BRIEF REPORTS

$\mathcal{L}^2$ stabilization theory of dynamics: Dissociative photoabsorption

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A conceptually simple and computationally economical, $\mathcal{L}^2$-discrete-basis-set stabilization method of computing a spectral density as a function of energy is presented. Photoabsorbtion to the continuum is emphasized in examples of model problems. The use of the method for computing rates and state-dependent cross sections is sketched. Traditional scattering solutions are avoided, as are dilatation analytic, imaging, and absorbing-potential techniques.

PACS number(s): 34.10.+x

I. INTRODUCTION

$\mathcal{L}^2$-discrete-basis-set stabilization methods are those that use the eigenfunctions and/or eigenvalues, which arise from a series of diagonalizations in ever larger spaces, to compute physical observables [1]. As always, $\mathcal{L}^2$ methods are "preferred" because they allow the full use of the developments in quantum chemistry and bound-state theory to be used in scattering theory. The method is useful when there is a physical reason to expect that the observable depends on the mechanics in a localized region of space. Once the localized space is exceeded, convergence is expected. Here the word "space" will refer to a configuration space, although the ideas are generalizable to Hilbert spaces. In this paper space refers to boxes of size L; as the examples here are one dimensional, the box size L will be the parameter that is increased as the space is increased. The method has been used for many years to compute the energies of resonances where the physical idea is that, since resonance wave functions are localized in space, the real part of their energy converges, i.e., "stabilizes," once the basis space spans this localized space. This will not be true for the energies of the nonresonant roots which decrease smoothly with L. Recently [2] the stabilization method, using ideas similar to those presented below, was extended to the computation of the resonance part of the density of states for the case of isolated resonances. The resulting Breit-Wigner form of that part of the density associated with resonances allowed the extraction of both the resonance energy and the total width of the resonance. The stabilized frequen-

cies that arise from a correlation function analysis of this same resonance part of the density of states was also used [3] to interpret the motions of the $\text{HeH}_2{}^+$ complex formed in $\text{He}+\text{H}_2{}^+$ reactive scattering. These motions give rise to many overlapping resonances being seen in the computed cross section [4] and to a corresponding classical chaotic motion in the reaction [5].

Here we apply the method to the well-studied one-channel photoionization problem [6,7] and to the photoabsorbtion into the excited states of a two-coupled square-well potential. Section II gives the method; Sec. III, the specific examples; Sec. IV is a discussion.

II. GENERAL THEORY

All the dynamic problems studied below require the energy eigenvalue set $\{E_j(L)\}$ versus L diagram as input. For resonance parameters this is the only input needed. For absorbtion cross section or rates which do not specify asymptotic states, the eigenfunctions $\phi_{j,L}$ resulting from the diagonalization which yields $E_j(L)$ are also required. For problems in which state-to-state information is sought it is also assumed that in each channel, uncoupled arrangement and perhaps uncoupled channel distorted waves $\Phi_{n_\alpha}(E)$ exist along with the distorting potentials V_α. For wave functions n_α refers to arrangements α and states therein n_α. In this Brief Report we concentrate on absorbtion cross section, but present the theory in a more generic manner.

The equation which underlies all our work is that for the spectral density operator

$$\langle \Phi_a | \delta(E - H) | \Phi_b \rangle$$

$$= \sum_{n_\alpha} \langle \Phi_a | \Psi_{n_\alpha}^+(E) \rangle \langle \Psi_{n_\alpha}^+(E) | \Phi_b \rangle$$

$$= \lim_{L \to \infty} \sum_j \delta(E - E_j(L)) \langle \Phi_a | \phi_{j,L} \rangle \langle \phi_{j,L} | \Phi_b \rangle. \qquad (1)$$

Here $\Psi_{n_\alpha}^+$ are the standard δ-function-normalized scattering functions, and Φ_a and Φ_b are testing functions to be specified for each problem. The third part of Eq. (1) comes from enclosing the system in a box and using the closure of the unit-normalized box eigenfunctions $\phi_{j,L}$. Equation (1) is understood in the sense that, for any fixed L, an averaging over a small L-dependent energy range ΔE is implied. In the limit L tends to infinity, $\Delta E(L)$ tends to zero.

Now the eigenfunctions, eigenvalues, and test functions on the right-hand side are known, but we face the problem of evaluating the sum of δ functions. The accepted way to do this is to take L so large that histograms can be made and evaluated. For example, if this is done for Eq. (1), large L ensures us that a large number Δn of lines appear in a small energy range ΔE and this yields the density of states $\Delta n / \Delta E$. Of course this method is not desirable, as working at such a large L is impractical. We evaluate the third term by assuming for each case, albeit for different physical reasons, that Eq. (1) involves only on a localized region of configuration space that runs from $L = 0$ to $L = L_{cv}$ (cv for convergence). If this is the case, then the right-hand side of Eq. (1) can be averaged over a range ΔL from $L - \Delta L/2$ to $L + \Delta L/2$ with $L - \Delta L/2 > L_{cv}$ without changing the value of the left-hand side. Carrying out the average with use of

$$\int dx \, \delta(f - f(x)) = \left| \frac{df}{dx} \right|_{f(x)=f}^{-1} \qquad (2)$$

allows a trivial evaluation of the integral of the δ functions and yields

$$\langle \Phi_a | \delta(E - H) | \Phi_b \rangle$$

$$= \frac{1}{\Delta L} \sum_j \left| \frac{dE_j(L')}{dL'} \right|_{E_j(L')=E}^{-1} \langle \Phi_a | \phi_{j,L'} \rangle \langle \phi_{j,L'} | \Phi_b \rangle. \qquad (3)$$

The index j sums the derivatives of the E_j versus L curves at the intersections of the curves with the constant line E, if they lie in the ΔL region over which we have averaged, i.e., all L' for which

$$E_j(L') = E, \quad L - \Delta L/2 < L' < L + \Delta L/2. \qquad (4)$$

In order to decrease statistical error we need to take ΔL large enough that the number of eigenenergies $E_j(L')$ satisfying condition (4) will be sufficient for convergence.

Clearly all quantities involved on right-hand side of Eq. (3) are known and the right-hand side is now a continuous function of energy. The limit in Eq. (1) has disappeared since it is reached at L_{cv}, which in turn must be found empirically for each problem. In a nutshell,

Eq. (3) is the key idea of our work. All else follows from it. It is also to be noted that the test functions Φ_a and Φ_b need not be the same as we have no positive-definite requirements, as is the case in other theories [7,8], that will prevent us from studying inelastic processes.

Our testing function for photodissociation is $\mu\Psi_0$, with μ being the operator coupling the initial state Ψ_0 to the continuum. Consequently, $\Phi_a = \Phi_b = \mu\Psi_0$. The resulting photoabsorption cross section is

$$\sigma_{\text{absorb}}(E) \sim \frac{1}{\Delta L} \sum_j \left| \frac{dE_j(L')}{dL'} \right|_{E_j(L')=E}^{-1} |\langle \mu\Psi_0 | \phi_{j,L'} \rangle|^2. \qquad (5)$$

The averaging over L is justified from the time-dependent point of view by the fact that $\mu\Psi_0$ is a packet whose return to its initial position causes peaks in frequency in the Fourier transform of the autocorrelation function of the propagating packet with itself [9]. As such there is a value of L which marks a point of no return for the leaving packet. This L acts as L_{cv}.

III. EXAMPLES

A. One-channel problem

Here we confine ourselves to a hydrogenic photoionization problem [6] where the usual Coulomb potential has been distorted to take the shape

$$V(r) = \begin{cases} -5 \text{ a.u.}, & 0 < r < 1.0 \text{ a.u.} \\ V_h, & 1.0 \text{ a.u.} < r < 1.2 \text{ a.u.} \\ 0, & r > 1.2 \text{ a.u.} \end{cases} \qquad (6)$$

For p-wave final states the effective potential is $V(r) + r^{-2}$. The expression for the photoionization can be written in the form

$$\sigma(E) = \tfrac{2}{3} \pi^2 \alpha a_0^2 (E - E_0) |\langle \Psi_0 | r | \Psi_p^+(E) \rangle|^2. \qquad (7)$$

Here α is the fine-structure constant $(1/137)$, a_0 is the Bohr radius, and E_0 and Ψ_0 are eigenenergy and eigenfunction of the ground s state of the system. This exactly solvable problem was chosen by others [6,7] to exemplify specific computational challenges to existing $\mathcal{L}^2$ methods. We refer the reader to these papers for these "challenges" and do not detail them here as we found no exceptionally difficult cases.

Figures 1(a) and 1(b) show the highest barrier (narrow resonance) case, $V_h = 40$ a.u. The solid line is always the numerically exact result; the squares are the result of our method. If Fig. 1(a) is compared to Fig. 3(d) of Ref. [7], one notes agreement between our results, the exact results, and the Feshbach-Fano method. The Stieljes method gives poor results. Notably our calculation was done with a sine basis set in boxes with $L \in [3, 9]$ a.u. while that of Ref. [7] required $L = 25$ a.u. Moreover, our method simultaneously produced evidence [Fig. 1(b)] of a much lower intensity resonance at about 18 a.u. and a "time" delay effect just above the barrier at about 43 a.u. Similar results are shown for $V_h = 5$ a.u. [Figs. 1(c) and
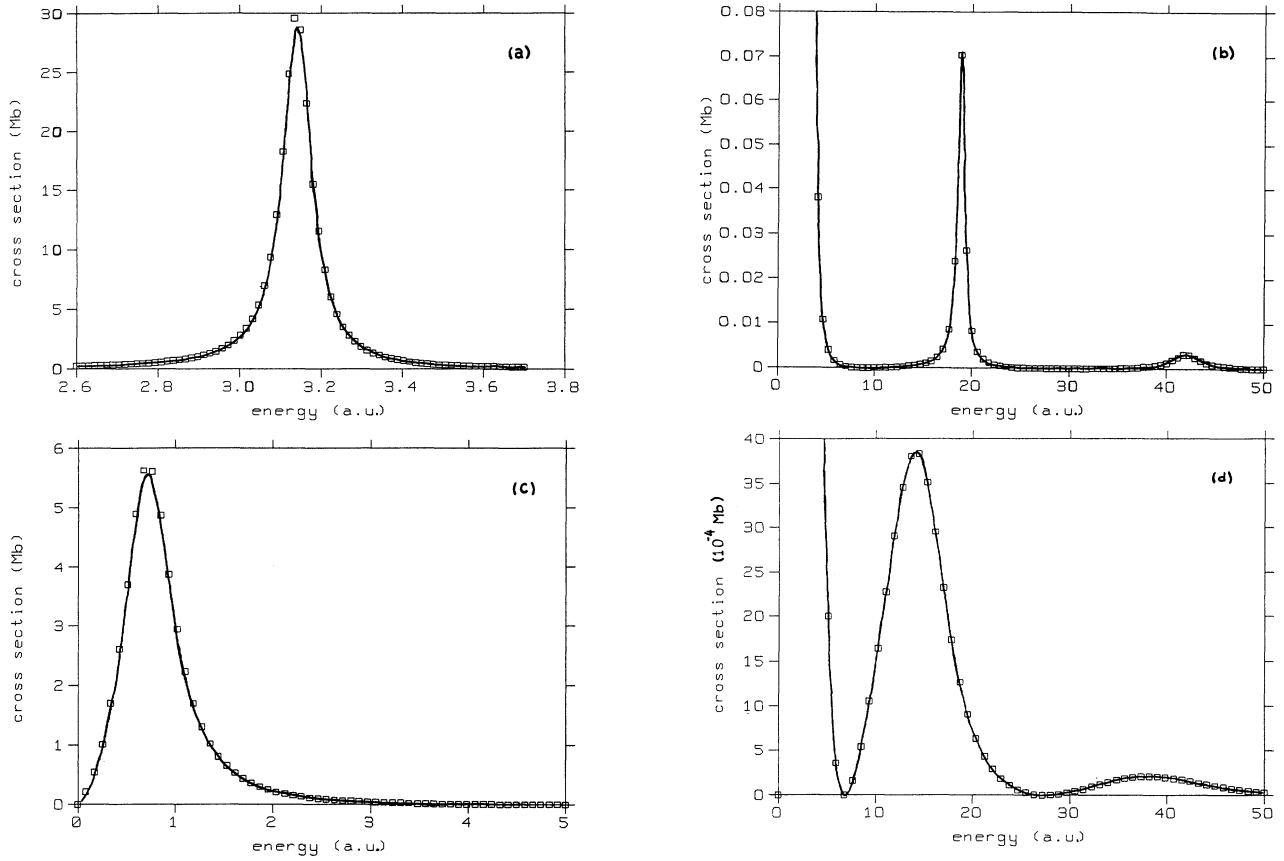
FIG. 1. The photoionization cross section for the one-channel problem: the continuous curve is the numerically exact calculation; the squares are calculations with Eq. (5). In (a) and (b) $V_h = 40$ a.u., and the averaging interval for L is [3,9] a.u., while in (c) and (d) $V_h = 5$ a.u. and the averaging interval is [4,14] a.u.

1(d)] with the averaging interval $L \in [4, 15]$ a.u.

It is also to be noted that larger boxes are needed in fixed single L methods to achieve a near continuous stream of eigenvalue in the desired energy range. If the eigenvalue gap is greater than that of a structure in the cross section, then the structure is missed [8]. Our method has no energy-gap problem as all energies appear in the stabilization graph in the range ΔL so we can use a much smaller L.

It is quite difficult to make a fair comparison of our method with the Feshbach-Fano approach [7]. The latter method treats the resonance and background separately and assumes that one knows a priori the short-range part of the scattering function at the resonance energy. The present method computes both parts simultaneously without such an assumption.

B. Two-channel problem

Here we apply our method for the calculation of the total photoabsorbtion into the excited states of a two-coupled square-well problem.

The two-channel Hamiltonian was taken in the form

$$H = -\tfrac{1}{2}(d^2/dr^2) + H_0(x) + V(x, r),   (8)$$

where $H_0(x)$ is assumed to have two states with energies

0 and 1 and r is associated with the reaction coordinate. The explicit form of the optical potential V (as a function of x) is not needed. It suffices to know the following matrix representation between states of H_0:

$$V_{ij} = \begin{cases} U_{ij} & \text{for } 0 < r < 1 \\ 0 & \text{for } r > 1, \end{cases}$$

where   (9)

$$U = \begin{pmatrix} -7 & -3 \\ -3 & -5 \end{pmatrix}.$$

As in Sec. II we used sine basis set for various values of the box size L. The stabilization diagram is shown in Fig. 2(a). The system has no resonances; the feature at the energy $E = 1$ corresponds to the one-two continua threshold.

For this model problem we chose a Gaussian initial state $\Psi_0 = 2\pi^{-1/4} \exp(-2r^2)$ with the coupling operator $\mu = 1$. The total photoabsorbtion cross section calculated using Eq. (5) is presented in Fig. 2(b) and is seen to agree with the exact result.

IV. SUMMARY

First, we note that our method solves problems usually associated with (i) coordinate rotation, i.e., dilatation an-
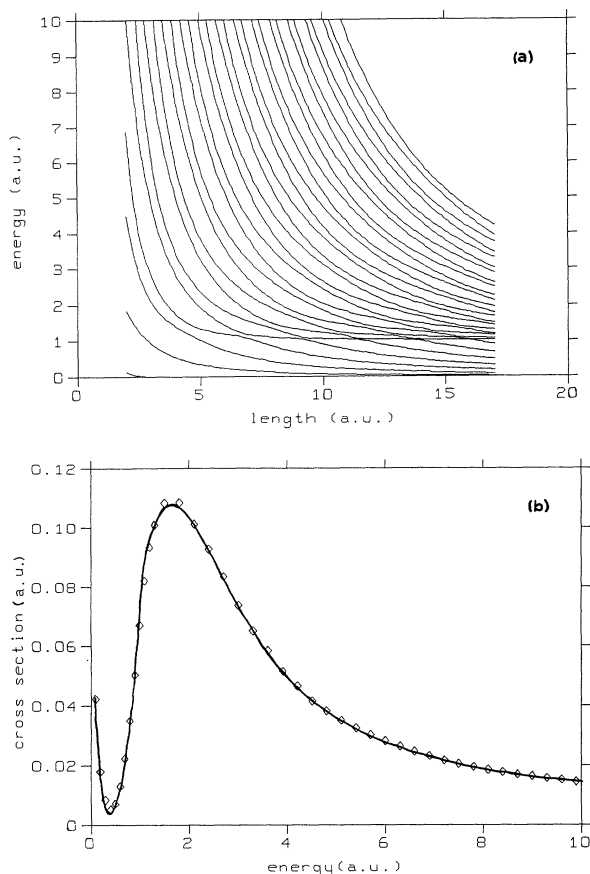
FIG. 2. (a) The stabilization diagram for the coupled, two-square-well problem. The feature at the energy $E = 1$ a.u. corresponds to the one-two continua threshold. (b) The total photoabsorbtion cross section calculated using Eq. (5) shown together with the exact result (continuous curve). The averaging procedure was carried out over the interval [2,9] a.u.

to be conceptually much simpler and no contact is lost with the quantum chemist's or the atomic and molecular physicist's "usual" bound-state computational experience, i.e., for computing the dynamics everything is simple Hamiltonian matrix diagonalization.

This approach, like the R-matrix method and the wave-packet propagation method, works at many energies simultaneously. We note that fixed-L methods need large L values and the large basis sets that go along with it because they try to mimic the continuum by a discrete set of eigenvalues. Our approach has eigenvalue input at all E, albeit at different L's with $L > L_{cv}$. We believe that this will result in the use of smaller basis sets than other methods; we have no gap problem and the N^3 diagonalization operation index is on our side.

Clearly the evaluation of $\langle \Phi_a | \delta(E-H) | \Phi_b \rangle$ by stabilization enables the evaluation of both microcanonical rates and the full Green's function G itself. The two depend on first evaluating the spectral density $\delta(E - H)$ (which is the imaginary part of the $\pi^{-1}G$) and then through the expression for the cumulative reaction probability [10] and the dispersion relation (which relates the real and imaginary parts of G) the microcanonical rate and the real part of the Green's function are evaluated respectively. Having $\langle \Phi_a | G | \Phi_b \rangle$ enables the evaluation of Raman processes, channel and arrangement specific photoabsorbtion processes, partial widths of resonances, and single-S-matrix elements for reactive and nonreactive processes; of course the averaging step and the appeal to the existence of an L_{cv} will have process specific justifications. The Smith lifetime matrix Q [14], which is the difference between the spectral density operator for H and H_0, may also be computed. Reference [2] shows how our method evaluates resonance energies and widths. Relative to the pictorial advantages of time-dependent methods, the Fourier transform of Eq. (5) gives a correlation function which in turn yields a formal expression for $\Psi(t)$ involving only the stabilization information. Hence one may recover such an advantage. All this will be developed in future papers.

ACKNOWLEDGMENTS

alytic approaches [8], (ii) absorbing potential approaches [10–12], (iii) imaging [7] or polynomial quadrature approaches, or (iv) studies of wave functions beyond the range of the potential [13]. The present method uses none of these, nor does it do the more difficult full scattering problem. Only real bound-state-type eigenvalues and eigenvectors are needed. As such, we claim the method

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