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Application of Toeplitz matrices to scattering processes. A NIP-Toeplitz approach to treating chemical reactions ☆

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Abstract

In this work a new approach to treating reactive (exchange) processes is presented. It is based on the ability of negative imaginary potentials (NIP) to decouple products arrangements without causing reflection and on the asymptotic behavior of the Hamiltonian which turns into a Toeplitz operator. The theory is developed within the discrete variable representation (DVR). This mixed approach is tested for the collinear $H + H_2$ reactive system for which accurate results were obtained.

1. Introduction

The formally accurate treatment of reactive (exchange) scattering problems had changed its course significantly since the late eighties – a trend that has been enhanced during the nineties. Instead of developing methods that take into account all available (i.e. the reagents and the products) arrangement channels (AC) [1–7], as for instance the one based on the hyperspherical coordinates [5–7], the trend now is to develop methods that avoid all products ACs without affecting the calculated (initial state-selected) reactive probabilities [8–20]. This has become possible following the application of negative imaginary (absorbing) potentials (NIP) which, under certain conditions, absorb quantum fluxes causing only negligible reflection. An important feature of a given NIP is its ability to absorb efficiently the quantum fluxes for a large range of kinetic energies (a crucial requirement for molecular dynamics). However, it turns out that in order to fulfil this requirement the NIP has to extend to a relatively large interval (of the order of 1 Å) which may sometimes double the range of the interaction to be considered.

We recently developed a method similar to the one employing NIPs but for which the above-mentioned difficulty is avoided. It is based on the asymptotic representation of the Hamiltonian, which assumes what is known in mathematics as a Toeplitz behavior [21–25]. So far we showed by considering single-coordinate models (two kinds, elastic [23] and 'reactive' [24,25]), that a method that takes advantage of this behavior can efficiently replace the NIP. In the present work we extend these ideas and apply them to a two-mathematical-coordinate reactive system, namely, the collinear configuration.

The previous method, based on the NIPs, and the present method, based on the Toeplitz feature, belong to the L^2 methods which were introduced in the

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late sixties and early seventies [26–29]. In our early version we employed Gaussians to present the (translational) wavefunction [23,24]. More recently [25] we based our treatment on the discrete variable representation (DVR) [30–32], which is used in the present study.

2. Theory

The theoretical derivation is based on the perturbative form of the Schrödinger equation (SE) [9], i.e.

$$(E-H)\chi_{n_0} = V\psi_{n_0}, \tag{1}$$

where E is the total energy, H is the Hamiltonian, n_0 is a given initial state, ψ_{n_0} is the unperturbed part of the wave function and is a solution of the SE defined in terms of the unperturbed Hamiltonian H_0,

$$(E-H_0)\psi_{n_0} = 0, \tag{2}$$

V is the perturbed potential defined as $(H-H_0)$ and χ_{n_0} is the perturbed part of the total wave function Ψ_{n_0}. Thus

$$\Psi_{n_0} = \psi_{n_0} + \chi_{n_0}. \tag{3}$$

In what follows we consider the collinear system expressed in terms of the reagents Jacobi coordinates and consequently the kinetic energy operator takes the form [33]

$$T = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}. \tag{4}$$

Here μ and m are the reduced masses of the atom–diatom system and the diatom system, respectively, and R and r are the corresponding translational and vibrational coordinates. Our approach, to be presented next, is based on two features which were already used in previous scattering studies:

(a) Along a certain range of the vibrational coordinate $[r_I, r_I + \Delta r_I]$ is defined a NIP [34]. This NIP is expected to absorb the (reactive) flux when $r > r_I$.

(b) Along the translational coordinate we make use of the fact that as R becomes larger than a given (asymptotic) value R_{as} the Hamiltonian H becomes a Toeplitz operator (to be shown later) and consequently the translational component of the wave function can be expanded in terms of L^2 basis sets [26–29].

To continue we employ the DVR within which the derivatives are expressed in terms of finite differences in the form [32]

$$f''(x_i) = \sum_{j=-\infty}^{\infty} t_{j-i} f(x_j), \tag{5}$$

where

$$t_k = \frac{-\pi^2}{3\sigma^2}, \quad k=0,$$

$$t_k = \frac{-2(-1)^k}{k^2\sigma^2}, \quad k \neq 0. \tag{6}$$

Here σ is the grid size and Eq. (5) is an 'infinite-point' formula to evaluate the second-order derivative. It may be important to mention that Eqs. (5) and (6) are for a fully infinite (rather than semi-infinite) interval with respect to R and r. Employing Eq. (5) one may convert Eq. (1) into a set of algebraic equations where the values of χ at the grid points $(R_p, r_q) = (p\sigma, q\sigma)$ are the unknown variables to be derived. Thus

$$\sum_{q'=0}^{\infty}\sum_{p'=0}^{\infty} A_{qpq'p'}\chi_{n_0q'p'} = Z_{n_0qp}, \tag{7}$$

where

$$A_{qpq'p'} = \left[E - U(R_p, r_q)\right]\delta_{qq'}\delta_{pp'} + \frac{\hbar^2}{2\mu}t_{p'-p}\delta_{qq'} + \frac{\hbar^2}{2m}t_{q'-q}\delta_{pp'} \tag{8}$$

and

$$Z_{n_0qp} = V(R_p, r_q)\psi_{n_0}(R_p, r_q). \tag{9}$$

Here $U(R, r)$ is the full potential. In the asymptotic region $U(R, r)$ becomes dependent on r only, namely

$$\lim_{R\to\infty} U(R, r) = v(r), \tag{10}$$

where $v(r)$ is the vibrational potential of the diatom. To make the calculation relevant for a reactive process a NIP, $v_I(r)$, is added to $U(R, r)$ in an ad-hoc way, thus forming $U_I(R, r)$. The potential $U_I(R, r)$ replaces $U(R, r)$ in Eq. (8) which causes the Hamiltonian to become complex. We now return to treat Eq. (7). Due to the above-mentioned asymptotic behavior we get for Eq. (7), once p becomes large

enough (larger than p_0), that (a) the matrix elements $A_{qpq'p'}$ become independent of p (or, in other words, the infinite part of **A** is independent of p) and (b) the perturbation potential $V(R_p, r)$ becomes zero. The above-mentioned feature of **A**, in addition to its other features as shown in Eq. (8), implies that this part of **A** has a Toeplitz structure [25], namely, for $p > p_0$ the matrix elements along the various diagonals become constants (not dependent on p). This and the fact that the inhomogeneity, for large values of p, becomes zero enable us to treat the infinite part of the system of equations given in Eq. (7) analytically. Such treatments were done in some of our previous publications [23–25] and we will refer to that here only briefly (in what follows the index n_0 will be omitted unless it is explicitly introduced again). For the asymptotic region we assume the solution χ_{qp} $(= \chi(R_p, r_q))$ to be of the form

$$\chi_{qp} = \exp(\mathrm{i}\theta p)\,\phi_q, \quad \text{for } p \geqslant p_0, \tag{11}$$

where θ and ϕ_q, $q = 0, 1\ldots$, are constants to be determined. Substituting Eq. (11) and Eq. (8) in Eq. (7), multiplying the resultant expression by $\exp(-\mathrm{i}\theta p)$ and changing the index of summation from p' to $j\ (= p' - p)$ yields for $p > p_0$

$$\sum_{j,q'}\left((E - v_{q'})\delta_{j0}\delta_{qq'} + \frac{\hbar^2}{2\mu}t_j\delta_{qq'} + \frac{\hbar^2}{2m}t_{q'-q}\delta_{j0}\right) \times \exp(\mathrm{i}\theta j)\,\phi_{q'} = 0, \tag{12}$$

or

$$\phi_q\left[\sum_j\left((E - v_q)\delta_{j0} + \frac{\hbar^2}{2\mu}t_j\right)\exp(\mathrm{i}\theta j)\right] + \frac{\hbar^2}{2m}\sum_{q'}t_{q'-q}\phi_{q'} = 0. \tag{13}$$

The summation over j can be done analytically (see Ref. [23]) and consequently Eq. (13) becomes

$$\frac{\hbar^2}{2m}\sum_{q'}t_{q'-q}\phi_{q'} + \left(E - \frac{\hbar^2\theta^2}{2\mu\sigma^2} - v_q\right)\phi_q = 0, \tag{14}$$

and recalling Eq. (5) we get for Eq. (14) the ordinary eigen-equation for the diatomic potential $v(r)$, namely,

$$\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}\phi(r) + \left(E - \frac{\hbar^2\theta^2}{2\mu\sigma^2} - v(r)\right)\phi(r) = 0. \tag{15}$$

Thus if ϵ_n are the eigenvalues of Eq. (15) then the values of θ, namely, θ_n are determined to be

$$\theta_n = \frac{\sigma}{\hbar}\sqrt{2\mu(E - \epsilon_n)}\,, \tag{16}$$

or in other words the θ_n, $n = 0, 1, \ldots$, are identified as $k_n\sigma$ where k_n is the nth wave vector. The eigenfunctions $\phi_n(r)$ which are solutions of Eq. (15) are assumed to be normalized.

The eigenvalue problem encountered in the process of solving θ and ϕ_q causes χ_{qp} to be presented, for any $p \geqslant p_0$, in the form

$$\chi_{qp} = \sum_n \exp(\mathrm{i}\theta_n p)\,\phi_{nq}T_{nn_0}, \tag{17}$$

where T_{nn_0}, $n = 0, 1, \ldots$, are coefficients still to be determined (as will be shown later their values will also depend on the initial state n_0). The fact that χ_{qp} is now analytically known will be used to convert the infinite system of equations (see Eq. (7)) to a finite system. For this purpose we consider the following (infinite) sum:

$$\sum_{p'=p_0}^{\infty}\sum_{q'}A_{qpq'p'}\chi_{q'p'} = \sum_{p'=p_0}^{\infty}\sum_{q'}A_{qpq'p'}\sum_n \exp(\mathrm{i}\theta_n p')\,\phi_{nq'}T_{nn_0}. \tag{18}$$

The next step is to eliminate the unknown T_{nn_0} coefficients and this we do by extracting them employing Eq. (17) at $p = p_0$. Multiplying Eq. (17) by $\exp(-\mathrm{i}\theta_{n'}p_0)\phi_{n'q}$ and summing over q (the ϕ_{nq} are an orthonormal set of functions with respect to the DVR grid points) yields for $T_{n'n_0}$ the result

$$T_{n'n_0} = \exp(-\mathrm{i}\theta_{n'}p)\sum_q \phi_{n'q}\chi_{qp}. \tag{19}$$

This is a correct result for each $p \geqslant p_0$ and therefore also for $p = p_0$. Substituting Eq. (19) in Eq. (18) yields the result

$$\sum_{p'=p_0}^{\infty}\sum_{q'}A_{qpq'p'}\chi_{q'p'} = \sum_{p'=p_0}^{\infty}\sum_{q'}A_{qpq'p'}\sum_{q''}\Lambda^{(p')}_{q'q''}\chi_{q''p_0}, \tag{20}$$

where $\Lambda^{(p')}_{q'q''}$ is defined as

$$\Lambda^{(p')}_{q'q''} = \sum_n \phi_{nq''}\exp[\mathrm{i}\theta_n(p' - p_0)]\,\phi_{nq'}. \tag{21}$$

Eq. (20) can also be written as

$$\sum_{p'=p_0}^{\infty} \sum_{q'} A_{qpq'p'} \chi_{q'p'} = \sum_{q'} \bar{A}_{qpq'p_0} \chi_{q'p_0}, \tag{22}$$

where

$$\bar{A}_{qpq'p_0} = \sum_{p'=p_0}^{\infty} \sum_{q''} A_{qpq''p_0} \Lambda_{q''q'}^{(p')}. \tag{23}$$

Following the above analytical treatment, Eq. (7) is reduced to a finite system of equations expressed in terms of the finite matrix $\bar{\mathbf{A}}$ which is defined as follows:

$$\bar{A}_{qpq'p'} = \sum_{p''=p_0}^{\infty} \sum_{q''} A_{qpq''p''} \Lambda_{q''q'}^{(p'')}, \quad \text{for } p' = p_0,$$

$$\bar{A}_{qpq'p'} = A_{qpq'p'} \quad \text{for } p' < p_0. \tag{24}$$

Although it may seen that the modified Eq. (7) is still infinite with respect to q' it is in fact finite due to the NIP defined along r, which causes the wave function χ to become zero for large values of q' (and q).

Once the modified Eq. (7) is solved, the values of χ become known for every grid point (p, q). This applies also for χ_{qp_0}, $q = 0, 1, \ldots$, which, by employing Eq. (19), will be used to calculate the T_{nm_0}, $n = 0, 1, \ldots$, coefficients. Having solved for the T_{nn_0}, it can be shown that the state-selected reactive transition probability from an initial state n_0 is given in the form

$$P_{n_0} = 1 - \sum_{n'} \left| \delta_{n'n_0} + \sqrt{k_n/k_{n_0}}\, T_{n'n_0} \times \exp\left[-\mathrm{i}(\theta_{n'} p_0 + \varphi_{n_0})\right] \right|^2, \tag{25}$$

where φ_{n_0} is the n_0th elastic phase shift (derived from Eq. (2)).

3. Results

In order check whether these ideas are applicable we present results for the collinear

$$\mathrm{H} + \mathrm{H}_2(v) \rightarrow \mathrm{H}_2 + \mathrm{H} \tag{26}$$

reaction. In Fig. 1 are presented state-selected reactive probabilities for three initial vibrational states i.e. $v = 0, 1, 2$ as computed for several different R_{p_0} values, namely, $R_{p_0} = 4.0, 3.5, 3.0, 2.5$ Å. All calculations were done for a linear ramp NIP (substituted along r only) which is 1 Å wide and 0.3 eV high.

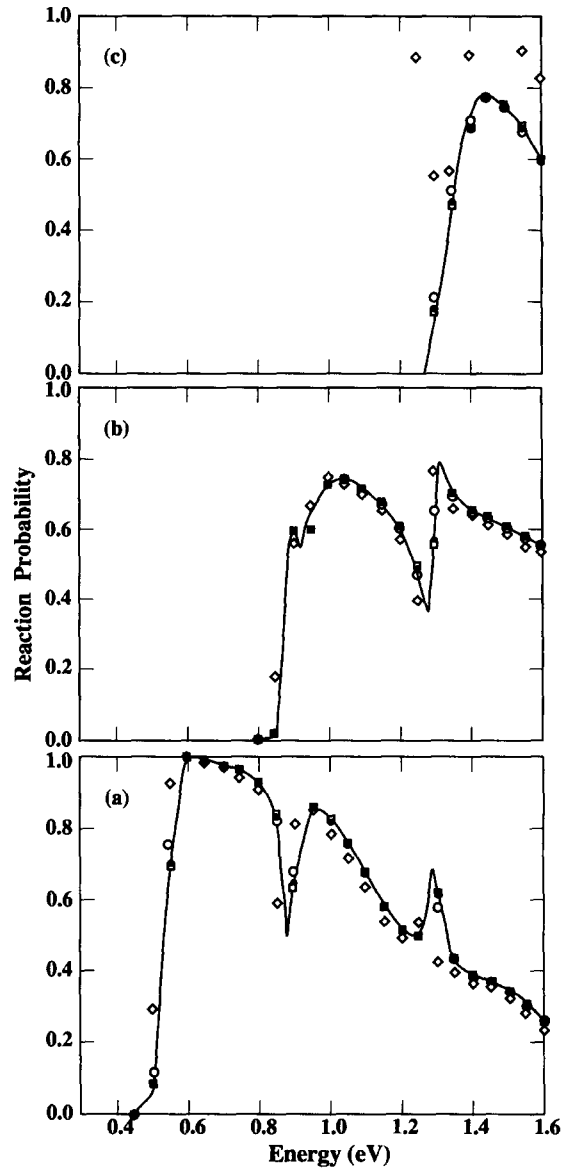

Fig. 1. State-selected reactive probability as a function of total energy as calculated for the collinear $\mathrm{H}+\mathrm{H}_2(v)$ system. (——) Accurate results (Ref. [35]); (●) present results as calculated for $R_p = 4.0$ Å; (□) present results as calculated for $R_p = 3.5$ Å; (○) present results as calculated for $R_p = 3.0$ Å; (◇) present results as calculated for $R_p = 2.5$ Å. (a) Probabilities for $v = 0$; (b) probabilities for $v = 1$; (c) probabilities for $v = 2$.

The present probabilities are compared with results obtained by an established method [35]. As can be seen, the results calculated for the three first R_{p_0} values are close to each other and for all practical applications are similar to the published ones. (We allow ourselves to claim that for $v = 2$ our results are probably more accurate than the ones found in Ref. [35].) It is also seen that as $R_{p_0} = 2.5$ Å the deviations from the accurate results increase but still in most cases the two types of results are reasonably close to each other. The only exceptions are the $v = 2$ probabilities which are off mainly because at $R_{p_0} = 2.5$ Å the second excited eigenvalue and eigenfunction are not accurate, enough, anymore. The fact that the results are hardly changing although the values of R_{p_0} are made relatively small is encouraging. For instance at $R = 2.5$ Å the system is rather far from being at the asymptotic region but nevertheless the assumption concerning the Toeplitz behavior seems to be satisfied.

An important outcome of this study is the fact that only 100–200 DVR points (depending on the energy and the value of R_{p_0}) were required to do the calculations. This small number does not only support our findings in the recent study of the Eckart potential [25] but is also similar to the number of the L^2 basis functions we employed in the treatment of the collinear $H + H_2$ system [11]. The fact that the dimensions of the matrices in both cases are comparable makes the DVR–Toeplitz approach, as compared to the basis set–NIP approach, much more attractive because no integrations (to form the matrix elements) are required.

4. Conclusions

In this work is presented a new numerical approach to treat reactive (exchange) processes, an approach which belongs to the L^2 family methods. It is based on a mixed procedure: along the vibrational coordinate of the reagent molecule a NIP is substituted to absorb the flux that flows into the products ACs whereas to treat the reagents (translational) asymptotic region we make use of the Toeplitz structure of the Hamiltonian operator. The actual numerical treatment is carried out within the DVR. To test this approach we calculated state-selected reactive probabilities that were found to be in good agreement with results of an established method.

The Toeplitz approach to treat scattering problems was introduced several years ago. Until recently it was only applied to single-coordinate systems [23–25]. Here, we applied it to a realistic reactive system. The approach as presented is based on both the NIPs and the Toeplitz behavior. It is our intention to extend this approach by eliminating the NIPs altogether (without losing any of the advantages gained by applying them) and base it on the Toeplitz features only.

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