Infinite Order Discrete Variable Representation for Quantum Scattering

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Abstract

A new approach to multi-dimensional quantum scattering by the infinite order discrete variable representation is presented. Determining the expansion coefficients of the wave function at the asymptotic regions by the solution of the differential Schrödinger equation, we reduce an infinite set of linear equations to a finite one. Application to the benchmark collinear H + H\(_2\) → H\(_2\) + H reaction is shown to yield precise reaction probabilities.

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One of the most common approach to the solution of quantum scattering problem is the application of square-integrable \((L^2)\) basis functions \([1,2]\). Of the \(L^2\) basis methods the discrete variable representation(DVR) method \([3]\) is proven to be highly successful \([7,8]\). The DVR is a grid-point representation in which the potential energy is diagonal and the kinetic energy is a sum of one-dimensional matrices. Hence the Hamiltonian matrix is extremely sparse, which means that iterative linear algebra methods \([10]\) can deal efficiently with extremely large systems.

Recently, Eisenberg et al. \([11]\) has developed an infinite order DVR method for one-dimensional quantum reactive scattering problems. They expanded the wave function in terms of an infinite set of \(L^2\) basis functions satisfying the conditions of DVR \([3,8,12]\). The matrix related to the resulting set of algebraic equations, though infinite, has been shown to have the structure of a Toeplitz matrix \([13]\). Using the analytical properties of the Toeplitz matrix, they reduced the infinite set of algebraic equations to a finite one and obtained very accurate results for one-dimensional potential scattering. However, their method is not likely to be extended to multi-dimensional systems due to the failure of the Toeplitz properties.

In this Letter, we show that the infinite order DVR can be properly converted into a finite DVR even for multi-dimensional reactive systems. Instead of investigating the analytical properties of the Toeplitz matrix, we use the solutions of the differential Schrödinger equations at the asymptotic regions.

The full scattering wave function \(\Psi_n\) is decomposed of the incoming distorted wave \(\theta_n^-\) and the outgoing wave \(\chi_n^+\),

\[
\Psi_n = -\theta_n^- + \chi_n^+, \tag{1}
\]

where \(n\) is a channel index, i.e., a superindex over the arrangement and rovibrational indices. The distorted wave \(\theta_n^-\) is any regular scattering solution corresponding to a simple nonreactive (i.e., arrangement conserving) Hamiltonian, \(H_0n\), in the asymptotic region in the arrangement channel \(n\):

\[
(H_0n - E)\theta_n^- = 0, \tag{2}
\]

where \(E\) is the energy.
while $\Psi_n$ is the solution of

$$ (H - E)\Psi_n = 0, \quad (3) $$

where $H$ is the full Hamiltonian. For the sake of later convenience, we impose the "totally incoming" boundary condition on $\theta_n^-$ as

$$ \theta_n^-(r, R) \sim \frac{e^{-ik_n R}}{\sqrt{v_n}} u_n(r) \quad (4) $$

for large $R$. Here $r$ denotes all possible internal coordinates of the system, thus excluding the channel radius (relative translation) $R$; $\{u_n(r)\}$, the channel eigenfunctions; $v_n$ the relative velocity for channel $n$, and $k_n$ the corresponding wave vector. The equation for $\chi_n^+$ is then, from (1)-(3),

$$ (E - H)\chi_n^+ = (H - E)\theta_n^-. \quad (5) $$

$\chi_n^+$ must obey "totally outgoing" boundary condition, i.e., the only incoming wave part in the full wave function is due to $\theta_n^-$. 

Using the infinite order uniform DVR [3], (5) is transformed into an infinite set of coupled linear algebraic equations. To do this, we introduce the following convenient sets of DVR basis functions $Q, R_0, P_0, R$ and $P$ as shown in Fig. 1: $Q$ be the set of $N$ DVR basis functions represented by the $N$ grid points in the reactive (strong) interaction region correspond; $R_0 = \{R_0(1), \ldots, R_0(N_r)\}$, the set of $N_r$ DVR basis functions in the reactant asymptotic (relatively weak interaction) region nearest to the region of reactive interaction; $P_0 = \{P_0(1), \ldots, P_0(N_p)\}$, the set of $N_p$ DVR basis functions in the product asymptotic regions nearest to the region of reactive interaction; $R$, the infinite set of DVR basis functions in the reactant asymptotic region except the functions in $R_0$, and $P$ the infinite set of DVR basis functions in the product asymptotic regions except the functions in $P_0$. Here $N_r(N_p)$ is the number of open channels in the reactant (product) arrangement. Using these sets, we can rewrite (5) as a set of coupled algebraic equations,

$$ A_{R_0 R} \langle R|\chi_n^+ \rangle + A_{R_0 R_0} \langle R_0|\chi_n^+ \rangle + A_{R_0 Q} \langle Q|\chi_n^+ \rangle + A_{R_0 P_0} \langle P_0|\chi_n^+ \rangle + A_{R_0 P} \langle P|\chi_n^+ \rangle = \langle R_0|H - E|\theta_n^- \rangle. \quad (6) $$
\[ A_{QR}(\mathcal{R}|\chi^+_{n_r}) + A_{QR_0}(\mathcal{R}_0|\chi^+_{n_r}) + A_{Q\mathcal{Q}}(\mathcal{Q}|\chi^+_{n_r}) + A_{Q\mathcal{P}_0}(\mathcal{P}_0|\chi^+_{n_r}) + A_{Q\mathcal{P}}(\mathcal{P}|\chi^+_{n_r}) = \langle \mathcal{Q}|H - E|\theta^-_{n_r} \rangle, \tag{7} \]

\[ A_{P\mathcal{R}_0}(\mathcal{R}|\chi^+_{n_r}) + A_{P\mathcal{R}_0}(\mathcal{R}_0|\chi^+_{n_r}) + A_{P\mathcal{Q}}(\mathcal{Q}|\chi^+_{n_r}) + A_{P\mathcal{P}_0}(\mathcal{P}_0|\chi^+_{n_r}) + A_{P\mathcal{P}}(\mathcal{P}|\chi^+_{n_r}) = \langle \mathcal{P}_0|H - E|\theta^-_{n_r} \rangle, \tag{8} \]

where

\[ A_{ij} = (E - V_j)\delta_{ij} - T_{ij}, \tag{9} \]

\( T_{ij} \) is the kinetic energy matrix element [8], which is analytically obtained, connecting the DVR grid points \( i \in \mathcal{R}_0 + \mathcal{Q} + \mathcal{P}_0 \) and \( j \in \mathcal{R} + \mathcal{R}_0 + \mathcal{Q} + \mathcal{P}_0 + \mathcal{P} \), \( V_j \) is the potential energy at the DVR grid point \( j \), and we omit the summation over the index \( j \) such that, e.g., \( A_{R_0 R}\langle \mathcal{R}|\chi^+_{n_r} \rangle = \sum_{j \in \mathcal{R}_0 + \mathcal{Q} + \mathcal{P} + \mathcal{P}_0} A_{ij} \langle j|\chi^+_{n_r} \rangle \) for \( i \in \mathcal{R}_0 \).

In the above we did not write explicitly the similar equations corresponding to the \( \mathcal{R} \) and \( \mathcal{P} \) component since we do not use them in order to eliminate \( \langle \mathcal{R}|\chi^+_{n_r} \rangle \) and \( \langle \mathcal{P}|\chi^+_{n_r} \rangle \) by searching for an analytical property as in the case of Toeplitz. Instead, for the asymptotic regions, we introduce,

\[ \langle \mathcal{P}|\chi^+_{n_r} \rangle = - \sum_{n_p=1}^{N_p} \langle \mathcal{P}|\theta^+_{n_p} \rangle S_{n_p n_r}, \tag{10} \]

\[ \langle \mathcal{R}|\chi^+_{n_r} \rangle = - \sum_{n'_r=1}^{N_r} \langle \mathcal{R}|\theta^+_{n'_r} \rangle S_{n'_r n_r}, \tag{11} \]

where \( \theta^+_{n} \) is the regular "totally outgoing" wave which satisfies (2), i.e., \( \langle \mathcal{P}|\theta^+_{n} \rangle = \langle \mathcal{P}|\theta^-_{n} \rangle^* \), and \( S \) is the scattering matrix to be determined. (10) and (11) can be rewritten as

\[ \langle \mathcal{P}|\chi^+_{n_r} \rangle = \sum_{n_p=1}^{N_p} \sum_{i=1}^{N_R} \langle \mathcal{P}|\theta^+_{n_p} \rangle \left(T^\mathcal{P}\right)_{n_p i}^{-1} \langle \mathcal{P}_0(i)|\chi^+_{n_r} \rangle, \tag{12} \]

\[ \langle \mathcal{R}|\chi^+_{n_r} \rangle = \sum_{n'_r=1}^{N_r} \sum_{i=1}^{N_R} \langle \mathcal{R}|\theta^+_{n'_r} \rangle \left(T^\mathcal{R}\right)_{n'_r i}^{-1} \langle \mathcal{R}_0(i)|\chi^+_{n_r} \rangle, \tag{13} \]

where

\[ T^\mathcal{P}_{i n_p} \equiv \langle \mathcal{P}_0(i)|\theta^+_{n_p} \rangle, \tag{14} \]

and

\[ T^\mathcal{R}_{i n_r} \equiv \langle \mathcal{R}_0(i)|\theta^+_{n_r} \rangle. \tag{15} \]
The above equations (12)-(15) are the key in this Letter. Substituting \( \langle \mathcal{P}|\chi^+_n \rangle \) and \( \langle \mathcal{R}|\chi^+_n \rangle \) in (12) and (13) into (6) through (8), we obtain the following set of \( N + N_r + N_p \) linear equations:

\[
\begin{align*}
(\epsilon + A)_{\mathcal{R}_0\mathcal{R}_0} \langle \mathcal{R}_0|\chi^+_n \rangle + A_{\mathcal{R}_0\mathcal{Q}} \langle \mathcal{Q}|\chi^+_n \rangle + (\epsilon + A)_{\mathcal{R}_0\mathcal{P}_0} \langle \mathcal{P}_0|\chi^+_n \rangle &= \langle \mathcal{R}_0|H - E|\theta^{-}_n \rangle, \\
(\epsilon + A)_{\mathcal{Q}\mathcal{R}_0} \langle \mathcal{R}_0|\chi^+_n \rangle + A_{\mathcal{Q}\mathcal{Q}} \langle \mathcal{Q}|\chi^+_n \rangle + (\epsilon + A)_{\mathcal{Q}\mathcal{P}_0} \langle \mathcal{P}_0|\chi^+_n \rangle &= \langle \mathcal{Q}|H - E|\theta^{-}_n \rangle, \\
(\epsilon + A)_{\mathcal{P}_0\mathcal{R}_0} \langle \mathcal{R}_0|\chi^+_n \rangle + A_{\mathcal{P}_0\mathcal{Q}} \langle \mathcal{Q}|\chi^+_n \rangle + (\epsilon + A)_{\mathcal{P}_0\mathcal{P}_0} \langle \mathcal{P}_0|\chi^+_n \rangle &= \langle \mathcal{P}_0|H - E|\theta^{-}_n \rangle,
\end{align*}
\]

where \( \epsilon \) is the matrix of which the non-vanishing elements are

\[
\epsilon_{i\mathcal{R}_0} = \sum_{j \in \mathcal{R}} \sum_{n'_r} A_{ij} \langle j|\theta^+_{n'_r} \rangle \left( T^\mathcal{R} \right)^{-1}_{n'_r \mathcal{R}_0}
\]

and

\[
\epsilon_{i\mathcal{P}_0} = \sum_{j \in \mathcal{P}} \sum_{n_p} A_{ij} \langle j|\theta^+_{n_p} \rangle \left( T^\mathcal{P} \right)^{-1}_{n_p \mathcal{P}_0},
\]

where \( i \) is a DVR grid point in the sets \( \mathcal{R}_0, \mathcal{Q}, \) and \( \mathcal{P}_0 \). Note that \( \epsilon_{ij} \) is nonvanishing only for \( j \) in the sets \( \mathcal{R}_0 \) and \( \mathcal{P}_0 \). Applying the complex conjugate of (12)-(15), (19) and (20), the right hand sides of expressions (16) through (18) can be expressed as

\[
\langle i|H - E|\theta^-_n \rangle = -(A + \epsilon^*)_{i\mathcal{R}_0} \langle \mathcal{R}_0|\theta^-_n \rangle.
\]

Hence, (16)-(18) can be expressed in the form of an \( (N + N_r + N_p) \times (N + N_r + N_p) \) matrix equation

\[
\tilde{A} \cdot \chi^+_n = -\tilde{A}^* \cdot \theta^-_n
\]

where \( \tilde{A} = A + \epsilon \). Let \( G^+ \) be the left-inverse of \( \tilde{A} \), i.e., \( G^+ \cdot \tilde{A} = 1 \). Then it can be shown that

\[
\chi^+_n = -\theta^-_n + G^+ \cdot (\epsilon - \epsilon^*) \cdot \theta^-_n.
\]

Finally we obtain the full scattering wave function and the scattering matrix,

\[
\Psi_n = G^+ \cdot (\epsilon - \epsilon^*) \cdot \theta^-_n.
\]
and

\[ S_{np} = \sum_{i \in P, j \in R_0} \left( T^T \right)^{-1}_{np} \left[ G^* \cdot (\epsilon^* - \epsilon) \right]_{ij} \left( \theta^*_{nr} \right)_j. \]  

(25)

For the calculation of \( \epsilon \), we need the overlaps \( \langle R|\theta^+_{nr'} \rangle \), \( \langle R_0|\theta^+_{nr'} \rangle \), \( \langle P|\theta^+_{np} \rangle \), and \( \langle P_0|\theta^+_{np} \rangle \). Using the property of the DVR basis functions,

\[ \langle i|\theta^+_{n} \rangle = \theta^+_{n} (r_i, R_i) \sqrt{w}, \]  

(26)

where \( r_i \) and \( R_i \) are respectively the values of \( r \) and \( R \) at the DVR grid point \( i \), and \( w \) is the quadrature weight [6–8,12], the above overlaps can be easily obtained by numerical integration of the differential Schrödinger equation (2) corresponding to the nonreactive scattering region discussed earlier.

Thus far we have shown that the derived scattering matrix (25) is completely general enough to deal with the fully three dimensional scattering processes. For the sake of comparison with other accurate calculations, we apply the method to the collinear \( \text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H} \) reaction in the energy range of 0.4–1.0 eV. The coordinate axes for the DVR are chosen to be the normal ones of the transition state [16] as shown in Fig. 1. We use the LSTH potential energy surface [14]. The distorted wave functions, \( \theta^+_{nr} \), are calculated by integrating the coupled differential equations (2) inward from \( R_{\text{asym}} (\geq 20.0 \text{ a.u.}) \) to \( R_{\text{max}} (\geq 6.0 \text{ a.u.}) \) for each arrangement, and then are interpolated at the DVR grid points in the asymptotic regions to obtain the overlaps \( \langle R|\theta^+_{nr'} \rangle \), \( \langle R_0|\theta^+_{nr'} \rangle \), etc. \( E_1=0.78629 \text{ eV} \) is the threshold of the vibrational quantum states with \( n = 1 \). Hence there are two linearly independent distorted wave functions \( \theta^+_{0} \) and \( \theta^+_{1} \) at the energies above \( E_1 \).

Fig. 2 illustrates the convergence of \( P_0(E) \) and \( P_1(E) \) at \( E = 0.9678 \text{ eV} \), where \( P_{nr}(E) \) is the total reaction probability from a given reactant molecular state \( n_r \) to any product molecular states at energy \( E \), i.e.,

\[ P_{nr}(E) = \sum_{n_p=1}^{N_p} |S_{np}^2|, \]  

(27)

as the size of the region of reactive interaction, \( R_{\text{max}} \), is increased, for different values of the grid constant \( n_B \) [8][16]. The percent error is calculated by comparison to the results of
Colbert and Miller [8]. The convergence for $E = 0.9678$ with respect to $n_B$ for $R_{\text{max}} = 8.0$ is also shown in Fig. 3. The total reaction probabilities, with $R_{\text{max}} = 8.0$ and $n_B = 3.4$, are converged to within 0.05% at this energy. Fig. 4 shows excellent agreement of the converged results for $P_0(E)$ and $P_1(E)$ with the exact results of Bondi and Connor [15] over a range of total energies including the resonance energy near 0.9 eV.

In summary, the infinite order DVR theory for multi-dimensional reactive scattering has been presented. By applying it to the collinear $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction, we obtained precise reaction probabilities comparable with the other results obtained from the direct integration of the differential Schrödinger equation (3) [15]. The advantages of the present theory are as follows: 1. iterative linear algebra methods are readily applicable, 2. no numerical integrals are needed for calculating the matrix elements, 3. as can be seen from (19),(20),(24) and (25), no regularization techniques [3,5] for the distorted wave functions are necessary since no informations on those functions in the reactive (strong) interaction region are required although they are set to be regular at $R = 0$ in the beginning (1), 4. the effective Green’s operator $\mathbf{G}^+$ in the reactive interaction region is obtained as a by-product, 5. the formalism is completely general and can be applied to any non-collinear scattering problems including collinear systems.

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FIGURES

FIG. 1. Schematic diagram showing the sets $R$ (plus), $R_0$ (diamond), $Q$ (dot), $P_0$ (square), and $P$ (cross) of the DVR basis functions, which are represented by the DVR grid points, for the collinear $H + H_2 \rightarrow H_2 + H$ reactive scattering problem. Three straight lines are drawn to divide the sets $R$, $Q$, and $P$ from each others. The potential energy contours and the $(x, y)$–coordinate system for the DVR are also depicted.

FIG. 2. Relative percent error of the total reaction probabilities $P_0(E)$ (solid lines) and $P_1(E)$ (dashed lines) at $E = 0.9678$ eV as a function of $R_{max}$ for different values of $n_B$; $n_B = 3.4$ (thick lines); and $n_B = 1.7$ (thin lines).

FIG. 3. Relative percent error of the total reaction probabilities $P_0(E)$ (solid lines) and $P_1(E)$ (dashed lines) at $E = 0.9678$ eV as a function of $n_B$ for $R_{max} = 8.0$.

FIG. 4. Total reaction probabilities (a) $P_0(E)$ and (b) $P_1(E)$ as a function of energy computed using $R_{max} = 8.0$ a.u. and $n_B = 3.4$ (circle) compared to the results of Bondi and Connor (solid line) (ref. [15]) and Thompson and Miller (triangle) (ref. [16]).
Fig. 1(b)