

## Stabilization theory for computing energies and widths of resonances

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(Received 9 February 1994)

For the purposes of computing resonance parameters an alternative version of the stabilization method is used in a simpler way than previously reported [V. A. Mandelshtam, T. R. Ravuri, and H. S. Taylor, *Phys. Rev. Lett.* **70**, 1932 (1993)]. The method is based on the calculation of the eigenphase sum, which, as is shown, can be extracted easily from a stabilization diagram.

PACS number(s): 34.10.+x

The stabilization method [1–5] obtains the energies and widths of resonances by a successive diagonalization of the system Hamiltonian in ever larger enclosing boxes. A recent paper [1] showed how these resonance parameters could be calculated by computing the density of resonance states from the data in the stabilization graph. The stabilization graph exhibits a plot of the eigenenergies,  $E_j(L)$ , as a function of the box size,  $L$ . A typical diagram is shown in Fig. 1.

The change in the density of states due to the interaction is given by

$$\Delta\rho = \text{Tr}[\delta(E - H) - \delta(E - H_0)], \quad (1)$$

where  $H_0$  is the Hamiltonian without interaction. Under

the box-normalization approach Eq. (1) can be replaced by

$$\begin{aligned} \Delta\rho &= \lim_{L \rightarrow \infty} \{ \rho_L(E) - \rho_{0L}(E) \} \\ &= \lim_{L \rightarrow \infty} \left\{ \sum_j \delta(E - E_j(L)) - \rho_{0L}(E) \right\}, \quad (2) \end{aligned}$$

where  $\rho_{0L}(E)$  is the density of states of the noninteracting system in the box of size  $L$ .

The next step is the averaging of  $\rho_L(E)$  over an interval of  $L_0 \leq L \leq L_0 + \Delta L$  and replacing of the limit  $L \rightarrow \infty$  by  $\Delta L \rightarrow \infty$ . That is

$$\begin{aligned} \Delta\rho(E) &= \lim_{\Delta L \rightarrow \infty} \left\{ \frac{1}{\Delta L} \int_{L_0}^{L_0 + \Delta L} dL \sum_j \delta(E - E_j(L)) - \rho_{0L}(E) \right\} \\ &\approx -\frac{1}{\Delta L} \sum_j \left( \frac{dE_j(L)}{dL} \right)^{-1} \Big|_{E_j=E} - \rho_0(E), \quad (3) \end{aligned}$$

where  $\rho_0(E)$  is the averaged density of states of the noninteracting system. Note in passing that since bigger boxes give lower eigenvalues and the derivatives  $dE_j(L)/dL$  are negative, the first term in the right hand side of Eq. (3) is always positive.

Inverting  $E_j(L)$  to  $L_j(E)$  gives

$$\Delta\rho(E) \approx -\frac{1}{\Delta L} \sum_j \frac{dL_j(E)}{dE} - \rho_0(E). \quad (4)$$

The index  $j$  sums the summand in Eq. (4) for all  $L_j(E)$  in the interval  $\Delta L$ .

To extract the resonance parameters  $\Delta\rho(E)$  is approximated by a Lorentzian plus a smooth background parametric form. The method has been applied successfully in [1] to a model systems and in Ref. [5] to compute the parameters of doubly excited states of Helium. Notably the method uses no analytic continuation nor introduces any

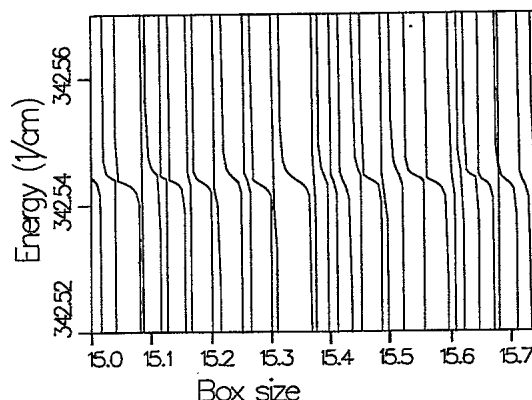


FIG. 1. A typical stabilization diagram for a generic 3D problem, NeICl van der Waals complex. The eigenenergies,  $E_j(L)$ , versus box size,  $L$ , have a plateau near the resonance energy ( $342.5438 \text{ cm}^{-1}$ ).

negative imaginary absorbing potentials. Thereby, it allows us to considerably reduce (factor 2) computer memory needed for complex diagonalizations and use very fast diagonalization codes for real symmetric matrices. Moreover, if only eigenvalues of the Hamiltonian in a small energy range are needed the diagonalization speed can be increased enormously. The latter becomes very important since the method requires multiple diagonalizations of the Hamiltonian matrices.

However, Eq. (4) has two features that could cause problems. The first is that if a resonance overlaps a threshold, the singularity occurring as  $\Delta\rho(E)$  diverges at the threshold causes the Lorentzian to be nearly unrecognizable, because of inadequate representation of the singularity at finite  $L$ . Furthermore, near threshold the density of resonance states may not be Lorentzian at all. Resonances with this overlap property have such problems in many methods and can only be treated either by direct searches for the resonance pole of the  $S$  matrix [6] or by the analytic continuation of the Hamiltonian [7] or by computing the collision lifetime matrix [8],  $Q$ . The eigenvalues of the  $Q$  matrix as a function of energy often assign resonance and threshold effects to different eigenvalues and resolve this problem (see, e.g., Ref. [9]). The maximum eigenvalue of  $Q$  as a function of energy then shows the unfettered Lorentzian shape. Since this first problem is far from generic the method remains of great use.

The second problem in using formula (4) is that since the number of  $L_j(E)$  points in the finite interval  $\Delta L$  is a step function of the energy,  $E$ , the calculated density of states  $\Delta\rho(E)$  is discontinuous. Now this problem is purely aesthetic because one could always smooth the "jumps" and fit  $\Delta\rho(E)$  to the Lorentzian with a good result for  $E_r$  and  $\Gamma$ .

In this paper, we show how to avoid this second problem and further show that an even greater computational simplification can be introduced. This simplification shows that the  $L_j(E)$  values completely determine the width. To see this result we propose here to calculate the eigenphase sum,  $\eta(E) = \frac{1}{2i} \ln(\det S)$ , which as proved in Ref. [10] can be defined by

$$\frac{\partial \eta(E)}{\partial E} = \pi \Delta\rho(E) \quad (5)$$

and consequently,

$$\eta(E) = \pi \int_0^E \Delta\rho(E') dE' \approx \varphi(E) - \varphi_0(E), \quad (6)$$

where the notation for the  $\Delta L$  dependent phase shifts  $\varphi(E)$  and  $\varphi_0(E)$  is obvious from Eq. (4). Realizing that the term  $\varphi_0(E)$  in  $\eta$  originating from the unperturbed  $\rho_0(E)$  cannot yield any resonance information we consider only the effective phase shift  $\varphi(E)$ . Carrying out the integration in Eq. (6) for the above component, we have

$$\varphi(E) = \pi N(E) + \frac{\pi}{\Delta L} \sum_j [L_0 + \Delta L - L_j(E)], \quad (7)$$

where  $N(E)$  is the number of eigenvalues for which

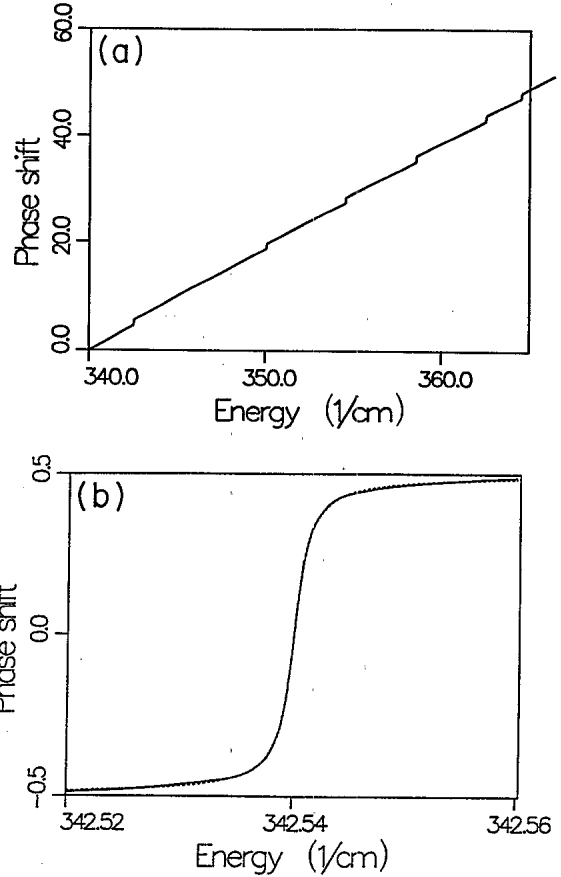


FIG. 2. (a) The phase shift  $\varphi(E)/\pi$  for the NeCl van der Waals complex calculated using Eq. (7). Sudden unit rises indicate the resonance positions. (b) The blowup of (a) for the lowest resonance (solid line) approximated by formula (8) (dashed line). The fitted parameters are  $E_r = 342.5438 \text{ cm}^{-1}$ ,  $\Gamma = 0.0021 \text{ cm}^{-1}$ .

$E_j(L_0) < E$ , and summation in Eq. (7) [as in Eq. (4)] is taken over all  $L_j(E)$  values in the interval  $\Delta L$ . As usual  $\Delta L$  is our convergence parameter as it moves to infinity.

Since the phase shift  $\varphi(E)$  has the same resonance part as the eigenphase sum  $\eta(E)$  but its background phase differs, after being computed it will be approximated by

$$\varphi(E) = \arctan\left(\frac{2(E - E_r)}{\Gamma}\right) + \varphi_b(E), \quad (8)$$

where the background term,  $\varphi_b(E)$ , is smooth function of energy. This analysis is based on the fact that when resonance energy and lifetime can be defined the resonance term in Eq. (8) can be separated from the background (see Ref. [11]).

$\varphi(E)$  calculated using Eq. (7) is continuous well behaved function of  $E$ . To see this we notice that at energy  $E$  each  $j$ th eigenvalue contributes continuously to the total phase shift,  $\varphi(E)$ , according to the formula

$$\varphi(E) = \sum_j \tilde{\varphi}_j(E), \quad (9)$$

where

$$\tilde{\varphi}_j(E) = \pi \begin{cases} 0 & \text{if } E < E_j(L_0 + \Delta L) \\ \frac{(L_0 + \Delta L) - L_j(E)}{\Delta L} & \text{if } E_j(L_0 + \Delta L) < E < E_j(L_0) \\ 1 & \text{if } E_j(L_0) < E. \end{cases} \quad (10)$$

For a generic three-dimensional (3D) problem, NeICl van der Waals complex on the  $B$  electronic surface, described in details in Refs. [12] and [13] a graph of  $\varphi(E)$  versus  $E$  is shown in Fig. 2(a) with sudden rises by  $\pi$  indicating the resonances. A blowup of the graph at one of the rises corresponding to a single resonance energy range of Fig. 1 is shown in Fig. 2(b). The calculated single resonant phase shift is then fitted by the form of Eq. (8). This gives the same result as gotten in Ref. [14] using complex rotation. Details of the calculation, specifically, how basis sets are chosen are saved for Ref. [14].

This work was supported by the Fund for the Promotion of Research at the Technion; by the Basic Research Foundation administrated by the Israeli Academy of Sciences and Humanities, and by NSF Grant No. 9120493. V.R. acknowledges support from the Center of Absorption of Science, Israel Ministry of Immigrant Absorption and from the Wolfson Family Charitable Trust Program. V.A.M. also acknowledges the hospitality of the Technion, where most of the stabilization results were obtained.

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