# Toeplitz matrices within discrete variable representation formulation: Application to collinear reactive scattering problems

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Recently, a new approach based on the features of the Toeplitz matrix was introduced for reactive scattering problems. So far these features were used only along the reagents translational coordinate (either for Eckart-type models or for collinear scattering). In this work, we show how to employ the Toeplitz features for the two asymptotic regions of the collinear system. © *1996 American Institute of Physics.* [S0021-9606(96)02102-8]

## I. INTRODUCTION

In the last few years the application of finite-range square-integrable ($L^2$) functions has become one of the more popular methods of handling multiarrangement channel scattering processes.[1–8] The expansion of the wave function in terms of $L^2$ functions enables one to convert the Schrodinger 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 way as straightforward as bound-state problems since scattering states are, in nature, *extended* states, and therefore an *infinite* number of finite-range functions is needed to expand these states.

Several approaches were suggested in recent years to overcome this difficulty. The most common one uses the explicit asymptotic form of the wave function, and matches these asymptotes to the wave function in the interaction region, which, in turn, can be expanded in terms of the localized $L^2$ functions.[1] Another approach is based on applying negative imaginary potentials (NIP), which absorb the wave function in the asymptotic region and at the same time do not cause any reflection back into the interaction region.[2] This unaffected part of the wave function is again solved using $L^2$ basis sets.[2b–d] A third method which was considered most recently involves expanding the wave function in terms of an *infinite* set of localized Gaussians.[3,4] It has been shown that the (infinite) matrix related to the resulting set of algebraic equations has (in the asymptotic region) the structure of a Toeplitz matrix.[9] Using the analytical properties of the Toeplitz matrix the infinite set of equations is reduced rigorously, without any further assumptions, to a finite (not too large) one.[3] This method was found to be more efficient, at least for the single-coordinate reactive problem, than the NIP approach.[4]

This new approach was recently modified by combining it to another technique, namely, the discrete variable representation (DVR) of the Hamiltonian[5] (in what follows we term this combined approach as the DVRTM). The advantage of the DVR approach is well known; the solution for the wave function does not require integrations to produce the matrix elements. The main difficulty with DVR is related to the accuracy in expanding the derivatives. This was recently partly overcome with the introduction of the infinite order grid point representation.[7] Since the infinite order grid point representation uses the values of the wave function at the asymptotic region, as well as at the interaction region, it cannot be efficiently applied unless one handles the wave function at the asymptotic region properly. One way of doing it is to employ the NIP and to force the wave function to vanish at some finite point.[8] A different way is to let the expansion of the derivative operators to go *ad infinitum* and treat the infinite matrix that follows analytically, employing methods applicable to Toeplitz matrices.[3–6,9] The DVRTM was applied to a reactive-single-coordinate Eckart-type potential, and more recently to a realistic (collinear) reactive system. For the Eckart potential, reactive transition probabilities were calculated as a function of energy as well as a function of the number of grid points per wavelength.[5] A similar study was carried out by Seideman and Miller,[8] but whereas within their approach (employing the NIPs) the (average) minimal number of points per wavelength required to obtain converged results was ∼3.5, we found it to be ∼2.5. For the collinear system, a mixed NIP–Toeplitz approach was used; namely, the Toeplitz behavior was used in the reagents (translational) asymptotic region, and an NIP was substituted along the vibrational coordinate.[6]

In this work we extend this approach by eliminating the NIP altogether, and employing the Toeplitz method for the two asymptotes. This, in turn, requires a new representation of the Hamiltonian.

## II. THEORY

The theoretical derivation is carried out in terms of the perturbative form of the SE,[10,2b–d] i.e.,

$$(E-H)\chi = V\psi, \tag{1}$$

where $E$ is the total energy, $V$ is the perturbation potential, $\psi$ is the unperturbed part of the wave function, $\chi$ is the perturbed part of the wave function (i.e., the entire wave function is given by $\psi+\chi$), and $H$ is the total Hamiltonian given in the form

$$H = T + U. \tag{2}$$

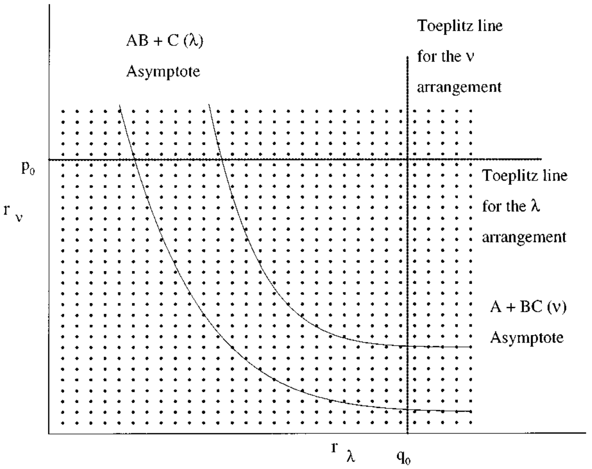

FIG. 1. The grid used for the DVR formulation. The solid lines present equal-potential lines, and the dotted lines are the "Toeplitz lines"—the limits of the asymptotic regions for the $\nu$ and λ AC.

Here $U$ is the full potential of the system and $T$ is the kinetic-energy operator that will be written, for the collinear three-atom case, in terms of the interatomic distances:[11]

$$T=-\frac{\hbar^2}{2\mu_{AB}}\frac{\partial^2}{\partial r_{AB}^2}-\frac{\hbar^2}{2\mu_{BC}}\frac{\partial^2}{\partial r_{BC}^2}+\frac{\hbar^2}{m_B}\frac{\partial^2}{\partial r_{AB}\,\partial r_{BC}}. \tag{3}$$

Here $A$, $B$, and $C$ are the three atoms ($B$ is the central atom), $\mu_{AB}$ and $\mu_{BC}$ are the reduced masses for the $A$ and $B$ atoms, and for the $B$ and $C$ atoms, respectively; $r_{AB}$ and $r_{BC}$ are the respective interatomic distances and $m_B$ is the mass of the central atom. In order to simplify our notation, we denote the two arrangement channels (AC) of the system by λ, $\nu$, such that the λ AC corresponds to the $AB+C$ configuration (with the asymptote $r_{BC}\rightarrow\infty$), and the $\nu$ AC corresponds to the $A+BC$ configuration (with the asymptote $r_{AB}\rightarrow\infty$). In what follows we replace $(r_{AB},r_{BC},\mu_{AB},\mu_{BC},m_B)$ by $(r_\lambda,r_\nu,\mu_\lambda,\mu_\nu,m)$ where $r_\alpha(\alpha=\lambda,\nu)$ is the vibrational coordinate in the $\alpha$ AC and $r_\beta(\beta\neq\alpha)$ is the translational coordinate of the $\alpha$ AC. Equation (3) then becomes

$$T=-\frac{\hbar^2}{2\mu_\lambda}\frac{\partial^2}{\partial r_\lambda^2}-\frac{\hbar^2}{2\mu_\nu}\frac{\partial^2}{\partial r_\nu^2}+\frac{\hbar^2}{m}\frac{\partial^2}{\partial r_\lambda\,\partial r_\nu}. \tag{4}$$

We now transform the differential equation (1) into an infinite set of algebraic equations using two-dimensional grid points $(r_{\lambda,q},r_{\nu,p})=(q\sigma,p\sigma)$ (see Fig. 1), and replacing the differential operators by their (one-dimensional) infinite order grid point representation

$$f'(x_i)=\sum_{j=-\infty}^{\infty}t^1_{j-i}f(x_j),\quad f''(x_i)=\sum_{j=-\infty}^{\infty}t^2_{j-i}f(x_j), \tag{5}$$

where

$$t_j^1=\begin{cases}0 & j=0,\\ \dfrac{-(-1)^j}{j\sigma} & j\neq 0,\end{cases}\qquad t_j^2=\begin{cases}\dfrac{-\pi^2}{3\sigma^2} & j=0,\\ \dfrac{-2(-1)^j}{j^2\sigma^2} & j\neq 0.\end{cases} \tag{6}$$

The expression for the second derivative was taken from Ref. 7, and the one for the first derivative is derived in Appendix A.

Note that we use the DVR expressions for the fully infinite intervals $(-\infty,\infty)$ with respect to the two variables, rather than the semi-infinite intervals. In fact, the incorporation of the negative range of $r_\alpha$; $\alpha=\lambda,\nu$ is crucial for the implementation of the DVRTM. Such an extension is not justified physically since $r_\alpha$; $\alpha=\lambda,\nu$ are non-negative distances, but is consistent from the formal mathematical point of view. Since the wave function vanishes for negative $r_\alpha$ (because of the infinite positive potential barrier at $r_\alpha\leqslant 0$), the sums in Eq. (5) are effectively taken only for positive $j$.

Using the above expressions, Eq. (1) takes the form

$$\sum_{q',p'}A_{q,p,q',p'}\chi_{q',p'}=Z^{(\nu)}_{q,p}, \tag{7}$$

where

$$A_{q,p,q',p'}=[E-U(r_{\lambda,q},r_{\nu,p})]\delta_{q,q'}\delta_{p,p'}-\frac{\hbar^2}{m}t^1_{q'-q}t^1_{p'-p}+\frac{\hbar^2}{2\mu_\lambda}t^2_{q'-q}\delta_{p,p'}+\frac{\hbar^2}{2\mu_\nu}t^2_{p'-p}\delta_{q,q'}, \tag{8}$$

$$Z^{(\nu)}_{q,p}=V(r_{\lambda,q},r_{\nu,p})\psi_{0\nu}(r_{\lambda,q},r_{\nu,p}). \tag{9}$$

In the $\nu$ asymptotic region, $U(r_{\lambda,q},r_{\nu,p})$ depends solely on $r_{BC}=r_{\nu,p}$, i.e.,

$$\lim_{r_{\lambda,q}\rightarrow\infty}U(r_{\lambda,q},r_{\nu,p})=v_\nu(r_{\nu,p}), \tag{10}$$

where $v_\nu$ is the vibrational potential in the $\nu$ asymptote. Consequently, the lhs of Eq. (7) depends only on the indices $q-q',p,p'$, and has a block-Toeplitz structure. Moreover, in this region the perturbation $V$, and therefore the rhs of Eq. (1), vanishes. It thus follows that the solution space is spanned by solutions with the asymptotic behavior

$$\chi_{q,p}=\exp(i\theta_\nu q)\phi_p^{(\nu)},\quad q\rightarrow\infty, \tag{11}$$

where $\theta_\nu$ and $\phi_p^{(\nu)}$ are constants yet to be determined.

Substituting Eq. (11) in Eq. (7) and multiplying by $\exp(-i\theta_\nu q)$ one obtains the equation (where $l=q'-q$)

$$\sum_{l,p'}\left\{[E-v_\nu(r_{\nu,p})]\delta_{l,0}\delta_{p,p'}-\frac{\hbar^2}{m}t^1_l t^1_{p'-p}+\frac{\hbar^2}{2\mu_\lambda}t^2_l\delta_{p,p'}+\frac{\hbar^2}{2\mu_\nu}t^2_{p'-p}\delta_{l,0}\right\}\exp(il\theta_\nu)\phi^{(\nu)}_{p'}=0. \tag{12}$$

The sum over $l$ can be done analytically[5,12] and yields

$$\sum_{p'}\left\{(E-\frac{\hbar^2\theta_\nu^2}{2\mu_\lambda\sigma^2}-v_\nu(r_{\nu,p}))\delta_{p,p'}+\frac{\hbar^2}{2\mu_\nu}t^2_{p'-p}-\frac{i\hbar^2\theta_\nu}{m\sigma}t^1_{p-p'}\right\}\phi^{(\nu)}_{p'}=0. \tag{13}$$

Using Eq. (5), we can transform this equation back into the differential equation

$$\left\{E-\frac{\hbar^2\theta_\nu^2}{2\mu_\lambda\sigma^2}-v_\nu(r_\nu)+\frac{\hbar^2}{2\mu_\nu}\frac{\partial^2}{\partial r_\nu^2}-\frac{i\hbar^2\theta_\nu}{m\sigma}\frac{\partial}{\partial r_\nu}\right\}\phi^{(\nu)}(r_\nu)=0. \tag{14}$$

The $\theta_\nu=0$ case is the equation for the vibrational states of the diatomic molecule $BC$. The solutions of this equation are given, i.e.,

$$\left\{\epsilon_{\nu,n}-v_\nu(r_\nu)+\frac{\hbar^2}{2\mu_\nu}\frac{\partial^2}{\partial r_\nu^2}\right\}\phi_0^{(\nu,n)}(r_\nu)=0, \tag{15}$$

where $\epsilon_{\nu,n}$ and $\phi_0^{(\nu,n)}(r_\nu)$ are the eigenenergies and eigenstates of the diatomic molecule $BC$, respectively. In order to treat the $\theta_\nu\neq 0$ case we define

$$\phi^{(\nu,n)}(r_\nu)=\phi_0^{(\nu,n)}(r_\nu)\exp\left(\frac{i\theta_\nu\mu_\nu r_\nu}{m\sigma}\right), \tag{16}$$

and show that these are the solutions of Eq. (14). From Eq. (16) it follows by direct differentiation that

$$\frac{\hbar^2}{2\mu_\nu}\frac{\partial^2\phi_0^{(\nu,n)}(r_\nu)}{\partial r_\nu^2}=\frac{\hbar^2}{2\mu_\nu}\exp\left(\frac{-i\theta_\nu\mu_\nu r_\nu}{m\sigma}\right)\left\{\frac{\partial^2}{\partial r_\nu^2}-\frac{2i\theta_\nu\mu_\nu}{m\sigma}\frac{\partial}{\partial r_\nu}-\left(\frac{\theta_\nu\mu_\nu}{m\sigma}\right)^2\right\}\times\phi^{(\nu,n)}(r_\nu). \tag{17}$$

On the other hand, from Eq. (15) we obtain

$$\begin{aligned}\frac{\hbar^2}{2\mu_\nu}\frac{\partial^2\phi_0^{(\nu,n)}(r_\nu)}{\partial r_\nu^2}&=[v_\nu(r_\nu)-\epsilon_{\nu,n}]\phi_0^{(\nu,n)}(r_\nu)\\&=\exp\left(\frac{-i\theta_\nu\mu_\nu r_\nu}{m\sigma}\right)[v_\nu(r_\nu)-\epsilon_{\nu,n}]\times\phi^{(\nu,n)}(r_\nu),\end{aligned} \tag{18}$$

where the second equality follows from Eq. (16). Comparing the rhs of Eqs. (17) and (18) we get

$$\frac{\hbar^2}{2\mu_\nu}\left\{\frac{\partial^2}{\partial r_\nu^2}-\frac{2i\theta_\nu\mu_\nu}{m\sigma}\frac{\partial}{\partial r_\nu}-\left(\frac{\theta_\nu\mu_\nu}{m\sigma}\right)^2-\frac{2\mu_\nu}{\hbar^2}v_\nu(r_\nu)\right\}\phi^{(\nu,n)}(r_\nu)=-\epsilon_{\nu,n}\phi^{(\nu,n)}(r_\nu). \tag{19}$$

Substituting Eq. (19) in Eq. (14), one sees that $\phi^{(\nu,n)}$ indeed solves this equation under the condition

$$\left[E-\epsilon_{\nu,n}+\frac{\hbar^2\theta_\nu^2}{2\mu_\lambda\sigma^2}\left(\frac{\mu_\lambda\mu_\nu-m^2}{m^2}\right)\right]\phi^{(\nu,n)}(r_\nu)=0, \tag{20}$$

which has to be fulfilled for each $r_\nu$. Consequently, the expression in the square brackets must vanish, thus yielding a solution for $\theta_n$ for each $n$,

$$\begin{aligned}\theta_{\nu,n}&=\frac{\sigma}{\hbar}\sqrt{2(E-\epsilon_{\nu,n})}\sqrt{\frac{\mu_\lambda m^2}{m^2-\mu_\lambda\mu_\nu}}\\&=\frac{\sigma}{\hbar}\sqrt{2\mu_{A,BC}(E-\epsilon_{\nu,n})}=\sigma k_{\nu,n},\end{aligned} \tag{21}$$

where

$$\mu_{A,BC}=\frac{m_A(m_B+m_C)}{m_A+m_B+m_C} \tag{22}$$

and $k_{\nu,n}$ is the wave number associated with the translational energy of the $n$th vibrational state in the $\nu$ asymptote, at total energy $E$. Collecting the results of Eqs. (11), (16), (20), and (21), and after transforming back to DVR form, we find that the space of solutions $\chi_{q,p}$ in the $\nu$ asymptote can be spanned by the functions [see Eq. (11)]

$$\begin{aligned}\chi_{q,p}&=\exp(i\theta_{\nu,n}q)\phi_p^{(\nu,n)}\\&=\exp(i\theta_{\nu,n}q)\phi_{0p}^{(\nu,n)}\exp(i\theta_{\nu,n}\mu_\nu p/m),\quad r_\lambda\to\infty,\end{aligned} \tag{23}$$

where $\phi_p^{(\nu,n)}$ and $\phi_{0p}^{(\nu,n)}$ are the values of these functions at the DVR points $r_{\nu,p}$.

The same considerations can be applied to the asymptotic λ AC, and the solution space in that region can be spanned by solutions of the form

$$\begin{aligned}\chi_{q,p}&=\exp(i\theta_{\lambda,n}p)\phi_q^{(\lambda,n)}\\&=\exp(i\theta_{\lambda,n}p)\phi_{0q}^{(\lambda,n)}\exp(i\theta_{\lambda,n}\mu_\lambda q/m),\quad r_\nu\to\infty,\end{aligned} \tag{24}$$

where $\phi_0^{\lambda,n}$ are the asymptotic vibrational states of the diatomic molecule $AB$.

We now introduce two integers $q_0,p_0$, such that the $\nu$-asymptotic region is reached for all grid points $q>q_0$, and the λ-asymptotic region is reached for all grid points $p>p_0$ (see Fig. 1). Consequently, $\chi_{q,p}$ will be written in this regions as a superposition of the solutions given by Eq. (11). Thus

$$\chi_{q,p}=\sum_n c_{\nu,n}\exp(i\theta_{\nu,n}q)\phi_p^{(\nu,n)},\quad q>q_0, \tag{25}$$

$$\chi_{q,p}=\sum_n c_{\lambda,n}\exp(i\theta_{\lambda,n}p)\phi_q^{(\lambda,n)},\quad p>p_0, \tag{26}$$

where $\phi_l^{(\alpha,n)}=\phi^{(\alpha,n)}(r_{\alpha,l})$ ($\alpha=\lambda,\nu$ and $l=p,q$, respectively), and the coefficients $c_{\nu,n}$ and $c_{\lambda,n}$ will be determined later. The $c_{\alpha,n}$ ($\alpha=\lambda,\nu$) are closely related to the $T$-matrix elements through the relation

$$c_{\alpha,n}=\sqrt{\frac{k_{\alpha,n}}{k_{n_0}}}\,T(\alpha,n\leftarrow\lambda,n_0), \tag{27}$$

where $k_{n_0},k_{\alpha,n}$ are the wave numbers of the incoming wave and outgoing wave in the $\alpha$ asymptote, respectively.

Note that the application of interatomic distances as independent variables is essential for the above derivation, since it yields at each asymptote a Toeplitz situation. This is not the case, for instance, if one employs the ordinary Jacobi $(R_\alpha, r_\alpha)$ coordinates.

We now use the above results to reduce the infinite set of algebraic equations (7) for the wave-function values at the grid points, to a finite set, only for the points in the interaction region (see also Ref. 3).

The sum on the lhs of Eq. (7) can be broken into three subsummations; two of them correspond to the two asymptotic regions and the third to the interaction region. The first term, which corresponds to the $\nu$ asymptote, is obtained from the sum over $q'>q_0$, and can be simplified using Eq. (25) as follows:

$$\sum_{q'>q_0,p'} A_{q,p,q',p'}\chi_{q',p'} = \sum_{q'>q_0,p'} \sum_n A_{q,p,q',p'} c_{\nu,n} \exp(i\theta_{\nu,n}q')\phi_{p'}^{(\nu,n)}. \tag{28}$$

The coefficients $c_{\nu,n}$ can be calculated by using the values of $\chi_{q_0,p}$ in the following way: Substituting $q=q_0$ in Eq. (25), we get

$$\chi_{q_0,p} = \sum_n b_{\nu,n}\phi_p^{(\nu,n)}, \tag{29}$$

where

$$b_{\nu,n} = c_{\nu,n}\exp(i\theta_{\nu,n}q_0). \tag{30}$$

We define the transformation matrix $\Gamma$ through its inverse whose elements are given by

$$(\mathbf{\Gamma}_\nu^{-1})_{p,n} = \phi_n^{(\nu,p)} = \phi_{0n}^{(\nu,p)}\exp(i\theta_{\nu,p}\mu_\nu n/m). \tag{31}$$

Accordingly,

$$(\mathbf{\Gamma}_\nu^{-1}\mathbf{b})_l = \sum_n (\Gamma_\nu^{-1})_{l,n} b_{\nu,n} = \sum_n b_{\nu,n}\phi_l^{(\nu,n)} = \chi_{q_0,l}, \tag{32}$$

and thus the matrix $\mathbf{\Gamma}_\nu$ gives the relation

$$b_{\nu,n} = \sum_l (\mathbf{\Gamma}_\nu)_{n,l}\chi_{q_0,l}. \tag{33}$$

Using the results (25) and (33) one obtains (for $q>q_0$)

$$\chi_{q,p} = \sum_{n,l} (\mathbf{\Gamma}_\nu)_{n,l}\chi_{q_0,l}\exp(i\theta_{\nu,n}(q-q_0))\phi_p^{(\nu,n)} = \sum_l \mathbf{\Lambda}_{p,l}^{(\nu,q)}\chi_{q_0,l}, \tag{34}$$

where

$$\mathbf{\Lambda}_{p,l}^{(\nu,q)} = \sum_n (\Gamma_\nu)_{n,l}\exp(i\theta_{\nu,n}(q-q_0))\phi_p^{(\nu,n)}. \tag{35}$$

We note here that while one employs the above procedure numerically, the matrix elements in the rows of the matrix $\Gamma_\nu^{-1}$ which correspond to the highly excited vibrational states, i.e., the high $p$ rows, are practically zero. This is due to the fact that for a closed state $\theta_\nu$ is pure imaginary, and thus the matrix elements are exponentially damped. This involves a severe numerical instability related to the existence of many eigenvalues of the matrix $\Gamma_\nu$ which are very close to zero. From a physical point of view, the way to bypass this obstacle is to consider only a few low states and not all the states given by the DVR solution to the vibrational problem (whose number is the same as the number of points). This can be done in two ways. The first is to restrict the index of the states to the lower states. Thus, in order to obtain a square matrix (such that it could be inverted), one does not use for the matrix $\Gamma_\nu$ all the points, but rather a selected set of points whose number is equal to the number of states taken. A more general way is to use an SVD-like method which projects the state $\chi_{q_0,l}$ onto the subspace spanned by the low vibrational states. We note that in this way, the matrix $\mathbf{\Lambda}^{(\nu,q)}$ which relates $\chi_{q,l}$ to $\chi_{q_0,m}$ is not the identity matrix even for $q=q_0$ but is rather an *idempotent* matrix (a projection operator) which eliminates the components of $\chi_{q_0,m}$ corresponding to the high-energy states.

A similar relation can be derived for the $\lambda(AB+C)$ asymptote, i.e.,

$$\chi_{q,p} = \sum_l \mathbf{\Lambda}_{q,l}^{(\lambda,p)}\chi_{l,p_0}, \tag{36}$$

where

$$\mathbf{\Lambda}_{q,l}^{(\lambda,p)} = \sum_n (\Gamma_\lambda)_{n,l}\exp[i\theta_{\lambda,n}(p-p_0)]\phi_q^{(\lambda,n)}, \tag{37}$$

$$(\Gamma_\lambda^{-1})_{lq} = \phi_q^{(\lambda,l)} = \phi_{0q}^{(\lambda,l)}\exp(i\theta_{\lambda,l}\mu_\lambda q/m). \tag{38}$$

Using the results (34), (36), the algebraic system (7) is reduced to the finite system

$$\sum_{q'=0}^{q_0}\sum_{p'=0}^{p_0}\tilde{A}_{q,p,q',p'}\chi_{q',p'} = V(r_{\lambda,q}, r_{\nu,p})\psi_0(r_{\lambda,q}, r_{\nu,p}), \quad 0\leqslant q\leqslant q_0, \quad 0\leqslant p\leqslant p_0, \tag{39}$$

where

$$\tilde{A}_{q,p,q',p'} = \begin{cases} \Sigma_{q''=q_0}^{\infty}\Sigma_{p''=0}^{p_0}A_{q,p,q'',p''}\mathbf{\Lambda}_{p',p''}^{(\nu,q'')} & q'=q_0, \\ A_{q,p,q',p'} & q'<q_0, \quad p'<p_0, \\ \Sigma_{p''=p_0}^{\infty}\Sigma_{q''=0}^{q_0}A_{q,p,q'',p''}\mathbf{\Lambda}_{q',q''}^{(\lambda,p'')} & p'=p_0. \end{cases} \tag{40}$$

## III. ANALYSIS AND RESULTS

We now turn to the problem of calculating the state-to-state probabilities out from the solution $\chi$ obtained by the method described in the previous section. Usually, when the wave function is evaluated employing $L^2$ methods, one has to perform integrations in order to calculate the $S$-matrix

TABLE I. Reactive transition probabilities for the colinear reaction $H_2+H\rightarrow H+H_2$ in the low-energy domain, where the vibrational ground state is the only one open in both reactants and products. The results are shown to converge as a function of $N$, the number of grid points.

| $N$ | $E_{tot}=0.50$ | 0.55 | 0.60 | 0.65 | 0.70 | 0.75 | 0.80 |
|---|---|---|---|---|---|---|---|
| 95 | 0.079 | 0.715 | 1.052 | 1.034 | 1.043 | 0.984 | 1.074 |
| 106 | 0.080 | 0.746 | 1.003 | 1.039 | 0.998 | 1.005 | 1.006 |
| 116 | 0.078 | 0.737 | 0.996 | 1.014 | 0.997 | 0.995 | 0.965 |
| 128 | 0.084 | 0.717 | 1.005 | 1.007 | 0.999 | 0.984 | 0.949 |
| 140 | 0.083 | 0.702 | 1.007 | 1.013 | 0.995 | 0.980 | 0.950 |
| 169 | 0.081 | 0.709 | 1.002 | 0.998 | 0.991 | 0.973 | 0.946 |
| exact[a] | 0.084 | 0.721 | 1.000 | 0.992 | 0.980 | 0.967 | 0.938 |

[a] See Ref. 14.

elements.[7,13] These methods are preferred since they apply the values of the wave function in the whole configuration space and not just at a limited region.

The DVR method yields wave-function values at a given set of discrete grid points. We have shown before[5] that the DVRTM approach requires a relatively small number of points to get converged results (~2.5 points per wavelength). Such a low density of points is far from enough for any accurate numerical integration. Consequently, obtaining $S$-matrix elements following an integration may not be compatible with the DVRTM approach if one wants to keep the number of points as small as possible. This difficulty can be overcome using the sampling theorem, which will be discussed elsewhere.

An alternative way is to apply a matching procedure to obtain the $S$-matrix elements. Usually matching methods involve a solution of an algebraic system for the coefficients of the different vibrational states. However, we show now that, employing the formalism derived in the previous section, this difficulty is easily overcome.

The initial state is determined by the boundary conditions for $\psi_0$ and is therefore known. For each final reactive state $n$, the coefficient $b_{\alpha n}$, $\alpha=\lambda,\nu$ presented in Eq. (29) is, in fact, closely related to the required $S$-matrix elements. These coefficients can be obtained using Eq. (33), once Eq. (39) is solved. Consequently, the reactive transition probabilities are [see Eqs. (27) and (30)]

$$P(\lambda\rightarrow\nu,n)=|T(\alpha,n\leftarrow\lambda,n_0)|^2$$

$$=\frac{k_{n_0}}{k_{\nu,n}}\left|\sum_p (\mathbf{\Gamma}_\nu)_{n,p}\chi_{q_0,p}\right|^2. \tag{41}$$

A similar expression can be obtained for the nonreactive probabilities.

In order to check the applicability and efficiency of the above method, we have tested it with respect to the collinear reaction

$$H+H_2(v_i)\rightarrow H_2(v_f)+H. \tag{42}$$

We calculated state-to-state and state-selected reactive probabilities for three initial vibrational states, i.e., $v=0,1,2$. Table I presents the results in the low-energy domain, where only one vibrational state is open. The results are shown as a function of $N$, the number of grid points. One can see that, in general, as the energy is lower, less points are needed for convergence. The results are compared with those obtained by Bondi *et al.*[14] In Table II are presented the high-energy cases, up to energies which allow three open vibrational states. The state-to-state and total state-selected reactive transition probabilities are shown for two different grids. The results for the more dense grid show a good agreement with those of Ref. 15.

## IV. CONCLUSION

In this work, we extended the recently introduced DVRTM approach to a system with two coordinates and accordingly two nonlinear asymptotes. This method employs the discrete grid representation of SE to get an *exact*, but *infinite*, set of algebraic equations. The asymptotic part of the matrix obtained has the structure of a Toeplitz matrix. The features of Toeplitz matrices are then employed in order to reduce the *infinite* set of equations to a *finite* one, whose solution is equivalent to a solution of the original SE. We have shown that for a two-coordinate reactive system, the matrix obtained has a block-Toeplitz rather than a single-element Toeplitz form, and consequently extended the DVRTM approach for this case. The reduced finite set of equations is employed to calculate the reactive state-to-state transition probabilities. We are now in the process of extending the approach to 3D, and hope to be able to report on results in the near future.

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## APPENDIX: DVR FOR THE FIRST DERIVATIVE

In this Appendix, we derive the DVR expression for the first derivative, which we need in order to get the DVR form of the kinetic-energy operator in terms of the interatomic distances. For this purpose, we consider (see Ref. 7) the $(2N+1)$-order Lagrangian interpolation formula:

$$f(x)=\sum_{k=-N}^{N} f_k \prod_{l=-N}^{N}{}' \left(\frac{x-x_l}{x_k-x_l}\right), \tag{A1}$$

TABLE II. State-to-state and total state-selected reactive transition probabilites for the colinear reaction $H_2(v_i)+H \rightarrow H+H_2(v_f)$. A comparison between present results (first row $N=162$; second row $N=209$) and those due to Ref. 15 (last row).

| $E_{tot}$ | 0→0 | 0→1 | 0→2 | Total | 1→0 | 1→1 | 1→2 | Total | 2→0 | 2→1 | 2→2 | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.85 | 0.845 | 0.010 | ⋯ | 0.855 | 0.010 | 0.001 | ⋯ | 0.011 | | | | |
| | 0.828 | 0.014 | ⋯ | 0.841 | 0.010 | 0.002 | ⋯ | 0.012 | | | | |
| | 0.834 | 0.013 | ⋯ | 0.847 | 0.012 | 0.003 | ⋯ | 0.016 | | | | |
| 0.9 | 0.401 | 0.290 | ⋯ | 0.691 | 0.281 | 0.286 | ⋯ | 0.567 | | | | |
| | 0.394 | 0.290 | ⋯ | 0.686 | 0.285 | 0.297 | ⋯ | 0.576 | | | | |
| | 0.380 | 0.290 | ⋯ | 0.670 | 0.289 | 0.298 | ⋯ | 0.586 | | | | |
| 1.0 | 0.581 | 0.290 | ⋯ | 0.871 | 0.268 | 0.432 | ⋯ | 0.701 | | | | |
| | 0.565 | 0.268 | ⋯ | 0.830 | 0.268 | 0.455 | ⋯ | 0.720 | | | | |
| | 0.537 | 0.283 | ⋯ | 0.820 | 0.275 | 0.468 | ⋯ | 0.744 | | | | |
| 1.1 | 0.335 | 0.378 | ⋯ | 0.713 | 0.373 | 0.331 | ⋯ | 0.704 | | | | |
| | 0.306 | 0.373 | ⋯ | 0.673 | 0.377 | 0.355 | ⋯ | 0.729 | | | | |
| | 0.289 | 0.393 | ⋯ | 0.682 | 0.371 | 0.363 | ⋯ | 0.734 | | | | |
| 1.2 | 0.163 | 0.369 | ⋯ | 0.532 | 0.367 | 0.245 | ⋯ | 0.611 | | | | |
| | 0.147 | 0.376 | ⋯ | 0.523 | 0.366 | 0.238 | ⋯ | 0.604 | | | | |
| | 0.133 | 0.371 | ⋯ | 0.504 | 0.386 | 0.238 | ⋯ | 0.625 | | | | |
| 1.3 | 0.527 | 0.067 | 0.114 | 0.708 | 0.040 | 0.401 | 0.105 | 0.546 | 0.075 | 0.063 | 0.032 | 0.170 |
| | 0.515 | 0.052 | 0.093 | 0.659 | 0.047 | 0.463 | 0.059 | 0.568 | 0.089 | 0.063 | 0.026 | 0.178 |
| | 0.513 | 0.059 | 0.065 | 0.637 | 0.063 | 0.489 | 0.045 | 0.597 | 0.105 | 0.071 | 0.021 | 0.197 |
| 1.4 | 0.050 | 0.227 | 0.070 | 0.347 | 0.206 | 0.353 | 0.195 | 0.754 | 0.106 | 0.116 | 0.576 | 0.798 |
| | 0.061 | 0.233 | 0.097 | 0.391 | 0.219 | 0.333 | 0.143 | 0.694 | 0.117 | 0.109 | 0.510 | 0.737 |
| | 0.059 | 0.231 | 0.106 | 0.396 | 0.223 | 0.302 | 0.122 | 0.648 | 0.112 | 0.136 | 0.512 | 0.759 |
| 1.5 | 0.056 | 0.199 | 0.125 | 0.380 | 0.149 | 0.320 | 0.329 | 0.798 | 0.123 | 0.218 | 0.552 | 0.893 |
| | 0.058 | 0.155 | 0.146 | 0.359 | 0.139 | 0.273 | 0.218 | 0.630 | 0.132 | 0.209 | 0.441 | 0.783 |
| | 0.064 | 0.147 | 0.138 | 0.350 | 0.137 | 0.263 | 0.206 | 0.606 | 0.136 | 0.210 | 0.396 | 0.742 |
| 1.6 | 0.039 | 0.053 | 0.187 | 0.278 | 0.051 | 0.199 | 0.259 | 0.509 | 0.135 | 0.397 | 0.375 | 0.907 |
| | 0.045 | 0.065 | 0.141 | 0.250 | 0.061 | 0.223 | 0.248 | 0.532 | 0.155 | 0.271 | 0.215 | 0.641 |
| | 0.049 | 0.078 | 0.169 | 0.296 | 0.070 | 0.248 | 0.288 | 0.605 | 0.140 | 0.242 | 0.214 | 0.596 |

where $f_k=f(x_k)$ and the prime on the product means that the factor $l=k$ is omitted. We consider the case of equally spaced grid points

$$x_k=\sigma k, \quad k=0,\pm 1,\ldots,\pm N. \tag{A2}$$

In what follows we evaluate the first derivative of $f(x)$ at the central grid point $x_0=0$.

Differentiating Eq. (A1) and setting $x=0$ gives

$$f'(0)=-\frac{1}{\sigma}\sum_{k=-N}^{N} f_k \sum_{j\neq k} \frac{1}{j} \prod_{l=-N}^{N}{}' \left(\frac{l}{l-k}\right). \tag{A3}$$

The product on the right hand side vanishes unless either $k=0$ or $j=0$. Thus the above expression is simplified to become

$$f'(0)=-\frac{1}{\sigma}\left\{ f_0 \sum_{j\neq 0} \frac{1}{j} \prod_{l=-N}^{N}{}' \left(\frac{l}{l-k}\right) + \sum_{k=-N}^{N}{}' f_k \prod_{l=-N}^{N}{}'' \left(\frac{l}{l-k}\right)\right\}, \tag{A4}$$

where the prime on the sum means that the term $k=0$ is omitted, and the double prime on the product means that both the $l=k$ and the $l=0$ terms are omitted. The sum over $j$ in the first term vanishes due to the cancellation of the terms $j$ and $-j$, and grouping together the terms $l$ and $-l$ in the product, one obtains

$$f'(0)=\frac{1}{\sigma}\sum_{k=1}^{N} \frac{1}{2k}(f_k-f_{-k})\prod_{l=1}^{N}{}' \left(\frac{l^2}{l^2-k^2}\right). \tag{A5}$$

$N=1$ and $N=2$, for example, give the three- and five-point results, respectively,

$$f'(0)\simeq \frac{1}{2\sigma}(f_1-f_{-1}), \tag{A6}$$

$$f'(0)\simeq \frac{1}{12\sigma}(-f_2+8f_1-8f_{-1}+f_{-2}). \tag{A7}$$

Applying the identity

$$\lim_{N\to\infty}\prod_{l=1}^{N}{}' \frac{l^2}{l^2-k^2}=\lim_{x\to k}\left(1-\frac{x^2}{k^2}\right)\frac{\pi x}{\sin(\pi x)}=-2(-1)^k, \tag{A8}$$

one obtains for $N\rightarrow\infty$ that $f'(0)$ is given by

$$f'(0)=-\frac{1}{\sigma}\sum_{k=1}^{\infty}\frac{(-1)^k}{k}(f_k-f_{-k}). \tag{A9}$$

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