple method for extracting the resonance energy and width.

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The stabilization method is usually presented as a method for obtaining resonance parameters, resonance energy $E_{\rm res}$, and total width Γ from $\mathcal{L}^2$ bound state type calculations [1–10]. For the purposes of obtaining exclusively $E_{\rm res}$ and Γ scattering methods are known to be more difficult than necessary.

The simple stabilization method repeatedly diagonalizes the Hamiltonian in the basis sets of ever larger extension (L) from what is believed to be the region where the resonance wave function is localized. (Q space [11], which is here taken as the localized space, operator Q projecting onto it. P space contains the asymptotes and is the orthogonal complement space.) Here for simplicity we use a basis set complete over the energy range of interest in a box of size L (see, e.g., [2, 3, 5]). The result is a stabilization diagram of the eigenenergies $E_j(L)$ vs L as seen in Fig. 1. The physical origin of the flat region hinges on the fact that the resonance scattering wave function, unlike other continuum solutions, is localized at short range and, as such, its energy converges, i.e., is stabilized, at L beyond the Q region. $\mathcal{L}^2$ states mimicking nonresonant scattering states do not have this property and their energies generally decrease with L.

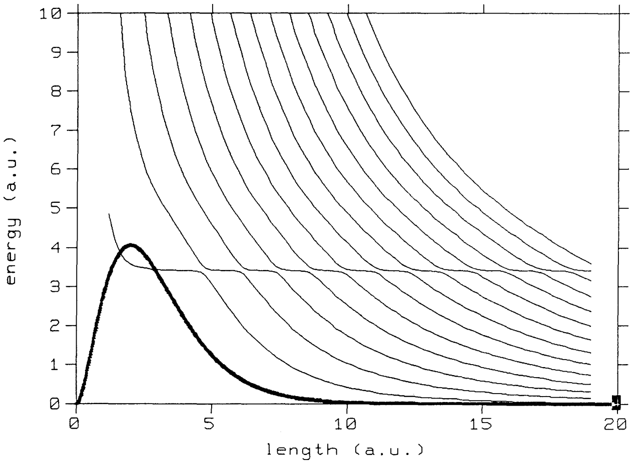

FIG. 1. Eigenenergies E_j as a function of the box size L for the potential in Eq. (10). The potential is shown as the thick curve.

In this paper we give a particularly simple way to extract from the stabilization diagram the density of resonance states $\rho^Q(E)$ which for isolated resonances gives $E_{\rm res}$ and Γ. The method does not need the wave functions [4, 10], nor does it use analytic continuation of the energy in the complex plane [7–9] or arguments about the asymptotic form of the wave functions [1–3]; it also does not have to calculate ρ^Q by first finding (in a scattering computation) the collision lifetime matrix [12]

$$Q = i\hbar S \frac{dS^*}{dE}\,, \tag{1}$$

then using the formula [13, 14]

$$\rho^Q = \pi^{-1} {\rm Tr} Q\,. \tag{2}$$

The method does not use imaging techniques [15] or complex potentials [16].

In the following we will present a novel approach for calculation of the density of resonance states using the stabilization method and then demonstrate its use on one- and two-channel model problems.

Calculation of the density of resonance states.—The method is based on the density of states obtained at a value of L. This density should have a contribution from two regions which we symbolize by writing

$$\rho_L(E) = \rho_L^Q(E) + \rho_L^P(E)\,. \tag{3}$$

$\rho^Q(E)$ is the expected resonant part which stabilizes, becoming independent of L, for L outside the Q region and which for a case of an isolated resonance is expected to be (see, e.g., [14])

$$\rho^Q(E) \simeq \pi^{-1} \frac{\Gamma/2}{(E_{\rm res} - E)^2 + \Gamma^2/4}\,. \tag{4}$$

Parenthetically, for overlapping resonances, where $E_{\rm res}$ and Γ cannot be defined, ρ^Q will stabilize with a shape that varies from problem to problem but which can be Fourier analyzed in various resolutions to give insights into the frequencies and dynamics of the finite lifetime complex whose states are the overlapping resonances. Here, for simplicity, we deal with the isolated resonance case although our approach should work for the overlapping resonance case.

Now, $\rho_L^P(E)$ is that part of the density of states that comes from the background and for fixed L it should vary smoothly with energy and, more importantly, be very small at the resonant energy and inside the range Q. Physically the P-space scattering does not start until the "packet" leaves the inner Q region. As such a method that computes $\rho_L(E)$ as a function of L should show a region of L where a Lorentzian shape exists for $\rho_L(E)$ itself; this defines the Q region.

The problem now reduces to calculation of $\rho_L(E)$, which is given by the formula

$$\rho_L(E) = \sum_j \delta(E_j(L) - E) \ , \tag{5}$$

where $E_j(L)$ are the box eigenvalues of the system. This formula, being represented by a stick diagram, is usually useful only at such large L , where the sticks are dense enough to generate a histogram of $\rho_L(E)$ and thereby get $\rho_L(E)$ as a smooth function of E. The use of large L forfeits the $\mathcal{L}^2$ advantage. In contrast, for small L expression (4) cannot be histogrammed and at first it is not clear how to evaluate it.

Since we expect that $\rho_L^Q(E)$, the desired part of $\rho_L(E)$, is independent of L in any range ΔL outside the Q region, we can average the right-hand side of (5) over parameter L [17]:

$$\langle\rho_L(E)\rangle \simeq \Delta L^{-1} \int_{L-\Delta L/2}^{L+\Delta L/2} dL\, \rho_L(E) \ . \tag{6}$$

Using

$$\int dx\, \delta(f - f(x)) = \left|\frac{df}{dx}\right|^{-1}_{f(x)=f} \tag{7}$$

results in the easily calculable [since $dE_j(L')/dL'$ are available from Fig. 1] formula

$$\langle\rho_L(E)\rangle = \frac{1}{\Delta L} \sum_j \left|\frac{dE_j(L')}{dL'}\right|^{-1}_{E_j(L')=E} \ . \tag{8}$$

The index j sums the derivatives of the E_j vs L curves in Fig. 1, at the intersections of the curves with the constant E line, if they lie in the ΔL region over which we have averaged

$$E_j(L') = E, \quad L - \Delta L/2 < L' < L + \Delta L/2 \ . \tag{9}$$

In order to decrease the statistical error we need to take ΔL large enough that the number of eigenenergies $E_j(L')$ satisfying condition (9) will be sufficient for convergence. In future papers, the above equations will be derived with more rigor using the averaging technique to get the spectral density whose trace is the density operator. We note here, and it shall be shown, that Eq. (6) converges in the limit ΔL approaching infinity. Up to Eq. (6), our method bears similarity in spirit to that of Kim and Ezra [17] who computed a density for use in a density-density correlation function but did not apply the idea to single isolated resonances. Kim and Ezra evaluated the average by first smoothing the delta functions with Gaussians and then by binning into histograms. This latter technique requires usage of data from many more L values than required by Eq. (8). Further it is not part of a larger theory to compute the spectral density [18].

It should be mentioned that the function $\langle\rho_L(E)\rangle$ is now a continuous function of energy [$\rho_L(E)$ is not] and can be processed to extract $\rho^Q(E)$. Note also that the resonances come in Eq. (8) due to the fact that the derivative $dE_j(L)/dL$ becomes very small in the neighborhood of a resonant energy.

We expect and, as will be seen, find that the averaging, which makes possible the evaluation of ρ_L at small L, will leave ρ^Q unaffected and recognizable as it is independent of L. Furthermore, making an assumption that the resonant part of $\langle\rho_L(E)\rangle$ stabilizes at relatively small L, where $\langle\rho_L^P(E)\rangle$ is negligible, we can approximate ρ^Q by the following formula:

$$\rho^Q(E) \simeq \langle\rho_L(E)\rangle \ . \tag{10}$$

In many real problems the part of $\langle\rho_L^P(E)\rangle$, $\langle\rho_L^0(E)\rangle$ that corresponds to the Hamiltonian for noninteracting reactants and products H_0 and which diverges at large L is almost always known. This allows us to make an approximation that is even better than Eq. (10)

$$\rho^Q(E) \simeq \langle\rho_L(E)\rangle - \langle\rho_L^0(E)\rangle \ . \tag{11}$$

What is left out here is that part of $\rho_L^P(E)$ in which the interaction still exists. This, as said, is small and is easy to remove, as will be seen.

The single channel problem.—Consider the radial Schrödinger equation with potential

$$V(r) = V_0 r^2 e^{-r} \ . \tag{12}$$

We restrict our analysis to the case with total angular momentum zero. We have used the same parameter V_0 =7.5 a.u. as was used in [2]. Eighty sine basis functions were taken to obtain the stabilization graph for boxes of radius L from 1 up to 20 a.u. The dependence of eigenenergies E_j on L is presented in Fig. 1. This system has a narrow resonance with energy $E_{\text{res}} = 3.42$ and width $\Gamma = 0.025$ [2].

In Fig. 2 we present our numerical calculation of $\langle\rho_L(E)\rangle$ for two different radii L using Eq. (8). Both curves are very similar (a Lorentzian on a pedestal) except for a small difference in the background (the pedestal) which depends on L and which can be easily subtracted (method A). For even greater accuracy in this simple case the divergent part of the ρ_L^P can be estimated by the formula for the free particle in a box,

$$\rho_L^0(E) \simeq \frac{L}{\pi\sqrt{2E}} \ , \tag{13}$$

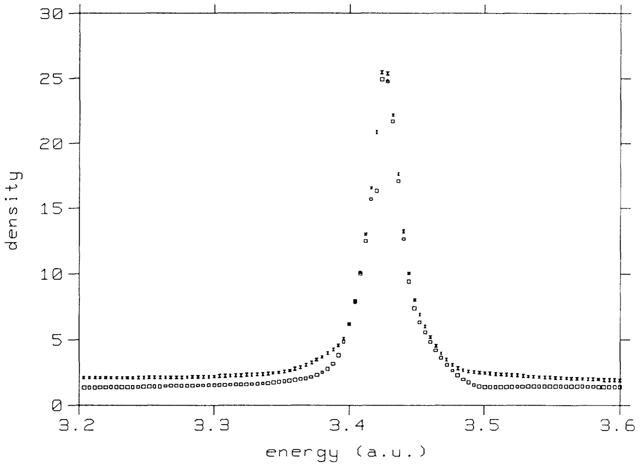

FIG. 2. The averaged density $\langle \rho_L(E) \rangle$ calculated using Eq. (8) for two different box sizes L_1=10 a.u. (squares) and L_2=16 a.u. (hourglasses) averaged over the interval ΔL=6 a.u.

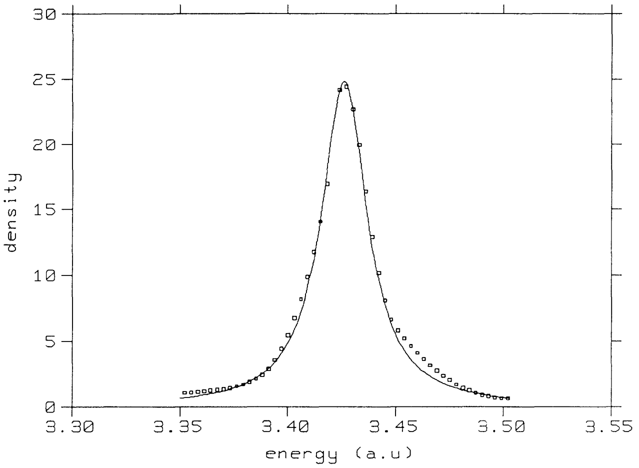

FIG. 3. The resonant density $\rho^Q(E)$ for the single-channel problem calculated using Eq. (9) (squares). The averaging procedure was carried out over the interval $L \in [7.0,13.0]$ a.u.; The Lorentzian in Eq. (2) (continuous curve) has $E_{\rm res}$=3.426 a.u. and Γ=0.0256.

and the resonant density $\rho^Q(E)$ is calculated with Eq. (11) (method B). The result is shown in Fig. 3. The theoretical density given by a Lorentzian [Eq. (4)] with $E_{\rm res}$ = 3.426 and Γ = 0.0256 is also presented in Fig. 3. Here both methods A and B give the same result. It is seen that the accuracy of the method is very high for even relatively small L where the potential $V(r)$ has not achieved its asymptotic value (see Fig. 1).

The two-channel problem.—Here we consider a two-channel model with Hamiltonian [19]

$$H = -\frac{1}{2}\frac{d^2}{dr^2} + H_0(x) + V(x,r) \ , \tag{14}$$

where $H_0(x)$ is assumed to have two states with energies 0.0 and 0.1 a.u. and r is associated with the reaction coordinate. The explicit form of the optical potential V (with x) is not needed. It suffices to know the following matrix representation between states of H_0:

$$V_{ij} = U_{ij} r^2 e^{-r}, \quad U = \begin{pmatrix} -1.0 & -7.5 \\ -7.5 & 7.5 \end{pmatrix} . \tag{15}$$

As in the previous section we used a sine basis set with 160 functions for various values of the box size L. The stabilization diagram is shown in Fig. 4 together with the potential curves for the two channels. The density of resonant states calculated using Eq. (11) is presented in Fig. 5. The averaging procedure was carried out over the parameter interval $L \in [9.0, 13.0]$ a.u. It turned out that the calculated result exactly coincides with the theoretical density given by the Lorentzian at $E_{\rm res}$=4.768 a.u. and Γ=0.00142 a.u. in agreement with the exact results.

In conclusion, we have proposed a new approach for calculation of the density of resonance states using the stabilization method. The advance has been in calculating the density of states using only information from the stabilization graph by a method that unlike other real axis methods is valid, and accurate, in multichannel cases. The method is numerically tested on two examples for one- and two-channel problems with isolated resonances. In both these cases we were able with minimal numerical effort to extract the resonance density, and for isolated resonances, $E_{\rm res}$ and Γ as well with a very high accuracy. The method is expected to work also for a general multichannel overlapping resonance situation. We have not, in this Letter, addressed the issue of the difficulty in computing the stabilization graph. This

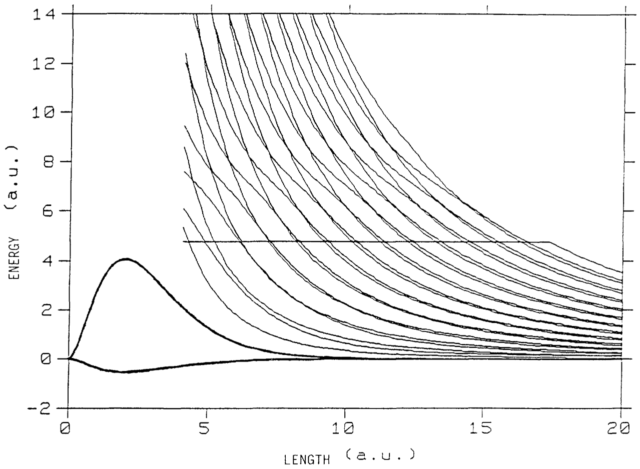

FIG. 4. The stabilization diagram for the two-channel problem shown with potential energies for the two channels (thick curves).

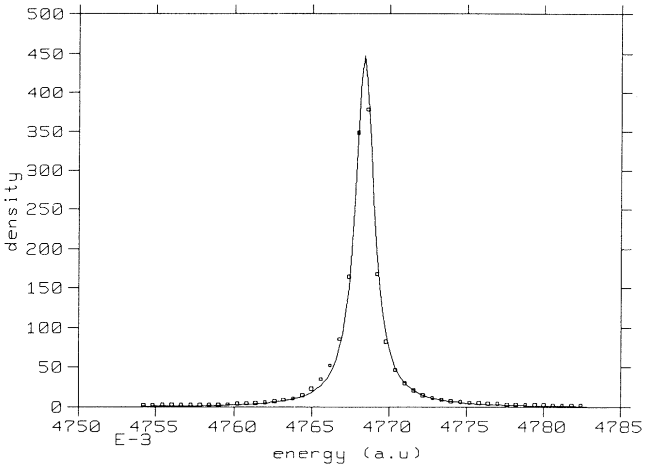

FIG. 5. The resonant density $\rho^Q(E)$ for the two-channel problem calculated using Eq. (9) (squares). The averaging procedure was carried out over the interval [9.0,13.0] a.u.; The Lorentzian in Eq. (2) (continuous curve) has $E_{\text{res}}=4.768$ a.u. and $\Gamma=0.001\,42$.

depends on the nature of the problem at hand (e.g., electron, heavy atom, ion-atom scattering, etc.) We also have not addressed the basis set representational problem, which again varies with the problem under study.

Applications of ideas similar to those given here can be made in any problem where the physics is localized at short distances. In future publications we shall discuss applications to the computation of absorption cross section in photodissociation and to the computation of microcanonical and thermal rate constants.

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