DISCRETE VARIABLE REPRESENTATIONS AND SUDDEN MODELS
IN QUANTUM SCATTERING THEORY *

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An exact formalism in which the scattering problem may be described by sets of coupled equations labeled either by basis functions or quadrature points is presented. Use of each frame and the simply evaluated unitary transformation which connects them results in an efficient procedure for performing quantum scattering calculations. Two approximations are compared with the IOS.

1. Introduction

Quantum-mechanical scattering calculations are most often performed in the close-coupled representation (CCR) in which the internal degrees of freedom are expanded in an appropriate set of basis functions resulting in a set of coupled differential equations in the scattering distance $R$ [1,2]. The method is exact to within a truncation error and convergence is obtained by increasing the size of the basis and hence the number of coupled equations ($N$). While considerable progress has been made in the development of efficient algorithms for the solution of these equations [3-7], as the number of equations is increased the computation time becomes proportional to $N^3$ due to the matrix work involved [8]. The primary cause of this increase is the proliferation of rotational states which become available at typical scattering energies.

In recent years a number of decoupled models for the quantum scattering problem have been proposed [9-13] (for a review, see ref. [14]). The centrifugal sudden (CS), energy sudden (ES), and infinite order sudden (IOS) models achieve their decoupling by replacement of orbital, rotational, or both orbital and rotational kinetic energy operators with constant “eigenvalue-like” expressions, respectively. In each case the potential is represented by the potential function itself evaluated at a set of points.

While these models have been shown to be effective in many problems, there are numerous ambiguities in their application, especially with regard to the choice of constants. Further, some models possess formal difficulties such as loss of time reversal symmetry, non-physical coupling, and non-conservation of energy and momentum [15-19]. In fact, it has never been demonstrated that sudden models fit into any exact framework for solution of the scattering problem.

This latter point is the reason for the use of the term “model” rather than “approximation” in the present work. The purpose of this paper is to introduce a new exact scattering formalism which includes sudden-type equations in a well-defined mathematical framework. In the following section the discrete variable and finite basis representations (DVR and FBR) are developed for a simple two-dimensional problem. The former variable-labeled representation is shown to be appropriate for small scattering distances while the latter function-labeled frame best describes the system at large scattering distances. Next the theory is applied to a standard rigid rotor problem. Finally a brief discussion will be given.
2. DVR and FBR

In order to introduce the DVR and FBR consider the simple two-dimensional scattering problem \( H(R,x) \times \psi^T(R,x) = E\psi^T(R,x) \) where the Hamiltonian is:

\[
H(R,x) = -\frac{d^2}{dR^2} + h(x) + V(R,x)
\] (1a)

and

\[
\lim_{R \to \infty} \psi(R,x) = 0.
\] (1b)

Here \( R \) is the scattering coordinate and \( x \) is the single internal variable. The internal Hamiltonian \( h(x) \) possesses a complete set of orthonormal eigenfunctions:

\[
h(x) \varphi_j(x) = \epsilon_j \varphi_j(x)
\] (2)

with orthonormality and completeness relations:

\[
\int dx \varphi_j(x) \varphi_k(x) = \delta_{jk}.
\] (3a)

\[
\sum_{k=1}^{\infty} \varphi_k(x) \varphi_k(x') = \delta(x-x').
\] (3b)

Here \( \delta_{jk} \) is the Kronecker delta and \( \delta(x-x') \) is the Dirac delta function, the range of \( x \) need not be specified.

Expansion of the wavefunction \( \psi(R,x) \) in the internal basis \( \{ \varphi_j(x) \} \):

\[
[\psi(R,x)] = \sum_{k=1}^{N} \{ f(R) \} \varphi_k(x).
\] (4)

where "\( n \)" indexes the "initial" quantum state, results in the truncated (\( N \)-dimensional) CCR equations:

\[
[d^2/dR^2 + L - \epsilon] f(R) = V(R) f(R),
\] (5a)

where:

\[
[\epsilon] = \delta \epsilon,
\] (5b)

and

\[
[V(R)]_{ij} = \int dx \varphi_i(x) V(R,x) \varphi_j(x).
\] (5c)

The DVR and FBR equations may now be developed in analogy to the partial differential and CCR equations by supposing there exists an \( N \)-point gaussian quadrature such that the first \( N \) orthogonality relations (3a) are reproduced exactly. Letting \( \{ x_\alpha \} \) and \( \{ \omega_\alpha \} \) denote the quadrature points and weights, respectively, the orthogonality and completeness relations [(3a) and (3b)] become:

\[
\sum_{\alpha=1}^{N} \varphi_\alpha(x_\alpha) \omega_\alpha \varphi_\alpha(x_\alpha) = \delta_\alpha^\prime,
\] (6a)

\[
\sum_{\alpha=1}^{N} \varphi_\alpha^T(x_\alpha) \omega_\alpha^T \varphi_\alpha^T(x_\alpha) = \delta_\alpha^T.
\] (6b)

In the language of numerical analysis the internal degree of freedom is now described by a discrete (as opposed to a continuous) orthogonal system [20].

The points and weights so described are unique, not only providing the discrete orthogonality condition (6a), but also minimizing the discrete rms error when quadrature approximations to the integrals (5c) are performed [21]. Such relations hold for any set of orthogonal polynomials.

Eq. (6b) is really just the Christoffel–Darboux identity in disguise (see eq. 8.4.18 in ref. [21]). It is clear that eqs. (6a) and (6b) define an orthogonal transformation:

\[
[T]_{\alpha}^T \equiv \varphi_\alpha(x_\alpha) \omega_\alpha^{1/2}.
\] (7a)

\[
T^T T = 1 = T T^T.
\] (7b)

This fact has been noted in an independent (and quite different) derivation [22] concerned with the efficient computation of matrix elements of unusual potential functions [23].

What is believed to be completely novel in the present approach is the use of the transformation (7a) to connect dual representations of the scattering problem. To this end it is convenient to define the \( N \)-dimensional diagonal matrix of the potential evaluated at the quadrature points:

\[
[U(R)]_{\alpha}^\beta = \delta_\alpha^\beta V(R,x_\alpha).
\] (8)

Now in analogy with the partial differential equation the DVR equations may be written as:

\[
[d^2/dR^2 + L - T T^T] f_{DVR}(R) = U(R) f_{DVR}(R)
\] (9a)

and in analogy with the CCR equations, the FBR equations may be written as:

\[
[d^2/dR^2 + L_1 - T T^T] f_{FBR}(R) = U(R) f_{FBR}(R)
\] (9b)
\[
\left[ \frac{d^2}{dR^2} + \mathcal{E} - \varepsilon \right] f_{\text{FBR}}(R) = \mathbf{T}^\dagger \mathbf{U}(R) \mathbf{T} f_{\text{FBR}}(R)
\]

(9b)

Note in particular that
\[
\varepsilon_i' = \int \varphi_i(x) h(x) \varphi_i(x) \, dx = \int \varphi_i(x) \varphi_i(x) \, dx = \delta_i^j \varepsilon_j,
\]

so the internal Hamiltonian is the same in the CCR and FBR. Further note that
\[
\left[ \mathbf{T} \mathbf{U}(R) \right] = \sum_{\alpha=1}^{N} \varphi_i(x_\alpha) \omega_{\alpha} \varphi_i(x_\alpha) = \delta_i^j \varepsilon_j,
\]
is just the usual potential matrix element except that now the inner product is the Gaussian quadrature instead of the integration as in (5c). Obviously as the number of quadrature points and basis functions go to infinity, the DVR and FBR results converge (in the mean) to the exact solution.

Since the dimensionality of the problem is unchanged the advantages of the DVR-FBR analysis are not immediately obvious. First note that the DVR provides an exact numerical method in which the potential matrix elements are merely given by the potential itself evaluated at the set of quadrature points. Since the internal Hamiltonian \( \mathbf{T} \mathbf{A} \mathbf{T}^\dagger \) is independent of \( R \) (this follows from the separation of variables in the original partial differential equation) it need only be calculated once. Thus there is much less work done in constructing the interaction in the DVR and this frame should always be preferable in exact calculations. In a quasi-adiabatic approach the eigenvalues obtained by diagonalization of the DVR and FBR interactions are exactly equivalent since they differ by only a unitary transformation; the eigenvalues so obtained approach those of the CCR in the limit of infinite dimensionality. Further, it may be shown that under a broad set of circumstances, the errors in the eigenvalues due to the replacement of the integration by the quadrature are of the same order as those introduced by truncation of the basis.

Secondly — and more importantly — the DVR-FBR analysis is an exact method which contains sudden-type equations and provides an approach to corrections to them. The diagonal portion of the DVR equations is in fact just a particular set of IOS equations with a particular set of “constants” dictated by the transformation of the internal Hamiltonian. Taking these equations as defining a zero-order problem, one may perform a series of calculations of varying degrees of accuracy by including the off-diagonal terms by various perturbation schemes.

Similarly the diagonal portion of the FBR equations defines the so-called distorted wave solution. This may similarly be improved through the use of perturbation theory. The DVR and FBR solutions may then be connected exactly at some value of the scattering coordinate \( R_s \) by the discrete variable transformation (7a).

The optimal choice of \( R_s \) involves determining which frame is more diagonally dominant. At small scattering distances where the potential dominates the collision the DVR is more diagonally dominant, at larger scattering distances where centrifugal effects dominate, the FBR is more diagonally dominant. A convenient measure of this dominance is the magnitude of the difference between the largest and smallest diagonal matrix elements. The frame with the larger splitting is more diagonally dominant since the largest and smallest diagonal elements are closer to the corresponding eigenvalues.

Finally the exact scattering boundary conditions may be applied in the FBR exactly as in the CCR:

\[
lm_{R \to \infty} f_{\text{FBR}}(R) = \lim_{R \to \infty} \left[ I(R) - O(R) S \right],
\]

where \( I(R) \) and \( O(R) \) are the appropriate incoming and outgoing waves, and \( S \) is the scattering matrix.

3. Example

As an example a 16-channel rigid rotor problem calculated by Tsien and Pack [24] was chosen. This is a relatively high energy system for which the “matrix diagonalization” sudden model of Tsien and Pack [9] is known to be quite accurate.

The DVR for this problem is defined in the body-fixed (helicity) frame of Pack [25]; the states for a total angular momentum \( J \) and space-fixed projection \( M \) are labeled by the body-fixed projection \( K \) and the
Table 1
Points and weights for the DVR–DVR transformation
\[ \cos \chi_\alpha \]
is the cosine of the atom–diatom angle

<table>
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<th>( k )</th>
<th>( \cos \chi_\alpha )</th>
<th>( \omega_\alpha )</th>
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<td>-0.9602899</td>
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Gauss–associated Legendre points as shown in table 1. Because the diatom is symmetric and the potential contains only \( P_0 \) and \( P_2 \) terms, the “trick” of using only negative points make all implied quadratures of basis functions over the potential equivalent to the corresponding integration. The DVR and FBR are thus each equivalent to the CCR for this type of problem.

Selected results of several calculations performed with the VISV integrator are presented in table 2. The first transition probability quoted is the exact result obtained by integration of either the CCR, FBR, or DVR equations. Differences between the results obtained in the various frames are due purely to numerical roundoff on the computer and do not appear in the numbers quoted. The second set of transition probabilities are obtained using the IOS model of Tsien and Pack with \( \eta = 0 \). These are slightly more accurate than the results with \( \eta = 0 \) and \( \eta = 6 \) quoted by those authors. The third set of transition probabilities are obtained by integration of the diagonal portions of the DVR and FBR equations and matching at \( R = 8.76 \) bohr with the discrete variable transformation

\[ [T]_\alpha^l = (1 - \cos^2 \chi_\alpha)^{-1} K^{1/2} \rho^K (\cos \chi_\alpha) \omega^{1/2} \].

Here \( (1 - \cos^2 \chi_\alpha) K^{1/2} \rho^K (\cos \chi_\alpha) \) is the polynomial part of the normalized associated Legendre function, and \( \cos \chi_\alpha \) and \( \omega_\alpha \) are the points and weights of table 1. In this diagonal calculation the coupling results from the phase built up in the DVR region and the discrete variable transformation itself.

Finally the fourth set of transition probabilities listed are obtained by inclusion of the off-diagonal coupling in the DVR and FBR regions to first order in perturbation theory and again matching at \( R = 8.76 \) bohr with the discrete variable transformation (11). In the language of the variable interval–variable step integrator, this is a two-interval calculation (one DVR and one FBR interval) with many steps in each interval. In more conventional language, the IOS-like equations are corrected to first order in the DVR internal and the distorted wave equations are corrected to first order in the FBR interval. The discrete variable transformation, being a transformation between Hilbert spaces, is independent of the accuracy of the solutions obtained in either region.

To avoid exponential growth in the closed channels, only the diagonal portion of the DVR equations were integrated in the non-classical region; one step per interval was taken up to the point where all channels were open to stabilize the solutions.

Root-mean-square (rms) errors are listed in table 3. Finally the variation in rms error of the perturbed cal-

Table 2
Selected transition probabilities. Here DDVR–DFBR and PDVR–PBR refer to the diagonal and perturbed DVR–FBR calculations, respectively. The numbers in parentheses are the powers of ten by which the value listed should be multiplied. All results have been rounded to the nearest \( 1 \times 10^{-3} \)

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486
Table 2 (continued)

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<td>2(-4)</td>
<td>2(-4)</td>
</tr>
<tr>
<td>PDVR-PTBR</td>
<td>8(-4)</td>
<td>3(-0)</td>
<td>1(-4)</td>
<td>0(-4)</td>
<td>1(-4)</td>
<td>0(-4)</td>
<td>0(-4)</td>
<td>0(-4)</td>
</tr>
</tbody>
</table>
4. Discussion

The values of $K$ and $\cos \chi_{\omega}$ in Table 1 label the DVR; in solving the DVR equations one is in effect working in a mixed partial-coupled ordinary frame, with the appropriate discretization given by the quadrature. Solution of the equations in the DVR would appear preferable for $R < 8.76$ bohr as is indicated in Table 4, past this point the FBR is more diagonally dominant. Table 4 also indicates only slight differences in the perturbed DVR--FBR results for reasonable choices of $R_S$.

Table 3 clearly indicates the superiority of the perturbed DVR--FBR results. The diagonal DVR--FBR results are very poor and consideration of Table 2 reveals the diagonal DVR--FBR transition probabilities to be much too elastic. Simply a change of frame is not enough to provide the coupling required by this problem.

Why then is the (uncoupled) IOS solution more accurate than the diagonal DVR--FBR? The essential difference between the IOS and DVR--FBR equations is in the asymptotic boundary conditions. In the IOS model “scattering-type” boundary conditions are applied in the variable-labeled frame and these boundary conditions are not equivalent to the exact scattering boundary conditions employed in the DVR--FBR analysis. It should be added that the non-physical boundary conditions of the IOS model are required to make the mathematical problem well posed; if the IOS boundary conditions were not dictated by the choice of “eigenvalue-like” constants the transition probabilities would keep changing with the endpoint of integration as $R \rightarrow \infty$. However this means that the sudden model is, strictly speaking, a scattering problem which is mathematically distinct from the exact problem. And there is no guarantee that performing an approximate calculation of the exact problem (as in the DVR--FBR calculation) will yield better results than an exact calculation of some model problem — such as the IOS model — for some specific problem.

The great benefit of using the DVR--FBR formalism is that one is guaranteed of converging to the exact result. This could be done with the diabatic VIVS integrator by simply taking more intervals in the DVR and FBR regions.

Finally it is interesting to note one final connection between IOS models and the DVR--FBR theory. The “matrix diagonalization” sudden used here uses a transformation which diagonalizes the potential matrix for all $R$. This transformation is in fact equivalent to the discrete variable transformation (11). In homonuclear diatomic scattering when there are potential terms higher than $P_1$, or in heteronuclear diatomic scattering when there are potential terms greater than $P_1$, no such diagonalizing transformation exists. However Secrest [11] has shown that in the limit of an infinite basis one can diagonalize the interaction matrix by transforming the CCR equations back to partial differential form. Similarly the discrete variable transformation (11) will diagonalize the FBR interaction matrix for all $R$ as the dimensions go to infinity. The DVR--FBR analysis is thus a synthesis of the matrix diagonalization and transformational approaches to the IOS equations included in an exact mathematical framework. It provides a unique representation in which the potential matrix is just a diagonal matrix of the potential itself evaluated at a specific set of points.
References