LETTER TO THE EDITOR

Calculation of the density of states using discrete variable representation and Toeplitz matrices

Eli Eisenberg†‡, Asher Baram† and Michael Baer†

† Department of Physics and Applied Mathematics, Soreq NRC, Yavne 81800, Israel
‡ Department of Physics, Bar-Ilan University, Ramat-Gan 52900, Israel

Abstract. A direct and exact method for calculating the density of states for systems with localized potentials is presented. The method is based on explicit inversion of the operator $E - H$. The operator is written in the discrete variable representation of the Hamiltonian, and the Toeplitz property of the asymptotic part of the *infinite* thus obtained matrix is used. Thus, the problem is reduced to the inversion of a *finite* matrix.

The evaluation of the density of states has been widely discussed for various physical systems in condensed matter and chemical physics [1–3]. In particular, one is interested in the exsistence of resonances, and their position and width. In the field of chemical physics, resonances play a role in electron–atom, and atom–molecule scattering processes, autoionization, associative detachment, dissociative attachment, and similar molecular resonant reactions [1, 4]. Recently, the subject of resonant tunnelling in semiconductors double-barrier structures has also been the subject of feverish activity [2], due to the technological interest of the properties of such structures, e.g. negative differential resistance and bistability in current–voltage response.

The common methods for finding the position of resonances are the complex scaling method [3] and the stabilization method [4, 5]. The complex scaling method, pioneered by the works of Aguilar, Balsve and Combes [6], and Simon [7] involves the analytic continuation of the energy into the complex plane using the transformation $r \rightarrow re^{i\theta}$, through diagonalization of the scaled (non-Hermitian) Hamiltonian. The following complex eigenvalues correspond to the resonant states, where the real part is the resonance energy, and the imaginary part is the life-time. The method was modified and extensively used by Certain, Moiseyev and co-workers [8], and has recently been applied to three body problems [9]. However, this method does not give the full density of states as a function of energy. Only an approximated form can be obtained through the sum of the Breit–Wigner functions of each resonance.

The stabilization method was developed in quantum chemistry for problems involving electron–atom and electron-molecule scattering. The basic idea is to repeatedly diagonalize the Hamiltonian in the basis sets of ever larger extension L, from what is believed to be the region where the resonance wavefunction is localized. The result is a stabilization diagram of the eigenenergies $E_j(L)$ versus L (see an example in figure 1 later). The characteristic plateaux which contain the pattern of avoided crossings between stable (with respect to L) and unstable eigenvalues, where the former correspond to the eigenvalues representing

resonances, and the latter to discretized continuum states. Briefly, the explanation of this method is as follows [10]. The wavefunctions for energies near the resonant energy are highly localized, and thus are very well described by the finite L^2 states. Therefore, they are stable with respect to changes in the range of the basis functions. In contrast, eigenvalues far from resonance correspond to extended states, and feel the modifications of the basis set. Thus, they will vary as L changes.

Some methods have been suggested for deriving the resonance parameters from the stabilization method [11–13]. More recently, Mandelshtam *et al* [14] have shown how the full density of states can be obtained using some kind of averaging over the parameter L. This method has been used for dissociative photoabsorbtion problems [15], for the calculation of microcanonical and canonical rate constants for one-dimensional [16] and three-body collinear problems [17], and for resonant tunnelling-time calculations [18]. A comparison of the above two methods is given in [19].

However, one would like to have a more direct way to calculate the density of states, without applying analytic continuation methods, or (somewhat artificial) averaging processes. For instance, the textbook definition of the density of states is

$$\rho(E) = \operatorname{Tr} \delta(E - H) = -\frac{1}{\pi} \operatorname{Im} \operatorname{Tr} G(E) \qquad (1)$$

where H is the Hamiltonian, and G is the (full) outgoing Green function defined via $G(E) = (E + i\epsilon - H)^{-1}$. A clear and simple derivation would be the evaluation of the Green function through the inversion of the matrix representing the operator $E - H$ in some L^2 basis set. Unfortunately, this naive approach is not directly applicable, since the physical systems in which resonant states occur are, in nature, of infinite extent, and accordingly, the matrices involved are *infinite*. A solution for this problem was given by Seideman and Miller [20], who applied the method of negative imaginary potentials as absorbing boundary conditions [21] to deal with the infinite asymptotes.

In this letter, we present an alternative approach for the above problem. We manage to invert the *infinite* matrix $E - H$ without applying to any truncations (as is done in the stabilization method) or imposing unphysical boundary conditions. This is accomplished using the discrete variable representation (DVR) [22–24] in which the asyptotic parts are well separated from the interaction region. It has been already recognized [25] that the asymptotic part of this matrix has a Toeplitz structure [26]. This structure is used here to reduce the problem to the inversion of a finite matrix whose dimension is proportional to the width of the interaction region. The only parameter in this method is the spacing σ between successive grid points of the DVR. We apply the method to two double-barrier problem, with parameter sets corresponding to typical mesoscopic resonant tunnelling and chemical reaction problems, respectively.

The essence of our method is that of employing the finite range of the potential through the separation between the asymptotic regions and the interaction region. In order to keep this separation, a localized basis set is desirable. Apparently, the most appropriate representation from this point of view is the DVR, in which the potential operator is diagonal. The representation of the kinetic energy part of the Hamiltonian is calculated through the infinite order grid point representation of the second derivative, and is (for an equally spaced grid) of the form [24]

$$T_{ij} = \frac{\hbar^2 (-1)^{i-j}}{2m\sigma^2} \begin{cases} \pi^2/3 & i = j \\ \dfrac{2}{(i-j)^2} & i \neq j \end{cases} \qquad (2)$$

where m is the mass. The corresponding Green function is thus given through

$$(G^{-1})_{ij} = (E - V(x_i))\delta_{ij} - T_{ij} \tag{3}$$

where the points $x_n = n\sigma$ are the basis grid points. In what follows we use only the outgoing Green function, and thus E has to be understood as $E + i\epsilon$.

We now look at the perturbative representation of G:

$$G = G^0 + G^0 V G^0 + G^0 V G^0 V G^0 + \cdots = SG^0 \tag{4}$$

where

$$S = \sum_{n=0}^{\infty} (G^0 V)^n. \tag{5}$$

In what follows, we use a block-form in which the vectors (which correspond to wavefunctions) are represented by three-dimensional super-vectors whose first (third) component corresponds to the left (right) asymptotic part of the vector (and is therefore an infinite-dimensional vector), and its second component corresponds to the interaction region (and is thus finite-dimensional). Accordingly, the matrices are represented by 3×3 super-matrices. In this notation, the potential matrix can be written (we use bold to indicate super-matrix elements, to stress that these are matrices themselves) as

$$V = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \mathbf{V}_{22} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{6}$$

Similarily, one can write the operator $G_0 V$ as

$$G^0 V = \begin{pmatrix} 0 & \mathbf{G}^0_{12}\mathbf{V}_{22} & 0 \\ 0 & \mathbf{G}^0_{22}\mathbf{V}_{22} & 0 \\ 0 & \mathbf{G}^0_{32}\mathbf{V}_{22} & 0 \end{pmatrix}. \tag{7}$$

Since this matrix has zero (first and third) columns, so does all its powers. One thus may write

$$S = \begin{pmatrix} \mathbf{I} & \mathbf{A} & 0 \\ 0 & \mathbf{B}+\mathbf{I} & 0 \\ 0 & \mathbf{C} & \mathbf{I} \end{pmatrix} \tag{8}$$

where the $\mathbf{I}$ operators are the identity operators of the appropriate order for each block.

It is easy to see from the definition of S, that it satisfies the equation

$$S - I = G^0 V S. \tag{9}$$

Explicit multiplication, and comparing term by term, gives the following relations:

$$\mathbf{A} = \mathbf{G}^0_{12}\mathbf{V}_{22}(\mathbf{I} + \mathbf{B}) \tag{10}$$

$$\mathbf{B} = \mathbf{G}^0_{22}\mathbf{V}_{22}(\mathbf{I} + \mathbf{B}) \tag{11}$$

$$\mathbf{C} = \mathbf{G}^0_{32}\mathbf{V}_{22}(\mathbf{I} + \mathbf{B}). \tag{12}$$

The solution of these relations is given by

$$\mathbf{B} = (\mathbf{I} - \mathbf{G}^0_{22}\mathbf{V}_{22})^{-1}\mathbf{G}^0_{22}\mathbf{V}_{22} \tag{13}$$

and consequently $\mathbf{A}$, $\mathbf{C}$ are given by (10), (12). Note that the matrix $\mathbf{I} - \mathbf{G}^0_{22}\mathbf{V}_{22}$ is *finite*, and thus its inversion is a simple numerical problem.

Using (4), the trace of G is easily obtained. One has

$$\text{Tr}(G - G^0) = \text{Tr}(AG_{21}^0) + \text{Tr}(BG_{22}^0) + \text{Tr}(CG_{23}^0). \tag{14}$$

The evaluation of the second trace involves simply a finite summation; however, the two other traces are infinite sums. We will now show that by using the explicit form of G^0 these sums can be reduced to finite ones.

For this purpose we now calculate the DVR form of G^0. By definition

$$G^0 = (E - T)^{-1} \tag{15}$$

where T stands for the kinetic energy operator. Using DVR, the matrix $E - T$ has the structure of a Toeplitz matrix, i.e. $(E - T)_{ij} = t_{i-j}$, where

$$t_n = \begin{cases} E - \dfrac{\hbar^2 \pi^2}{6m\sigma^2} & n = 0 \\[2mm] -\dfrac{\hbar^2 (-1)^n}{n^2 m\sigma^2} & n \neq 0. \end{cases} \tag{16}$$

The eigenvalues and eigenvectors are thus given by

$$\lambda^{(q)} = \sum_{n=-\infty}^{\infty} t_n e^{inq} = E - \frac{\hbar^2 q^2}{2m\sigma^2} \tag{17}$$

$$v_n^{(q)} = \frac{1}{\sqrt{2\pi}} e^{iqn} \tag{18}$$

where q is a continuous index in the region $-\pi < q < \pi$†. The inverse matrix is thus given by

$$G_{ln}^0 = \int_{-\pi}^{\pi} dq \, v_l^{(q)} v_n^{(q)*} \frac{1}{\lambda^{(q)}} = -\frac{2m\sigma^2}{\pi \hbar^2} \int_0^{\pi} dq \, \frac{\cos((l - n)q)}{\alpha^2 + q^2} \tag{19}$$

where $\alpha^2 = -(\sigma k)^2 - i\epsilon$, and k is the wavenumber corresponding to the energy E. The integrand is highly peaked around $q = |\alpha|$, and therefore, whenever $|\alpha| < \pi$ and this peak is inside the integration region, one can extend the integration region to infinity and obtain

$$G_{ln}^0 = -\frac{im\sigma}{\hbar^2 k} e^{i\theta|l-n|} \tag{20}$$

where $\theta = \sigma k$. The condition $\theta < \pi$ means that the number of grid points per (free) wavelength is > 2. This is a relatively sparse grid compared with those used in usual DVR applications.
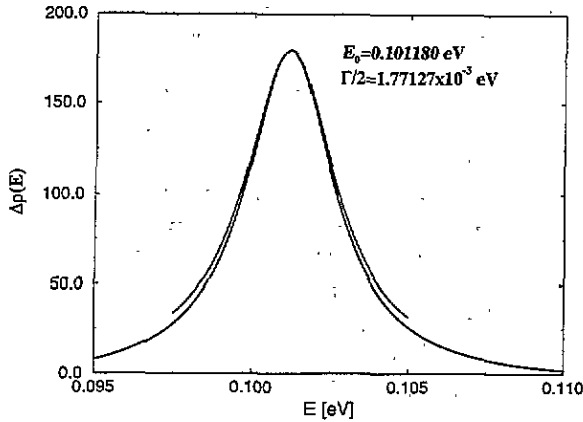
The free particle density of states per unit length is obtained from (20) as

$$\rho^0(E) = -\frac{1}{\pi} \text{Im} \, \text{Tr} \, G^0 = \sqrt{\frac{m}{2E}} \frac{1}{\pi \hbar}. \tag{21}$$

Substituting (20) in (14), the infinite sums reduce to geometric series, and one obtains the formula

$$\rho(E) = -\frac{1}{\pi} \sum_{m,n=n_0+1}^{n_1-1} B_{mn} G_{nm}^0 + V_m (B + I)_{mn} \left(e^{i\theta(m+n-2n_0)} + e^{-i\theta(m+n-2n_1)} \right) \frac{(G_{00}^0)^2}{1 - e^{2i\theta}} \tag{22}$$

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† This (exact) result can also be derived as the $N \to \infty$ limit of the spectrum of a *finite* Toeplitz matrix, given in [27].

Figure 1. The resonant part of the density of states, i.e. $\Delta\rho(E) = \rho(E) - \rho^0(E)$ for the potential (23). The full curve corresponds to our results, and the dotted one is the best Lorentzian fit. The parameters used are $V_0 = 0.5$ eV, $x_0 = 50$ A, $\alpha = 4 \times 10^{-3}$ A^{-2} and $m^* = 0.041 m_e$.
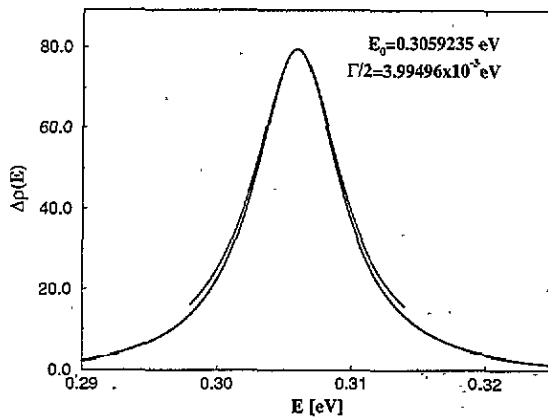
Figure 2. As figure 1, but with parameters $V_0 = 0.5$ eV, $x_0 = 0.2$ A, $\alpha = 50$ A^{-2} and $m = m_p$.

where n_0 (n_1) is the first point of the left (right) asymptotic region. Thus, after inverting the matrix $\mathbf{B} + \mathbf{I}$, all that one has to do is to sum according to (22).

As an example, we consider here a (symmetric) double-barrier structure, typical of the problems treated in mesoscopic resonant tunnelling problems [18]. The potential is of the form

$$V(x) = V_0(\exp(\alpha(x - x_0)^2) + \exp(\alpha(x + x_0)^2)). \tag{23}$$

The parameters used are $V_0 = 0.5$ eV, $x_0 = 50$ A and $\alpha = 4 \times 10^{-3}$ A^{-2} (corresponding to a quantum well of width ~ 60 A, with barriers of width ~ 40 A). The mass is $m^* = 0.041\ m_e$, corresponding to the $Ga_{0.47}In_{0.53}As$ well. Figure 1 shows the full density of states, as calculated from (22). The resulting line shape is a Lorenzian centred at $E_0 = 0.101\ 180$ eV whose half-width is $\Gamma/2 = 1.771\ 27 \times 10^{-3}$ eV. Figure 2 presents the same graph for the same potential with set of parameters suitable for a chemical physics problem, i.e. $V_0 = 0.5$ eV, $x_0 = 0.2$ A, $\alpha = 50$ A^{-2} and $m = m_p$. The resulting line shape is a Lorenzian

centred at $E_0 = 0.305\,9235$ eV whose half-width is $\Gamma/2 = 3.994\,96 \times 10^{-3}$ eV.

In conclusion, a direct and exact method for the calculation of the density of states for localized-potential systems has been derived. The method evaluates the inverse of the matrix representing the operator $E - H$ in the DVR, employing its asymptotic Toeplitz structure. As usual in DVR treatments, no integration is needed in constructing the matrix elements. The numerical effort needed involves only the inversion of one matrix (for each energy) whose dimensionality is proportional to the range of the interaction region. We have considered an explicit example of a one-dimensional double-barrier structure, typical of those considered in the field of resonant tunnelling. However, the derivation is completely general and can be applied also to more complicated (e.g. three-body, three-dimensional) problems.

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