

# Toeplitz matrices within DVR formulation: Application to quantum scattering problems

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(Received 3 February 1994; accepted 20 May 1994)

It is shown that the matrix obtained from the infinite order discrete variable representation (DVR) of a scattering problem has the structure of a Toeplitz matrix. The resulting properties can be used to reduce the associated infinite system of algebraic equations to a finite (and relatively small) one. An example is worked out to show the efficiency of the combined Toeplitz DVR approach.

## I. INTRODUCTION

Recently, the application of finite-range square-integrable ( $L^2$ ) functions has become one of the more popular methods of handling multiarrangement scattering processes.<sup>1-8</sup> The expansion of the wave function in terms of  $L^2$  functions enables one to convert the Schrödinger equation (SE) into a set of algebraic equations, whose numerical solution has many advantages over the propagative methods originally used to solve the differential SE. However, employing  $L^2$  functions for scattering problems cannot be done in a straightforward way, as for a bound-state problem, since scattering states are, in nature, *extended* states, and therefore an *infinite* number of finite-range functions is needed, generally, to expand these states.

Several approaches were suggested in recent years to overcome this difficulty. The most common one is making use of the explicit asymptotic form of the wave function, and carrying out some kind of matching these asymptotes to the wave function in the interaction region, which, in turn, can be expanded in terms of the localized  $L^2$  functions.<sup>1</sup> Another approach is based on applying negative imaginary potentials (NIP), which absorb the wave function in the asymptotic region and in the same time do not cause any reflection to the interaction region. This unaffected part of the wave function is again solved using  $L^2$  basis sets.<sup>2</sup> A third method which was considered most recently involves expanding the wave function in terms of an *infinite* set of localized Gaussians.<sup>3</sup> It has been shown that the matrix related to the resulting set of algebraic equations, though infinite, has (in the asymptotic regime) the structure of a Toeplitz matrix. Using the analytical properties of the Toeplitz matrix the infinite set of equations is reduced to a finite (not too large) one. This method was studied and was found to be more efficient, at least for a one-dimensional reactive problem, than the NIP approach.<sup>4</sup>

One of the  $L^2$  basis methods, which attracts more and more attention in recent years, is the discrete variable representation (DVR) method, which was pioneered in the last decade by Light and co-workers<sup>5</sup> (although its origin goes back to the 1960s<sup>6</sup>) for use in vibrational eigenvalue calculations. Applying the DVR formalism, no integration is needed to form the relevant matrix elements, and in addition, the matrix is (for more than one-dimensional problems) extremely sparse. Thus many of the numerical problems which can be treated by the  $L^2$  methods are solved in this approach.

However, the extension to scattering problems has to

solve the problem discussed in the preceding paragraphs, namely the infinite number of basis elements which are required to span the extended scattering states. Light and co-workers used a somewhat arbitrary truncation of the Hilbert space to the subspace spanned by the first  $n$  states of the  $L^2$  basis set;<sup>5(b),5(d)</sup> Colbert and Miller showed that the DVR method can be derived by replacing the differential operators by their finite-differences approximations and used an energy cut-off criterion to obtain a spatial truncation of the grid. This method was used to calculate the  $S$  matrix via the Kohn variational principle.<sup>7</sup> A more recent development in this direction was the application of NIPs which provides a more systematic way of getting a finite system out of the DVR method.<sup>8</sup>

In this work, we wish to show that the DVR method can be converted into a finite system *exactly*, i.e., without any truncations or absorbing boundary conditions, via the Toeplitz method.<sup>9</sup> This new approach therefore has the advantages of both methods; on the one hand, no integration is needed and the general structure of the matrix is almost the same as in usual DVR treatment, while at the same time, the reduction of the problem to a finite matrix is done rigorously with no need in any assumptions or approximations.

## II. THEORY

In the following we present the theory for a one-dimensional reactive scattering problem. The generalization to more realistic (three-dimensional, atom plus diatom) systems will be discussed elsewhere. The positive part of the real axis will be termed as the  $\lambda$  arrangement channel (AC), and the negative part as the  $\nu$  AC.

The relevant SE is

$$(E - H)\psi_\nu = 0, \quad (1)$$

where  $E$  is the energy,  $H$  is the full Hamiltonian, and  $\psi_\nu$  is the complete wave function calculated for an asymptotic boundary condition at the  $\nu$  AC. In order to solve this equation we apply the perturbative approach.<sup>2,10</sup> We define two (nonreactive) unperturbed potentials  $W_\alpha(\alpha=\lambda, \nu)$  such that the scattering potential  $U$  approaches  $W_\alpha$  at the asymptote of the  $\alpha$  AC, and solve by some propagative method the two unperturbed SEs:

$$(E - H_{0\alpha})\psi_{0\alpha} = 0; \quad \alpha = \lambda, \nu, \quad (2)$$

where

$$H_{0\alpha} = H - U + W_\alpha; \quad \alpha = \lambda, \nu. \quad (3)$$

Now writing  $\psi_\nu$  as

$$\psi_\nu = \psi_{0\nu} + \chi_\nu, \quad (4)$$

one obtains the inhomogeneous equation for  $\chi_\nu$ :

$$(E - H)\chi_\nu = V_\nu \psi_{0\nu}, \quad (5)$$

where  $V_\nu$  is defined by

$$V_\nu = H - H_{0\nu} = U - W_\nu. \quad (6)$$

Once  $\chi_\nu$  is solved, the "reactive"  $S$ -matrix element (i.e., the transmission coefficient) is obtained from the asymptotic behavior of the wave function

$$\psi_\lambda = S(\nu \rightarrow \lambda) \exp(ik_\lambda x), \quad (7)$$

where  $k_\lambda$  is given in the form

$$k_\lambda = \sqrt{\frac{2\mu}{\hbar^2} (E - U_0)}. \quad (8)$$

Here  $\mu$  is the reduced mass and  $U_0$  is the asymptotic value of the potential at  $x \rightarrow \infty$  (in the  $\nu$  AC).

For our one-dimensional system,  $H$  is given in the form

$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + U(x), \quad (9)$$

and consequently Eq. (1) becomes

$$\left[ E + \frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} - U(x) \right] \chi = V \psi_{0\nu}. \quad (10)$$

We now wish to transform the differential equation (10) to a set of coupled linear equations. This is done using equally spaced grid points  $x_n = n\sigma$ , and replacing the derivative term in Eq. (10) by its infinite order grid point representation.<sup>7</sup>

$$f''(x_n) = -\frac{1}{\sigma^2} \left\{ f(x_n) \pi^2/3 + 2 \sum_{k=1}^{\infty} [f(x_{n+k}) + f(x_{n-k})] \frac{(-1)^k}{k^2} \right\}. \quad (11)$$

Equation (10) therefore gets the DVR form

$$\sum_j A_{ij} \chi_j = \sum_j (E \delta_{ij} - T_{ij} - U_{ij}) \chi_j = V(x_i) \psi_{0\nu}(x_i), \quad (12)$$

where

$$T_{ij} = \frac{\hbar^2 (-1)^{i-j}}{2\mu\sigma^2} \begin{cases} \pi^2/3, & i=j \\ \frac{2}{(i-j)^2}, & i \neq j \end{cases}, \quad (13)$$

and the potential energy matrix is (as usual in DVR treatments) diagonal,

$$U_{ij} = \delta_{ij} U(x_i). \quad (14)$$

Note that the kinetic term  $T_{ij}$  is a Toeplitz matrix, i.e., it has the form  $T_{ij} = t_k$  where  $k = i - j$ ; this property is crucial for the following derivation.<sup>9</sup>

We wish to show now that the infinite algebraic system can be reduced analytically to an equivalent finite system, which, in turn, can be solved numerically. We first consider the  $\lambda$  AC where  $x \rightarrow \infty$ . Since the potentials  $U(x)$  and  $V(x)$  approach a constant  $U_0$  after some finite range, there exists an  $m_0$  such that once  $m > m_0$ ,  $A_{mn} = (E - U_0) \delta_{mn} - T_{mn} = \tau(m - n)$ , and the inhomogeneous term of Eq. (10) vanishes. Consequently, for  $m > m_0$  the equations have the form

$$\sum_{j=-\infty}^{\infty} A_{m,m-j} \chi_{m-j} = (E - U_0) \chi_m - \sum_{j=-\infty}^{\infty} t_j \chi_{m-j} = 0. \quad (15)$$

Since the equations are the same for each  $m > m_0$ , we seek for solutions which are the same up to a constant, i.e.,  $\chi_{m+1} = \beta \chi_m$  and therefore

$$\chi_{m_0+j} = \beta^j \chi_{m_0}. \quad (16)$$

We find below two independent solutions of this form, corresponding to incoming and outgoing waves, and therefore these (and superposition of them) are the only solutions. Since the solutions must not be asymptotically increasing nor asymptotically decreasing,  $\beta$  has to be of the form

$$\beta = \exp(i\theta). \quad (17)$$

Substituting Eqs. (16) and (17) in Eq. (15) yields the equation for  $\theta$ ,

$$E - U_0 - t_0 - 2 \sum_{j=-\infty}^{\infty} \cos(\theta j) t_j = 0. \quad (18)$$

The sum on the right-hand side can be done analytically<sup>11</sup> using the expression for  $t_j$ ,

$$\frac{2\mu\sigma^2(E - U_0)}{\hbar^2} - \pi^2/3 - \sum_{j=-\infty}^{\infty} 4 \cos(\theta j) \frac{(-1)^k}{k^2} = \frac{2\mu\sigma^2(E - U_0)}{\hbar^2} - \theta^2 = 0, \quad (19)$$

and therefore we find for  $\theta$

$$\theta = \sigma \sqrt{\frac{2\mu(E - U_0)}{\hbar^2}} = \sigma k_\lambda, \quad (20)$$

where  $k_\lambda$  was defined in Eq. (8). We thus have expressed all the coefficients  $\chi_m$  ( $m > m_0$ ) in terms of  $\chi_{m_0}$ :

$$\chi_n = \chi_{m_0} \exp[i\sigma k_\lambda(n - m_0)], \quad n > m_0. \quad (21)$$

In fact, Eq. (19) has two independent solutions, which follow from different sign choices for  $\theta$ . As mentioned above, this ensures us that all the solutions may be obtained through the form of Eq. (16). In the following the positive sign is used, in order to impose outgoing wave boundary conditions.

A similar treatment is applied to the  $\nu$  asymptote where  $x \rightarrow -\infty$ , and one can express  $\chi_n$  ( $n < n_0$ ) in terms of  $\chi_{n_0}$ ,

$$\chi_n = \chi_{n_0} \exp[i\sigma k_\nu(n - n_0)], \quad n < n_0, \quad (22)$$

where  $k_\nu$  is the wave number associated with the energy  $E$ .

We now consider Eq. (10) for  $n_0 \leq m \leq m_0$ . These equations can now be greatly simplified by substituting the previous expressions (16) and (17), and one therefore obtains the following *finite* system:

$$\sum_{j=n_0}^{m_0} \tilde{A}_{ij} \chi_j = V(x_i) \psi_{0\nu}(x_i), \quad i=n_0, \dots, m_0, \quad (23)$$

where

$$\tilde{A}_{ij} = \begin{cases} \sum_{l=0}^{\infty} A_{i, n_0-l} \exp(-i\sigma k_\nu l), & j=n_0 \\ A_{ij}, & n_0 < j < m_0 \\ \sum_{l=0}^{\infty} A_{i, m_0+l} \exp(i\sigma k_\nu l), & j=m_0 \end{cases} \quad (24)$$

The transmission is then given by the asymptotic behavior of  $\chi$  [see Eq. (7)]:

$$T = |S(\nu \rightarrow \lambda)|^2 = |\chi_{m_0}|^2, \quad (25)$$

which can also be expressed as

$$T = \left| \sum_{j=n_0}^{m_0} (\tilde{A}^{-1})_{m_0, j} V(x_j) \psi_{0\nu}(x_j) \right|^2. \quad (26)$$

### III. NUMERICAL TEST

We have taken a preliminary numerical test of the above described method in order to check its validity. A more detailed study will be presented elsewhere. The numerical work is carried out for an Eckart potential:<sup>12</sup>

$$U(x) = \frac{Ay}{1-y} - \frac{By}{(1-y)^2}, \quad (27)$$

where  $y = \exp(2\pi x/l)$ . The exact reactive (transmission) probability is given in the form<sup>12</sup>

$$P = 1 - \frac{\cosh[2\pi(\alpha - \beta)] + \Gamma}{\cosh[2\pi(\alpha + \beta)] + \Gamma}, \quad (28)$$

where

$$\alpha = \frac{1}{2} \left( \frac{E}{C} \right)^2, \quad (29)$$

$$\beta = \frac{1}{2} \left( \frac{E-A}{C} \right)^2, \quad (30)$$

$$C = \frac{\hbar^2}{8\mu l^2}, \quad (31)$$

$$\Gamma = \cosh(2\pi\delta), \quad (32)$$

$$\delta = \frac{1}{2} \left( \frac{B-C}{C} \right)^{1/2}. \quad (33)$$

In the present application we assumed  $\mu = 1/\sqrt{3}$ ;  $A = 0$ ;  $B = 1.7$  eV;  $l = 2\pi$  Å. Figure 1 presents the comparison between the exact results and the results obtained from the Toeplitz version of the DVR. The number of grid points per wavelength taken, which we denote  $N$ , was  $N = 2.5$ .

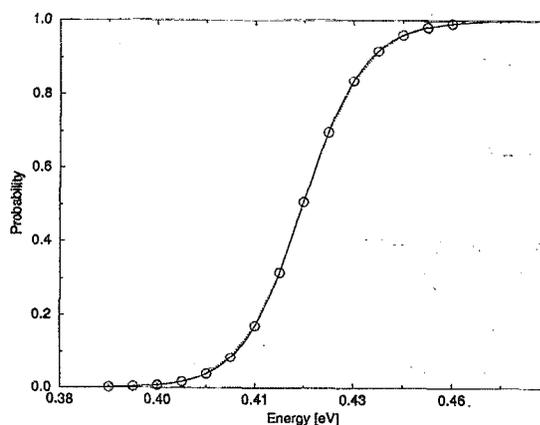


FIG. 1. Transmission probabilities for the Eckart potential. The solid line refers to the exact results of Eq. (25), while the circles correspond to the numerical results.

Figure 2 examines the convergence rate of the reactive probability with respect to the grid points density. The relative error is plotted for three different energies as a function of the number of grid points per wavelength. The energies were chosen to cover the whole range of interest: the high energy is far above the threshold, i.e.,  $E = 0.76$  eV ( $P = 1.000$ ), the intermediate energy is equal to the energy barrier, i.e.,  $E = 0.425$  eV ( $P = 0.501$ ), and the third energy was taken to be in the deep tunneling regime, namely  $E = 0.4$  eV ( $P = 0.017$ ). As one can clearly see, an excellent convergence is attained already for  $N \sim 2.5$  (for which the relative error is about 0.1%).

These results can be compared with those of Seideman and Miller (SM)<sup>8</sup> [who used the DVR approach combined with negative imaginary potentials (NIPs)]. SM achieved this kind of accuracy for a similar potential only for  $N \geq 3.5$ . (In both cases the interaction region was taken  $-10 \text{ \AA} \leq x \leq 10 \text{ \AA}$ .) It is important to mention that in this respect the accuracy of SM was so far the highest. We attribute our achievement to the analytic treatment of the second derivative in the asymptotic region. Whereas in the SM

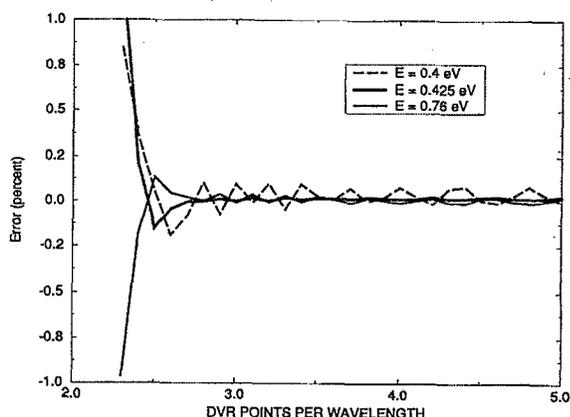


FIG. 2. Relative error in transmission probability for three different energies as a function of the grid points density.

case the expansion is stopped at some (large)  $x$  value and the asymptotes are taken care by the NIPs, we never really stop, and in this sense our treatment goes *ad infinitum*. The reduction to a finite case is done rigorously taking into account the features of the Toeplitz matrix which were recently applied by us in other scattering problems.<sup>3</sup>

#### IV. CONCLUSIONS

In this work, a new approach for treating scattering processes by the DVR method is described. The problem of dealing with an infinite number of equations, which follow from the usage of  $L^2$  functions, is solved in a rigorous way using the features of Toeplitz matrices. It is shown that all the wave function values at the asymptotic regions (where the potentials vanish) are connected to its values at the boundary of these regions, and thus one obtains a linear system of equations whose variables are the values of the wave function in the interaction region only. We thus presented an exact, but still finite, set of equations whose solution is equivalent to the exact solution of the original SE. Application of this method for a one-dimensional reactive system yields very accurate results, with an extremely sparse grid. This method is now extended to realistic three-atom reactive systems.

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