Applications of square-integrable basis functions for scattering problems: A comparison between approaches based on Toeplitz matrices and negative imaginary potentials

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In this work are considered two quantum-mechanical approaches to treat a single-coordinate (Eckart-type) potential scattering process. The one approach is based on the application of Toeplitz matrices and the other on the application of negative imaginary (absorbing) potentials. It was found that for this type of "reactive" process, the method based on the Toeplitz matrices performed better.

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I. INTRODUCTION

The application of finite-range square-integrable (L^2) functions has become, during the past few years, one of the more popular ways to handle multiarrangement channel scattering problems [1–4]. These methods have their origin in studies of the late 1960's and early 1970's [5]. Recently, several new approaches were introduced [6,7] and in the present study we would like to concentrate on the one that applies Toeplitz matrices [7] (TM). This approach is based on two ideas: (a) The equation to be considered is a perturbative-type equation [8] and (b) the unknown function is expanded in terms of an infinite set of localized basis functions (e.g., Gaussians). Such a set leads to a potential matrix of infinite dimensions where the "lower" infinite part takes the form of a Toeplitz matrix. The relevant set of algebraic equations can be treated analytically and, once completed, the remaining finite set of the algebraic equations is solved with ordinary methods.

This approach was applied to a single-coordinate elastic-scattering problem and was shown to lead to accurate phase shifts [7(a)]. In this work we concentrate on two aspects: (a) The previous elastic-scattering problem is extended to a "reactive" model employing Eckart-type potentials [9] defined along the infinite range $-\infty \le s \le \infty$ and (b) the calculations will be done twice, once employing the Toeplitz approach (TA) and once employing negative imaginary potentials (NIP). The results obtained by the two approaches will be compared, followed by a discussion of the advantages and disadvantages of each.

II. THE MODEL

In this work we study a single-coordinate(s) reactive model where s is defined along the range $-\infty \le s \le \infty$. In what follows, the positive part of the s axis will be termed the λ arrangement channel (AC) and the negative part as the ν AC. The relevant Schrödinger equation (SE) to be considered is

$$(E-H)\Psi_\lambda = 0 \ , \tag{1}$$

where Ψ_λ is the complete wave function calculated for an asymptotic boundary condition at the λ AC and H, the Hamiltonian, takes the form

$$H = -\frac{1}{2\mu}\frac{d^2}{ds^2} + U(s) \ . \tag{2}$$

Here, $U(s)$ is a potential defined in such a way that

$$\lim U(s) = \begin{cases} 0 \ , & s \to \infty \\ \text{const} \ , & s \to -\infty \end{cases} \tag{3}$$

and is nonzero in the vicinity of $s \sim 0$ (see Fig. 1).

To obtain Ψ_λ, we employ a perturbative approach [8] going through the following steps.

(a) We define two (nonreactive) unperturbed potentials $W_\alpha(s)$ where for $\alpha = \lambda$, we have

$$W_\lambda(s) = \begin{cases} \neq 0 \ , & s > 0 \\ = 0 \ , & s < 0 \end{cases} \tag{4a}$$

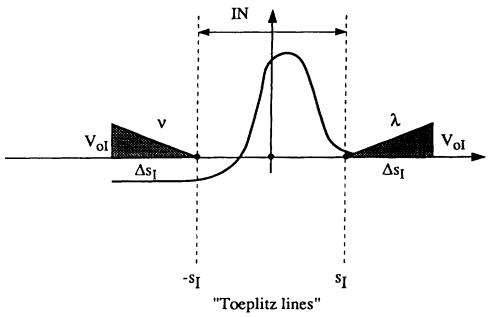

FIG. 1. The single-coordinate reaction system. The two "Toeplitz lines" are border lines for the reagents (λ) region, for the interaction (IN) region, and the products (ν) region. Also shown are the two NIP's: one in the λ region and the other in the ν region.

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and for $\alpha=\nu$,

$$W_\nu(s)=\begin{cases}=0\ , & s>0\\ \neq 0\ , & s<0\end{cases} \tag{4b}$$

and both potentials are relatively large in the vicinity of $s=0$ so that $W_\alpha(s)\gg E$; $\alpha=\lambda,\nu$.

(b) We solve the following two unperturbed SE's:

$$(E-H_{0\alpha})\Psi_{0\alpha}(s)=0\ ,\quad \alpha=\lambda,\nu \tag{5}$$

where

$$H_{0\alpha}=-\frac{1}{2\mu}\frac{d^2}{ds^2}+W_\alpha(s)\ ,\quad \alpha=\lambda,\nu \tag{6}$$

by some propagative method.

(c) We now write Ψ_λ as

$$\Psi_\lambda=\chi_\lambda+\psi_{0\lambda}\ , \tag{7}$$

substituting this expression in Eq. (2), and employing Eq. (5) for $\alpha=\lambda$, we get the inhomogeneous equation for χ_λ [2(a)]:

$$(E-H)\chi_\lambda=V_\lambda\psi_{0\lambda}\ . \tag{8}$$

(d) Once χ_λ is solved, the "reactive" S-matrix element is obtained from the expression [2(b)]

$$S(\nu\leftarrow\lambda)=i\langle\psi_{0\nu}|V_\nu|(\chi_\lambda+\psi_{0\lambda})\rangle\ , \tag{9}$$

where

$$V_\nu=U-W_\nu\ . \tag{10}$$

To solve Eq. (8), χ_λ is expanded in terms of a localized basis set (e.g., Gaussians):

$$\chi_\lambda=\sum_n a_n\zeta_n(s)\ . \tag{11}$$

Substituting Eq. (11) in Eq. (8), multiplying from the left by $\zeta_m(s)$, and integrating over s lead to the following set of algebraic equations:

$$\sum_{n=-\infty}^{\infty}A_{mn}a_n=Z_m\ ,\quad m=-\infty,\ldots,\infty \tag{12}$$

where

$$A_{mn}=\langle\zeta_m|E-H|\zeta_n\rangle \tag{13}$$

and

$$Z_m=\langle\zeta_m|V_\lambda|\psi_{0\lambda}\rangle\ . \tag{14}$$

Here,

$$V_\lambda=U-W_\lambda\ . \tag{10'}$$

Equation (12) will be solved in two different ways: Once applying the features of the Toeplitz matrix and once employing NIP's. In what follows we mainly concentrate on the TA, whereas the approach based on NIP's will be only briefly discussed.

A. The Toeplitz approach

To solve the infinite system of algebraic equations given in Eq. (12), we choose $\{\zeta_n(s)\}$ to be Gaussians of the form

$$\zeta_n(s)=\left[\frac{\alpha}{\sigma\sqrt{\pi}}\right]^{1/2}\exp\left[-\frac{\alpha^2}{2\sigma^2}(s-s_n)^2\right]\ ,$$
$$n=-\infty,\ldots,0,\ldots,\infty\ . \tag{15}$$

Here, $\{s_n\}$ is a set of equidistant grid points defined along the range $-\infty\le s\le\infty$, σ is the grid interval, and α is a constant. This choice of functions and the fact that $U(s)$ is of a finite range (in both directions) lead to the following analysis: We define two integers n_α, $\alpha=\lambda,\nu$ (n_ν is negative) such that once $s>s_{n_\lambda}$ and $s<s_{n_\nu}$, $U(s)$ is for all practical purposes identically zero. In addition, $V_\lambda(s)$ and $V_\nu(s)$ are identically zero once $s>s_{n_\lambda}$ and $s<s_{n_\nu}$, respectively. In such a case, for $n\gg n_\lambda$ and $n\ll n_\nu$, the inhomogeneous term Z_n becomes zero [see Eq. (14)] and if we consider the cases where also $m\gg n_\lambda$ or $m\ll n_\nu$, we obtain for A_{nm}, the expression

$$A_{nm}=\left\langle\zeta_n\left|\frac{1}{2\mu}\frac{\partial^2}{\partial s^2}+E_{\rm tr}\right|\zeta_m\right\rangle\ , \tag{13'}$$

where $E_{\rm tr}$ is the translational energy in the respective asymptotic region.

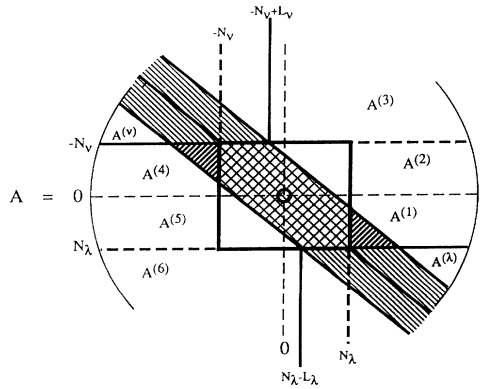
Substituting Eq. (15) in Eq. (13') leads to the expression

$$A_{nm}=A_{|n-m|}=t_j\ , \tag{16}$$

where $j=|n-m|$ and t_j is given in the form

$$t_j=\left[E_{\rm tr}-\frac{\alpha^2}{2\sigma^2}\frac{1}{2\mu}\left[1-\frac{\alpha^2}{2}j^2\right]\right]\exp\left[-\frac{\alpha^2j^2}{4}\right]\ . \tag{17}$$

In other words, for $|n|,|m|>N_\alpha$, $\alpha=\lambda,\nu$ (where $N_\alpha\gg n_\alpha$), all elements along a given diagonal are constant and the rest depend only on their distance from the main diagonal. Thus, **A** can be shown to have the following structure (the shaded area stands for nonzero numerical values and the empty areas are, for all practical purposes, zeros):



(18)

The matrix **A** is made up of nine matrices $\mathbf{A}^{(M)}$, $\mathbf{A}^{(\lambda)}$, $\mathbf{A}^{(\nu)}$, and $\mathbf{A}^{(i)}$, $i=1,\ldots,6$. Here, $\mathbf{A}^{(M)}$ is the central (square) matrix responsible for most of the potential coupling; its order is $(N_\lambda+N_\nu)\times(N_\lambda+N_\nu)$ with elements $\mathbf{A}_{mn}$ defined in Eq. (13). The matrices $\mathbf{A}^{(\lambda)}$ and $\mathbf{A}^{(\nu)}$ are *rectangular* matrices with the elements A_{mn} defined in Eqs. (13'), (16), and (17). The matrices $\mathbf{A}^{(1)}$ and $\mathbf{A}^{(4)}$ are

rectangular matrices responsible for the coupling of $\mathbf{A}^{(\lambda)}$ and $\mathbf{A}^{(\nu)}$, respectively, with $\mathbf{A}^{(M)}$, and the other remaining matrices, i.e., $\mathbf{A}^{(2)}$, $\mathbf{A}^{(3)}$, $\mathbf{A}^{(5)}$, and $\mathbf{A}^{(6)}$, are rectangular zero matrices. The matrices $\mathbf{A}^{(\lambda)}$ and $\mathbf{A}^{(\nu)}$ with the features just described are known as Toeplitz matrices, the analytic properties of which are well defined.

To solve Eq. (12), we start by considering first its lower part, namely, from row $n \geq N_\lambda + 1$ and downwards, then next its upper part, namely, from row $n' \leq -(N_\nu + 1)$ and upwards, and finally the central part, namely, all the rows in the range $-N_\nu \leq n'' \leq N_\lambda$. Recalling that for $n > N_\lambda + 1$ and for $n' \leq -(N_\nu + 1)$ the inhomogeneous term is $Z_n = 0$, we obtain for the lower and the upper parts of Eq. (12), respectively, the following expressions:

$$\sum_{j=-L_\lambda}^{L_\lambda} A^{(\lambda)}_{nn+j} a_{n+j} = \sum_{j=-L_\lambda}^{L_\lambda} t^{(\lambda)}_{n+j} a_{n+j} = 0 \ , \quad n > N_\lambda \tag{19a}$$

$$\sum_{j=-L_\nu}^{L_\nu} A^{(\nu)}_{-n'-(n'+j')} a_{-(n'+j')} = \sum_{j'=-L_\nu}^{L_\nu} t^{(\nu)}_{-(n'+j')} a_{-(n'+j')} = 0 \ , \quad n' > N_\nu \tag{19b}$$

where L_λ and L_ν are the number of nonzero off-diagonal terms in the lower and the upper part of $\mathbf{A}$, respectively. Since the elements of $\mathbf{A}^{(\alpha)}$, $\alpha = \lambda, \nu$, don't depend on n and since $\mathbf{A}$ is symmetric, Eqs. (19) become

$$t^{(\lambda)}_0 a_n + \sum_{j=1}^{L_\lambda} t^{(\lambda)}_j (a_{n-j} + a_{n+j}) = 0 \ , \quad n > N_\lambda \tag{20a}$$

$$t^{(\nu)}_0 a_{-n'} + \sum_{j'=1}^{L_\nu} t^{(\nu)}_{j'} (a_{-(n'-j')} + a_{-(n'+j')}) = 0 \ , \quad n' > N_\nu \ . \tag{20b}$$

From Eq. (19) it can be seen that $t^{(\lambda)}_j$ and $t^{(\nu)}_{j'}$ differ from each other only due to $E_{\rm tr}$, which may be different in the two asymptotic regions.

Each set in Eq. (20) stands for an independent system of homogeneous equations for the $(2L_\alpha + 1)$, $\alpha = \lambda, \nu$ unknowns $\mathbf{a}^{(n)}$ and $\mathbf{a}^{(n')}$ [here, $\mathbf{a}^{(n)}$ stands for $\mathbf{a}^{(n)} \equiv (a_{n-L}, \ldots, a_{n+L})$ and $\mathbf{a}^{(n')}$ for $\mathbf{a}^{(n')} \equiv (a_{n'-L}, \ldots, a_{n'+L})$]. Equation (20a) is formed at the grid point s_n and Eq. (20b) at grid point $s_{n'}$. Similar equations can be formed at grid points s_m and $s_{m'}$, respectively, for the similar unknowns $\mathbf{a}^{(m)}$ and $\mathbf{a}^{(m')}$. However, since the respective coefficients are identical, the equations at s_n and s_m (as well as those at $s_{n'}$ and $s_{m'}$) must have the same solutions (up to a constant), and, consequently, a sufficient and necessary condition to obtain a valid solution at all grid points is that

$$\frac{a_{n+j}}{a_n} = \beta^j_\lambda \ , \quad n > N_\lambda \tag{21a}$$

and

$$\frac{a_{-(n'+j')}}{a_{-n'}} = \beta^{j'}_\nu \ , \quad n' > N_\nu \ . \tag{21b}$$

where β_α and $\alpha = \lambda, \nu$ are constants to be determined. However, in order for the solution not to be increasing or decreasing in the two asymptotes, the absolute values of β_α, $\alpha = \lambda, \nu$, must be equal to 1. Thus,

$$|\beta_\lambda| = |\beta_\nu| = 1 \ , \tag{22}$$

which implies

$$\beta_\alpha = \exp(i\theta_\alpha) \ , \quad \alpha = \lambda, \nu \tag{23}$$

where θ_α, $\alpha = \lambda, \nu$, is real.

Substituting Eqs. (21a) and (21b) in Eqs. (20a) and (20b) yields the equations for β_α, $\alpha = \lambda, \nu$:

$$t^{(\alpha)}_0 + \sum_{j=1}^{L_\lambda} t^{(\alpha)}_j (\beta^{-j}_\alpha + \beta^j_\alpha) = 0 \ , \quad \alpha = \lambda, \nu \ . \tag{24}$$

Equations (24) stand for two polynomials, one for β_λ and the other for β_ν. In what follows they will be termed the Toeplitz polynomials (TP). Once the roots of the two polynomials in Eqs. (24) are obtained, the algebraic equations for the $(N_\lambda + N_\nu + 1)$ components of $\mathbf{a}^{(M)}$,

$$\mathbf{a}^{(M)} = (a_{-N_\nu}, \ldots, a_{-1}, a_0, a_1, \ldots, a_{N_\lambda}) \ , \tag{25}$$

are given in the form (see definition of $\mathbf{A}$ in Eq. (18):

$$\mathbf{A}^{(4)} \mathbf{a}^{(\nu)} + \mathbf{A}^{(M)} \mathbf{a}^{(M)} + \mathbf{A}^{(1)} \mathbf{a}^{(\lambda)} = \mathbf{Z} \ , \tag{26}$$

where

$$\mathbf{Z} = (z_{-N_\nu}, \ldots, z-1, z_0, z_1, \ldots, z_{N_\lambda}) \ , \tag{27}$$

$$\mathbf{a}^{(\nu)} = (a_{-(N_\nu + L_\nu)}, \ldots, a_{-(N_\nu + 1)}) \ , \tag{28a}$$

$$\mathbf{a}^{(\lambda)} = (a_{N_\lambda + 1}, \ldots, a_{N_\nu + L_\lambda}) \ . \tag{28b}$$

From Eqs. (21) we have

$$a_{-(N_\nu + j)} = \beta^j_\nu a_{-N_\nu} \tag{29a}$$

and

$$a_{N_\lambda + j} = \beta^j_\lambda a_{N_\lambda} \ . \tag{29b}$$

Substituting Eqs. (29) in Eq. (26) yields the following system of equations:

$$\sum_{m=-N_\nu}^{N_\lambda} \tilde{A}_{nm} a_m = Z_n \ , \quad n = -N_\nu, \ldots, N_\lambda \tag{30}$$

where

$$\tilde{A}_{nm} = \begin{cases} \sum_{j=1}^{L_\nu} A_{n-(N_\nu + j)} \beta^j_\nu, & -N_\nu \leq n \leq N_\lambda, \quad m = -N_\nu \\ A_{nm}, & N_\nu \leq n \leq N_\lambda, \quad -N_\nu < m < N_\lambda \\ \sum_{j=1}^{L_\lambda} A_{n-(N_\lambda + j)} \beta^j_\lambda, & -N_\nu \leq n \leq N_\lambda, \quad m = N_\lambda \ . \end{cases} \tag{31}$$

To complete the derivation, we still have to extract the relevant roots of the two TP's given in Eq. (24). This was

done in our previous publication [7(a)], namely,

$$\beta_\alpha = \exp i(k_\alpha \sigma) , \quad \alpha=\lambda,\nu \tag{32}$$

where

$$k_\alpha = (2\mu E_{\rm tr}^{(\alpha)})^{1/2} , \quad \alpha=\lambda,\nu . \tag{33}$$

Here, $E_{\rm tr}^{(\alpha)}$ is the translational energy in the α asymptotic region. In the Appendix we show that this behavior is also related to the expansion of $\exp(iks)$ in terms of localized Gaussians.

B. The NIP approach

Since this approach has been frequently discussed, we will just refer to it briefly.

To solve Eq. (12), a NIP of the following form is considered:

$$V_I(s) = \begin{cases} -iV_{0\lambda}\dfrac{s-s_\lambda}{\Delta s_\lambda} , & s_\lambda \le s \le (s_\lambda + \Delta s_\lambda) \\ iV_{0\nu}\dfrac{s+s_\nu}{\Delta s_\nu} , & -(s_\nu+\Delta s_\nu) \le s \le -s_\nu \\ 0 \quad \text{otherwise} . \end{cases} \tag{34}$$

The values of s_α, $\alpha=\lambda,\nu$, are determined in such a way that

$$V_\lambda(s)=0 \quad \text{for } s \ge s_\lambda \tag{35a}$$

and

$$V_\nu(s)=0 \quad \text{for } s \le -s_\nu , \tag{35b}$$

and the values of Δs_α and $V_{0\alpha}$, $\alpha=\lambda,\nu$, can be estimated from the two inequalities [10(a)]

$$\frac{E_{\rm tr}^{(\alpha)1/2}}{\Delta s_\alpha \sqrt{8\mu}} \le V_{0\alpha} \le E_{\rm tr}^{(\alpha)3/2} \Delta s_\alpha \sqrt{8\mu} . \tag{36}$$

Next, $V_I(s)$ is added to H to form H_I:

$$H_I = H + V_I(s) , \tag{37}$$

and, consequently, Eq. (12) is modified to become

$$\sum_n A_{mn}^{(I)} a_n = Z_m , \tag{12'}$$

where

$$A_{mn}^{(I)} = \langle |\xi_m (E - H_I)| \xi_n \rangle . \tag{13'}$$

The system of equations given in Eq. (12') is finite because the range for which $\chi_\lambda \neq 0$ is limited, i.e.,

$$\sim(s_\nu+\Delta s_\nu) \le s \le (s_\lambda + \Delta s_\lambda) .$$

III. THE NUMERICAL STUDY

The aim of the numerical study is not only to show that the application of the TA is capable of yielding formally accurate results but also to probe its efficiency as compared with the NIP approach. The main drawback in applying the NIP's is the need to assume a relatively wide range Δs (~ 1 Å) along which the NIP has to be defined so that it properly absorbs the encountered flux.

As mentioned earlier, the numerical study is carried out for an Eckart potential [9]:

$$U(s) = \frac{Ay}{1-y} - \frac{By}{(1-y)^2} , \tag{38}$$

where

$$y = \exp(2\pi s / l) . \tag{39}$$

The reactive (transmission) probability is given in the form [9]

$$P = 1 - \rho , \tag{40}$$

where

$$\rho = \frac{\cosh[2\pi(\alpha-\beta)] + \Gamma}{\cosh[2\pi(\alpha+\beta)] + \Gamma} . \tag{41}$$

Here,

$$\alpha = \frac{1}{2}\left|\frac{E}{C}\right|^{1/2} , \tag{42a}$$

$$\beta = \frac{1}{2}\left|\frac{E-A}{C}\right|^{1/2} , \tag{42b}$$

$$C = \frac{h^2}{8ml^2} , \tag{42c}$$

$$\Gamma = \cosh(2\pi\delta) \tag{42d}$$

where

$$\delta = \frac{1}{2}\left|\frac{B-C}{C}\right|^{1/2} . \tag{42e}$$

In the present application we assumed

$$A = 0 , \quad B = 1.5 \text{ eV} , \quad l = 1 \text{ Å} .$$

Reactive probabilities, calculated from Eqs. (40) and (41), as a function of energy are given in Table I (and Table II). In Table I we also present reactive probabilities employing the TM and the NIP approaches. These calculations are carried out for s_λ ($=-s_\nu$) $=3.0$ Å, for fixed values of σ ($=0.1$ Å) and α ($=1.2$) [in all calculations the number of Gaussians per angstrom was taken to be equal to 11 but for a varying number of Gaussians beyond s_λ and $(-s_\nu)$]. This number for the NIP case is proportional to Δs_α and the larger this number is, the larger the Δs_α's, $\alpha=\lambda,\nu$, are. In the case of the TA, the number of Gaussians is equal to L_λ (and L_ν) and therefore is a measure for the convergence of the series given in Eqs. (19)].

In Table I we present reactive probabilities as a function of energy calculated in three different ways: (a) Employing the NIP approach, (b) employing the TA approach, and (c) employing the analytical expression [Eqs. (40) and (41)]. The calculations for the NIP case were carried out twice: once for $V=0.5$ eV and once for

TABLE I. Reactive transition probabilities as calculated for Eckart potential. Analytic results and those obtained applying Toeplitz matrices and negative imaginary potentials are compared. The numerical calculations were done with 11 Gaussians per Å. Higher accuracies can be obtained by increasing the density of the Gaussians. All calculations were done for $s_\lambda=-s_\nu=3$ Å. The numbers in brackets denote multiplicative powers of ten.

Method	No. of additional Gaussians	E (eV) 0.30	0.32	0.34	0.36	0.37	0.38	0.39	0.40	0.41	0.42
NIP	6	0.194[−3]	0.232[−2]	0.0249	0.132	0.341	0.787	0.988	0.929	0.874	0.879
$V_{I0}=0.5$ eV	11	0.208[−3]	0.227[−2]	0.0229	0.157	0.367	0.687	0.889	0.942	0.947	0.950
	22	0.210[−3]	0.226[−2]	0.0224	0.165	0.375	0.664	0.863	0.939	0.961	0.971
NIP	6	0.182[−3]	0.235[−2]	0.0250	0.127	0.273	0.827	1.180	0.974	0.788	0.750
$V_{I0}=0.3$ eV	11	0.208[−3]	0.227[−2]	0.0227	0.160	0.375	0.685	0.864	0.922	0.952	0.980
	22	0.211[−3]	0.296[−2]	0.0226	0.168	0.378	0.656	0.853	0.938	0.967	0.979
Toeplitz	2	0.247[−3]	0.228[−2]	0.0298	0.0836	0.478	1.410	1.100	0.681	0.589	0.692
	4	0.209[−3]	0.224[−2]	0.0219	0.172	0.377	0.633	0.835	0.940	0.979	0.987
	7	0.209[−3]	0.224[−2]	0.0219	0.171	0.376	0.637	0.839	0.940	0.976	0.983
Analytic		0.212[−3]	0.226[−2]	0.0220	0.172	0.383	0.645	0.840	0.938	0.977	0.992

$V=0.3$ eV.

The analytic results are considered to be the accurate probabilities. From the Table it is easily seen that the NIP approach requires many more additional Gaussians to attain the same accuracy that is achieved by the TA approach. This seems to hint at the fact that in heavy close-coupling calculations the application of TM's could lead to a reduced numerical effort. Still, this outcome has to be carefully probed in relevant cases.

Another subject that was considered is the effect of varying s_λ and s_ν on the accuracy of the results. This study was carried out with respect to the TA only, but two aspects were checked, both of which are related to the expression of β_α given in Eq. (32). In Eq. (32), β_α is defined in terms of k_α which is assumed to be the asymptotic value (and therefore independent of s). Since our aim is to make s_α, $\alpha=\lambda,\nu$, as small as possible (and to do that without significantly affecting the final outcomes), both k_α and β_α may become s_α dependent, namely,

$$\beta_\alpha(s_\alpha)=\exp[i\sigma k(s_\alpha)] , \tag{32'}$$

where

$$k_\alpha(s_\alpha)=\sqrt{2\mu[E-U(s_\alpha)]} . \tag{33'}$$

Consequently, in forming the $(\beta_\alpha)^j$, $\alpha=\lambda,\nu$, required for constructing the **A** matrix [see Eq. (29)], we can use one of two possibilities:

(a) The ordinary choice, namely,

$$\beta_\alpha^j(s_\alpha)=\exp[(ij\sigma k(s_\alpha)] . \tag{32''}$$

(b) The other possibility, which is to replace $(\beta_\alpha)^j$ by $\beta_\alpha^{(j)}$, namely,

$$\beta_\alpha^{(j)}(s_\alpha)=\exp\left[i\sigma\sum_{l=0}^{j-1}k_l^{(\alpha)}\right] , \quad \alpha=\lambda,\nu \tag{43}$$

where

$$k_l^{(\alpha)}=k[\pm(|s_\alpha|+l\sigma)] , \quad \alpha=\lambda,\nu . \tag{44}$$

The plus and minus signs are for $\alpha=\lambda$ and $\alpha=\nu$, respectively. This choice leads, in fact, to the JWKB approximation [11], i.e.,

$$\beta_\alpha^{(j)}(s_\alpha)=\exp\left[i\int_{s_\alpha^{(0)}}^{s_\alpha^{(j)}}k(s)ds\right] . \tag{45}$$

Reactive probabilities employing the TA as a function of energy for various values of s_ν and s_λ are presented in Table II where they are compared, again, with exact re-

TABLE II. Reactive transition probabilities as calculated employing the Toeplitz approach. Analytic results and those obtained with fixed k_α values [Eq. (32'') and varying k_α values [Eqs. (43) and (44)] are compared.

Type of k_α	s_λ (Å)	s_ν (Å)	E (eV) 0.30	0.32	0.34	0.36	0.37	0.38	0.39	0.40	0.41	0.42
Fixed	+3.0	−2.0	0.194[−3]	0.220[−2]	0.0221	0.165	0.362	0.604	0.780	0.873	0.925	0.960
	+3.0	−1.0	0.248[−3]	0.222[−2]	0.0190	0.157	0.355	0.582	0.724	0.799	0.833	0.858
	+2.0	−1.0	0.258[−3]	0.243[−2]	0.0198	0.146	0.330	0.556	0.708	0.796	0.843	0.876
Varying	+3.0	−2.0	0.192[−3]	0.219[−2]	0.0221	0.169	0.363	0.593	0.766	0.864	0.921	0.961
	+3.0	−1.0	0.236[−3]	0.254[−2]	0.0234	0.163	0.340	0.555	0.701	0.766	0.779	0.788
	+2.0	−1.0	0.230[−3]	0.260[−2]	0.0243	0.166	0.341	0.550	0.698	0.776	0.801	0.812
Analytic			0.212[−3]	0.226[−2]	0.0220	0.172	0.383	0.645	0.840	0.938	0.977	0.992

sults due to Eqs. (40) and (41). Two types of results are shown, namely, those obtained with fixed values of k_α applying Eq. (32'') and those obtained with varying values of k_α employing Eqs. (43) and (44). It is seen, in general, that as the values of $|s_\alpha|$ decrease, the results become worse. The reason is related to the fact that as $|s_\alpha|$ decreases, the potential becomes less different from zero and, consequently, the matrices $\mathbf{A}^{(\alpha)}$, $\alpha=\lambda,\nu$, are no longer pure Toeplitz matrices. However, the two types of calculations, namely, those with fixed k_α values and those with varying ones, yield different types of results. It is easily seen that the fixed k_α probabilities are, in most cases, in better agreement with the analytic ones.

IV. CONCLUSIONS

In this work we compare the efficiencies of two approaches to yield quantum mechanical (reactive) transition probabilities for a single-coordinate reactive (Eckart-) type potential: one based on the application of TM's and the other based on the application of NIP's. It was found that, at least for this type of system, the TM approach is more efficient. This may hint at the possibility of replacing, in heavy multiarrangement-channel calculations, the NIP approach by the TM approach. However, the present indication is by far not enough. The main achievement in applying the NIP's was in creating the decoupling of a given arrangement channel from all the rest. Therefore, the crucial question is whether the TM's can create a similar decoupling. This subject is now being studied in our group and we hope to be able to report on our findings in the near future.

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APPENDIX

In this appendix we wish to show that the periodic behavior of the Gaussian coefficients in the asymptotic regime, namely, $a_n=C\exp(i\sigma kn)$, can be obtained from the free wave solution of the original Schrödinger equation, i.e., $\psi(r)=C\exp(ikr)$.

Consider an expansion of the free wave in terms of Gaussians:

$$\exp(ikr)=\sum_n a_n\xi_n \ , \tag{A1}$$

where ξ_n were defined in Eq. (15). Multiplying both sides by ξ_m and integrating over r yield the following set of equations:

$$\sum_n \exp\left[\frac{-\alpha^2(m-n)^2}{4}\right]a_n=B(k)\exp(ik\sigma m) \ , \tag{A2}$$

where $B(k)$ is given by

$$B(k)=\left[\frac{2\sigma\sqrt{\pi}}{\alpha}\right]^{1/2}\exp\left[-\frac{\sigma^2k^2}{2\alpha^2}\right] \ , \tag{A3}$$

and does not depend on either m or n. Multiplying both sides of Eq. (A2) by $\exp(ifm)$ and summing over m, one obtains

$$\begin{aligned}\mathcal{A}&\equiv\sum_{m,n}\exp\left[\frac{-\alpha^2(m-n)^2}{4}\right]\exp(ifm)a_n\\&=B(k)\sum_m\exp[i(k\sigma+f)m]\\&=2\pi B(k)\sum_m\delta(k\sigma+f-2\pi m) \ ,\end{aligned} \tag{A4}$$

where, so far, f is an undefined variable. Changing, on the left-hand summation, the summation indices to be n and $l=m-n$, we have

$$\mathcal{A}=\left\{\sum_l\exp\left[\frac{-\alpha^2l^2}{4}\right]e^{ifl}\right\}\sum_n e^{inf}a_n \ . \tag{A5}$$

The expression in the curly brackets (which is a function of f only) will be termed $A(f)$, while the sum is the Fourier representation of a function $\hat{a}(f)$. From Eqs. (A4) and (A5), one obtains that

$$\hat{a}(f)=2\pi A^{-1}(f)B(k)\sum_m\delta(k\sigma+f-2\pi m) \ , \tag{A6}$$

and, consequently, the coefficients a_n are given in the form

$$\begin{aligned}a_n&=\frac{1}{2\pi}\int_{-\pi}^{\pi}e^{-ifn}\hat{a}(f)df\\&=B(k)\sum_m\int_{-\pi}^{\pi}A^{-1}(f)\delta(k\sigma+f-2\pi m)e^{-ifn}df \ .\end{aligned} \tag{A7}$$

For each fixed m, the integral over the δ function vanishes unless

$$-\pi\le f_0=2\pi m-k\sigma<\pi \ ,$$

in which case it has the value $A^{-1}(f_0)e^{-if_0n}$. Since the difference between each f_0 to the following one (corresponding to higher m) is equal to the integration interval length, i.e., 2π, exactly one element of the sum over m does not vanish, namely, where $f_0=-k\sigma(\mathrm{mod}2\pi)$. However, since the exponent e^{-ifn} is periodic with 2π period and, according to the definition of $A(f)$ [see Eq. (A5)], so is $A^{-1}(f)$, it follows that

$$a_n=B(k)A^{-1}(-k\sigma)\exp(ik\sigma n)=C(k)\exp(ik\sigma n) \ . \tag{A8}$$

Thus, the Gaussian coefficients obtained from the exact expansion of the free wave coincide with those obtained from the Toeplitz method.

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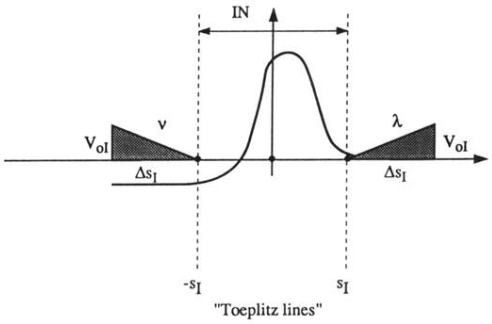

FIG. 1. The single-coordinate reaction system. The two "Toeplitz lines" are border lines for the reagents (λ) region, for the interaction (IN) region, and the products (ν) region. Also shown are the two NIP's: one in the λ region and the other in the ν region.