Theor Chem Acc (2002) 108:125–133
DOI 10.1007/s00214-002-0359-5

Theoretical
Chemistry Accounts

Feature article

Overview of reduced dimensionality quantum approaches to reactive scattering

Joel M. Bowman

Department of Chemistry and Cherry L. Emerson Center for Scientific Computation, Emory University, Atlanta, GA 30322, USA

Received: 3 February 2002 / Accepted: 8 April 2002 / Published online: 19 August 2002

Abstract. In this overview I discuss recent advances as well as outstanding issues in reduced dimensionality quantum approaches to reactive scattering. "Reduced dimensionality" in the present context signifies treating a subset of all degrees of freedom (the most strongly coupled ones) by rigorous quantum methods and treating the remaining (weakly coupled) degrees of freedom by a variety of approximate methods, ranging from simple, so-called energy shifts to more elaborate adiabatic treatments. The most widely used example of this approach is termed "*J*-shifting", and this overview will concentrate on this method and discuss its application and generalization to both "direct" and "complex" reactions, exemplified by $O(^3P)$ + HCl and $O(^1D)$ + HCl, respectively. In addition, for $O(^3P)$ + HCl, resonances in the tunneling region, due to van der Waals wells, are discussed and their challenge to reduced dimensionality methods is stressed. Another new aspect of the reduced dimensionality treatment of polyatomic reactions is the need to describe anharmonicity in a consistent fashion. This is exemplified by the H + CH_4 reaction.

Key words: Reaction dynamics – Reduced dimensionality – Resonances – van der Waals interactions

1 Introduction

There has been dramatic progress in doing quantum reactive scattering calculations for three-atom and some four-atom reactions [1, 2, 3, 4]. Codes for doing such calculations are freely available using both time-independent [5] and time-dependent methods [6]. The most widely used time-independent methods are based on coupled-channel representation(s) of the wavefunction. This results in a large set of coupled, second-order differential equations, the solutions to which yield the entire state-to-state scattering matrix at a given total energy. Time-dependent approaches generally are formulated on grids, and the scattering matrix is obtained for a range of energies; however, for a single initial state.

Depending on the particular application one method has advantages over the other; however, both methods scale exponentially with the number of degrees of freedom, and so these exact methods have been limited to triatomic and some tetraatomic systems. (For the specific calculation of the thermal rate constant the situation is less bleak, as discussed later.) There is an additional scaling with overall rotation. This latter scaling is essentially independent of the number of internal degrees of freedom, but it is quite significant nevertheless. An exact treatment of overall rotation scales nonlinearly with the total angular momentum quantum number J [as much as $O(J^6)$]. In favorable cases, this scaling occurs only for low values of J and then becomes constant for larger J values. Thus, for observables, such as the reaction cross section and rate constant, for which values of J up to several hundred or more are typical, this results in a huge increase in computational effort relative to a $J = 0$ calculation.

Faced with this unfavorable scaling, we and others have developed approximate, so-called reduced dimensionality methods that scale much less drastically with J and the number of internal degrees of freedom. The basic approach taken in these methods is to treat a subset of all the degrees of freedom (the most strongly coupled ones) by rigorous quantum methods and to treat the remaining (weakly coupled) degrees of freedom by a variety of approximate methods, ranging from simple, so-called energy shifts to more elaborate adiabatic treatments. Further, a useful distinction is made between the $3N$–6 internal degrees of freedom and the three rotational degrees of freedom. These approaches have been reviewed over the years [7, 8, 9, 10, 11, 12] and so this review will focus on new tests and challenges for these types of approximations. Also, although these approximation methods apply to all observables, the emphasis here is on the thermal rate constant, $k(T)$.

Correspondence to: J.M. Bowman
e-mail: bowman@euch4e.chem.emory.edu

In the next section I review recent applications, tests and further developments in dealing with the J-scaling for two quite challenging reactions, $O(^3P) + HCl \rightarrow OH + Cl$ and $O(^1D) + HCl \rightarrow OH + Cl$, $ClO + H$. Following that, I review recent reduced dimensionality quantum calculations of $k(T)$ for the $H + CH_4$ reaction and comparisons with full dimensionality calculations (which used J-shifting). I also discuss the importance of an appropriate treatment of the reactant vibrational partition function in full and reduced dimensionality methods. I summarize with some comments on challenges to reduced dimensionality methods.

2 The thermal rate constant

The thermal rate constant for a bimolecular reaction can be written as

$$k(T) = \frac{1}{hQ_{\mathrm{react}}(T)} \int_0^\infty \mathrm{d}E N(E) \mathrm{e}^{-E/k_{\mathrm{B}}T}, \tag{1}$$

where E is the total energy, Q_{react} is the reactant partition function, and $N(E)$ is the cumulative reaction probability (CRP). $N(E)$ is given exactly by

$$N(E) = \sum_i \sum_f \sum_{J=0} (2J+1) \sum_{KK'=-J}^{J} P_{i\rightarrow f}^{J,K,K'}, \tag{2}$$

where $P_{i\rightarrow f}^{J}$is the exact state-to-state (i to f) reaction probability for a given value of the total angular momentum J, and K (K') are initial (final) values of the body-fixed projection quantum number of J. For further use it is convenient to rewrite $N(E)$ as

$$N(E) = \sum_{J=0} (2J+1) N^J(E), \tag{3}$$

where $N^J(E)$ is just the sum over i, f, K and K' of the state-to-state reaction probability.

Clearly an exact calculation of $N(E)$ is equivalent to an exact solution of the Schrödinger equation, and the summations in Eq. (2) may involve thousands of terms. As emphasized by Miller and coworkers, it would be highly desirable to formulate a theory in which $N(E)$ could be obtained exactly and directly, i.e., without having to obtain the detailed state-to-state probabilities. That goal has been attained brilliantly by Miller and coworkers [13, 14]. This is a great advance; however, the exact calculation of $N(E)$ is still challenged by the unfavorable scaling with J, and so approximations for this scaling are still needed.

I review two approximations to deal with the J-scaling problem and present applications and tests of these approximations to two quite different reactions, $O(^3P) + HCl \rightarrow OH + Cl$ and $O(^1D) + HCl \rightarrow OH + Cl$, $ClO + H$. The first reaction is an example of a "direct" reaction (although a very challenging one), and the second is an example of a "complex", barrierless reaction.

3 J-shifting and adiabatic rotation approximations

The simplest reduced dimensionality quantum theory of reactive scattering is one in which a subset of degrees of freedom is treated rigorously while the remaining degrees of freedom are treated by standard (separable) transition-state theory (TST) [7, 8]. This results in simple energy-shift approximations to treat the degrees of freedom not treated dynamically. In the case of the rotational degrees of freedom, this approximation amounts to first making the (sufficient) assumption that K is a good quantum number and thus

$$N^J(E) = \sum_{K=-J}^{J} N^{J,K}(E), \tag{4}$$

and then approximating $N^{J,K}(E)$ as

$$N^{J,K}(E) \approx N^{J=0}\left(E - E_{J,K}^{\ddagger}\right), \tag{5}$$

where $N^{J=0}(E)$ is the exact CRP for $J = 0$ and $E_{J,K}^{\ddagger}$ is the rotational energy of the TS, for example, for a symmetric top

$$E_{J,K}^{\ddagger} = \bar{B}^{\ddagger} J(J+1) + \left(A^{\ddagger} - \bar{B}^{\ddagger}\right) K^2. \tag{6}$$

Equation (5) is known as J-shifting, and it has become fairly widely used because it greatly simplifies the calculation of the thermal rate constant compared to an exact (or other approximate) treatment of overall rotation. It is easily shown that the rate constant that results from J-shifting is

$$k(T) = k^{J=0}(T) Q_{\mathrm{rot}}^{\ddagger}(T), \tag{7}$$

where $Q_{\mathrm{rot}}^{\ddagger}$is the rotational partition function of the TS and

$$k^{J=0}(T) = \frac{1}{hQ_{\mathrm{react}}(T)} \int_0^\infty \mathrm{d}E N^{J=0}(E) \mathrm{e}^{-E/k_{\mathrm{B}}T}. \tag{8}$$

J-shifting for the thermal rate constant has been shown to be accurate to 10–30% for direct reactions, i.e., reactions with a barrier much larger than $k_{\mathrm{B}}T$ [15, 16]. (A modification of Eq. 7 is necessary for reactions with a linear TS to account for the fact the odd bending states of the TS are not accounted for in a $J = 0$ calculation. The simplest modification, in the spirit of reduced dimensionality theory, is to multiply the right-hand side of Eq. 7 by a partition function containing the odd-numbered bending states. More sophisticated approaches are also possible as reviewed elsewhere [8], and also see later.) A very recent, rigorous test for $O(^3P) + HCl$ is presented in the next section.

As already stated, J-shifting results from using separable TST to describe overall rotation. It is possible to describe some interaction between rotation and vibration of the TS. To see how this can be done, we need only continue with the assumption of TST that $N^{J,K}(E)$ can be written in terms of quantized TSs as follows:

$$N^{J,K}(E) = \sum_{i=0} N_i^{J,K}(E), \tag{9}$$

where the sum over i refers to the vibration/bending states of the TS. For example, $i = 0$ refers to the zero-point state of the TS. (There is convincing evidence from a variety of exact calculations that supports the concept of quantized TSs [17, 18], and so this assumption is on firm ground.) On the basis of Eq. (9) a generalized J-shifting approximation [19] can be made for each quantized TS, i.e.,

$$N_i^{J,K} \approx N_i^{J=0}\left(E - E^{\ddagger}_{J,K,i}\right), \tag{10}$$

where, for example $E^{\ddagger}_{J,K,i}$is still given by Eq. (6) but now the TS rotation constants are state-dependent.

Of course it is not obvious how to obtain these state-dependent rotation constants since, unlike the usual, separable rigid-rotor ones, vibration/rotation coupling of the TS must be included in the analysis of the TS vibration/rotation energies. We have done this for the OH + H_2 reaction [19], using the code, "MULTIMODE", which we developed with Carter [20, 21]. This code does calculations of coupled ro-vibrational states of polyatomic molecules, including saddle points. The potential used [22] in these calculations (which has since been superceded by more accurate ones) has a relatively "floppy" TS which resulted in strong vibration/rotation coupling and a significant variation of the rotation constants with a quantized TS. This in turn resulted in the thermal rate constant being reduced by roughly 20 % relative to the standard J-shifting result. This relatively large effect of vibration/rotation coupling is not typical.

Finally, it should be noted that J-shifting can be done using a CRP for J greater than zero [15, 23, 24, 25]. This requires more computational effort of course than J-shifting based on $N^{J=0}$; however, as expected the resulting rate constant is more accurate.

4 Adiabatic rotation approximation and a generalization of *J*-shifting

For reactions that proceed via complexes and with no potential barrier(s), it appears that standard J-shifting is not applicable, since no TS exists on the potential. However, rotational barriers do form on the effective potential, i.e., the sum of the potential plus the rotational energy. These barriers define a TS; however, one that may shift considerably in configuration with the total energy and with J. The existence and importance of these effective barriers is well known, and they play a central role in approximate dynamical and statistical models of unimolecular and bimolecular reactions [26, 27, 28]. These models treat the dynamics approximately, and it is clearly desirable to have a method that is based on quantum dynamics but which incorporates rotational energy barriers in the spirit of J-shifting.

An important step in this direction is the ℓ-shifting model of Gray et al. [29], which was developed for and applied to the O(^{1}D) + $H_2(v = 0, j = 0)$ reaction. In this method quantum reaction probabilities for nonzero orbital angular momentum ℓ were related to exact ones for $\ell = 0$ using an expression like Eq. (5); however, with J replaced by ℓ. This was justified for the specific case of $H_2(v = 0, j = 0)$ because in this case $\ell = J$. The value of the rotation constant used in the energy-shifting depends on ℓ, because the location of the barrier on the effective potential depends on ℓ. This model is applicable for describing rotational barriers in the entrance channel of a reaction, and for a reactant diatomic in the ground rotational state. In the case that these barriers determine the overall reactivity, as in the case of O(^{1}D) + H_2, the model is quite reasonable.

In the general case where the reactant diatomic is rotationally excited and/or where there are multiple product channels, the ℓ-shifting model needs to be generalized. We have proposed such a generalization [30] based on the adiabatic rotation approximation [31, 32, 33, 34]. In this approximation the rotational energy of the collision system is calculated at a given configuration, and the resulting (adiabatic) rotational energy is added to the electronic potential to form the effective potential. This treatment of overall rotation can be combined with the exact Hamiltonian for zero total angular momentum to obtain an approximate Hamiltonian for J greater than zero, given by

$$H^{J,K} = H^{J=0} + E^{J,K}(Q), \tag{11}$$

where Q represents the collection of internal coordinates and $H^{J=0}$ is the exact Hamiltonian for zero total angular momentum. Scattering calculations can be done for each J and K and, for example, the partial wave CRP, $N^{\mathrm{J,K}}(E)$, can be obtained from these calculations.

For example, consider a triatomic reaction $A + BC \rightarrow AB + C$, $AC + B$, and for simplicity assume a prolate symmetric top approximation so that K is a good quantum number. (This applies for reactions of the type X + HY, where X and Y are not hydrogen atoms.) Then, in standard Jacobi coordinates (R the distance of A to the center of mass of BC, r the BC internuclear distance and γ the angle between the vectors R and r) the adiabatic rotational energy is given by

$$\begin{aligned} E^{J,K}(R_\alpha, r_\alpha, \gamma_\alpha) = {} & \bar{B}(R_\alpha, r_\alpha, \gamma_\alpha)J(J+1) \\ & + [A(R_\alpha, r_\alpha, \gamma_\alpha) - \bar{B}(R_\alpha, r_\alpha, \gamma_\alpha)]K^2, \end{aligned} \tag{12}$$

where α denotes an arrangement channel and the rotation constants $A(R_\alpha, r_\alpha, \gamma_\alpha)$ and $\bar{B}(R_\alpha, r_\alpha, \gamma_\alpha)$ (the average of the B and C rotation constants) are functions of the coordinates. Adding this rotational energy to the potential $V(R_\alpha, r_\alpha, \gamma_\alpha)$ gives effective potentials in the three arrangement channels,

$$V^{J,K}_{\mathrm{eff},\alpha}(R_\alpha, r_\alpha, \gamma_\alpha) = V(R_\alpha, r_\alpha, \gamma_\alpha) + E^{J,K}(R_\alpha, r_\alpha, \gamma_\alpha). \tag{13}$$

Note that in this expression K is the spectroscopic quantum number, K_a, i.e., the projection quantum number on the a-axis, and thus the rotational energy is independent of the choice of arrangement channel coordinates.

Dynamics calculations using this effective potential have been done and very good results have been obtained [35, 36]; however, they are still quite computationally intensive. Clearly, these effective potentials can be used to determine the properties of rotational barriers as a function of J and K, and this forms the basis of the generalization of the J-shifting model [30], as illustrated for the O(^{1}D) + HCl reaction later. In brief, the method recognizes that barriers exist owing to the rotational motion in the various arrangement channels. From the characteristics of these barriers (including the zero-point energy) it is straightforward to determine which barrier controls a given reaction, α to β, for a given value of the total energy, J and K. Then, denoting the energy of the relevant, controlling barrier by $E^{\ddagger\alpha\beta}_{J,K}$, the generalized J-shifting approximation for the CRP for the reaction is given by

$$N^{J,K}_{\alpha\to\beta}(E) \approx N^{J=0}_{\alpha\to\beta}\left(E - E^{\ddagger\alpha\beta}_{J,K}\right), \qquad (14)$$

J- and K-shifting can also be used to estimate initial state-selected cross sections to form a given product. For example, for initial rotational states with $K = 0$ the cross section can be estimated using the expression

$$\sigma_{vj}(E) = \frac{\pi}{k_{vj}^2}\sum_{j=0}(2J+1)P^{J=0}_{vj}\left(E - E^{\ddagger}_{J,K=0}\right), \qquad (15)$$

where $P^{J=0}_{vj}$ is the initial state-selected reaction probability to form a given product (for simplicity we drop the α,β notation) and k_{vj} is the wavenumber. Degeneracy-averaged cross sections can also be estimated using J- and K-shifting; however, in this case the minimum value of J for an exact calculation has to be $J = K$ and then energy shifting is done relative to that value of J.

Finally, note that in general there will be minimum values of J and K where a positive energy barrier on the effective potential exists. For J and K less than these minimum values no energy shifting is done in Eq. (15).

Next I present an application and rigorous test of the standard J-shifting method to the "direct" reaction O(^{3}P) + HCl → OH + Cl. This reaction is quite challenging owing to the presence of low-energy resonances. Generalized J-shifting is illustrated by the "complex" reaction O(^{1}D) + HCl → OH + Cl, ClO + H.

5 O(^{3}P) + HCl: example of a "direct" reaction

The O(^{3}P) + HCl reaction has been widely studied quantum mechanically over the past decade [15, 16, 37, 38, 39, 40, 41, 42]. Most of these calculations were done using the potential of Koizumi et al. [37] (KSG), and until 1998 these quantum calculations made use of some version of J-shifting to obtain the thermal rate constant.

Very recently two groups [41, 42] reconsidered the quantum dynamics of this reaction using the KSG potential and a newer potential of Ramachandran et al. (denoted S4) [43]. Unlike the KSG potential this newer surface contains a van der Waals well in both the entrance and exit channels. The quantum scattering calculations (which were done for zero total angular momentum) found prominent resonances in the CRP at energies below the ground-state vibrationally adiabatic barrier (0.54 eV). Such resonances were not seen using the KSG potential and this led to the speculation that these low-energy resonances were due to the presence of the van der Waals well(s). Standard J-shifting (Eqs. 7, 8) was done to obtain the thermal rate constant, which was (surprisingly) in very good agreement with that obtained using the KSG potential, even though the ground-state adiabatic barrier on S4 is 1.3 kcal/mol higher than on KSG.

This surprising result clearly called for further investigation to determine if standard J-shifting might be inaccurate for a reaction with low-energy resonances. This was done in very recent work where resonances were further investigated using exact quantum scattering calculations (using the code ABC [6]) and also quasibound state calculations [44]. Exact and standard J-shifting calculations of the CRP were done to investigate the J dependence of these resonances. These calculations were done for J up to 100 in order to obtain the exact rate constant.

The CRP for zero total angular momentum is plotted in Fig. 1 versus the total energy, E. The barrier height of the S4 potential is 0.424 eV, measured relative to O(^{3}P) + HCl(r_e), and the (harmonic) ground-state adiabatic barrier height is 0.536 eV. Thus, the calculations are focused in the tunneling region of this reaction, where nine resonances are clearly seen. These resonances have been carefully characterized and assigned to quasibound states of van der Waals wells in either the entrance or exit channel [44].

The shift of resonance, r, with J and K can be predicted by J-shifting, which for this reaction is given by the prolate top expression, where the rotation constants

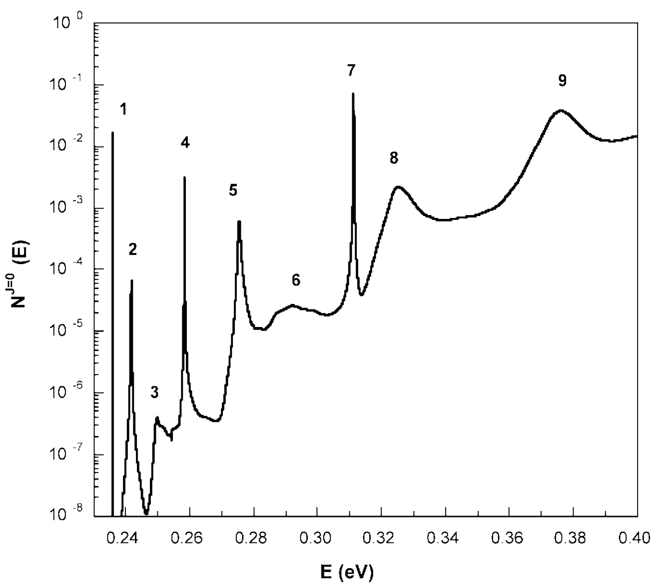

Fig. 1. Semilogarithmic plot of the cumulative reaction probability for zero total angular momentum for the O(^{3}P) + HCl reaction versus the total energy, E, in the tunneling region. The peaks numbered *1–9* correspond to quasibound states of the van der Waals minima, as explained in the text

could either be determined numerically by fitting the exact resonance energy [45] or approximated by the TS values. To check this prediction consider the exact CRP for $J = 1$ for the even and odd parity states; these are plotted in Fig. 2. As seen, there are clear resonance structures for the two parities, and both sets of resonances shift to higher energies relative to the $J = 0$ results, as expected from J-shifting. The $P = 1$ resonances are single peaks, but the narrow resonances for $\mathrm{P} = -1$ clearly split into doublets. The broad resonances for $P = -1$ are also doublets, which because they overlap are not clearly resolved. These detailed features of the resonances can be rationalized using a J-shifting argument. For $J = 1$ and $P = 1$, only $K = 1$ contributes to the CRP, but for $P = -1$, both $\mathrm{K} = 1$ and 0 contribute. Thus, the $P = -1$ CRP shows doublet behavior owing to the contributions of two K values. Thus, at least qualitatively the shift in the $J = 1$ resonances is given correctly by J-shifting. The exact shifts in the resonance positions can be used to numerically determine A and B.

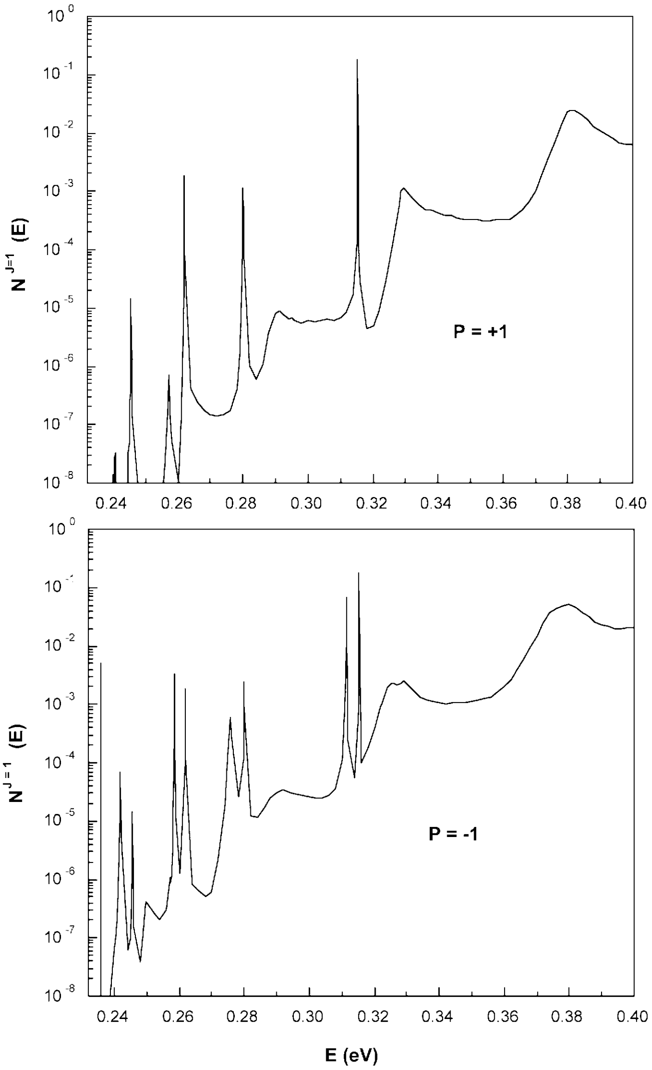

Fig. 2. Semilogarithmic plot of the cumulative reaction probability for $J = 1$ and the two parities, P, indicated for the $O(^3P)$ + HCl reaction versus the total energy, E, in the tunneling region

This was done and the agreement with TS rotation constants was only semiquantitative [44].

The exact and J-shifting CRPs, summed over J and K are compared in Fig. 3. The average relative error of the J-shifting CRP over the energy range shown is 19%, although the agreement deteriorates to around 30% at higher energies. The corresponding exact and J-shifted thermal rate constants were calculated using the CRPs shown in Fig. 3, and the approximate one was found to be on average 30 % higher than the exact result over the temperature range 200–800 K. Thus, the J-shifting calculation, which took roughly 10^4 times less computation time than the exact calculation, does provide a very useful and reliable level of accuracy for this challenging reaction. It should be noted though that other reduced-dimensionality approximations which make further approximations to obtain the $J = 0$ CRP do not give a rate constant in good agreement with either the exact result or the J-shifted one for this reaction [46]. These methods significantly underestimate the degree of tunneling and it is not completely clear why this is so. One speculation was that the van der Waals wells cause significant non-adiabatic coupling between the bending mode of the triatomic reaction system and the two stretching modes. This coupling is captured in an exact $J = 0$ calculation but is absent in adiabatic treatment(s) of the bend.

6 $O(^1D)$ + HCl: example of a "complex" reaction

The $O(^1D) + HCl \rightarrow ClO + H$, $OH + Cl$, reaction is described by a potential without barriers but with two deep minima corresponding to HOCl and HClO. These minima are expected to result in "sticky" collisions, and for this reason the reaction is termed complex. For such reactions, the computational challenges are even greater than those for direct reactions, because the

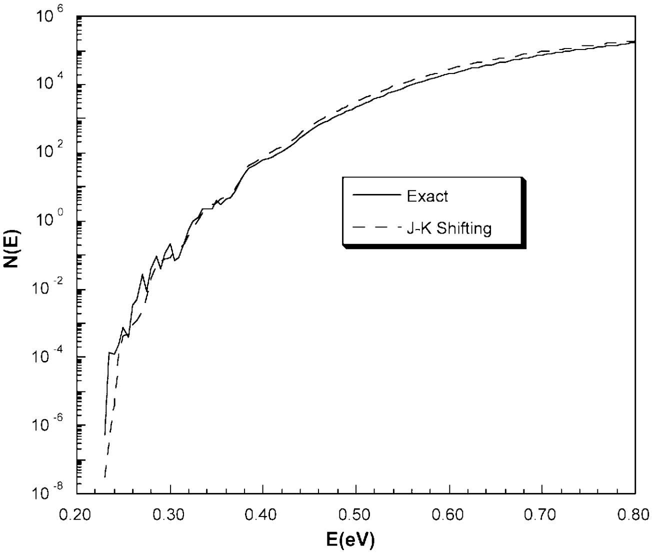

Fig. 3. Comparison of exact and J-shifting full cumulative reaction probability versus the total energy, E, for the $O(^3P)$ + HCl reaction

wavefunctions are highly oscillatory owing to the complex regions, and many initial states contribute to the CRP. Even direct methods to obtain the CRP [13] become of comparable difficulty to those that do an explicit sum of initial state-selected probabilities for such reactions because of the absence of a substantial potential barrier that limits the reactive flux. Thus, the need for some kind of *J*-shifting is perhaps even more compelling than for direct reactions. However, complex-forming reactions present new challenges to *J*-shifting approaches, precisely owing to the absence of a potential barrier. Thus, generalizations of *J*-shifting are necessary for this class of reaction, and our efforts to do this, motivated by a study of the O(^{1}D) + HCl reaction, are described next.

Global potential-energy surfaces, based on ab initio calculations, and subsequent quasiclassical trajectory and quantum wavepacket calculations for this reaction have been reported by two groups [30, 47, 48, 49, 50, 51]. A sketch of the energetics of the various minima and reaction channels is given in Fig. 4. Very roughly the OH + Cl product correlates with the HOCl minimum, while the ClO + H product correlates with HClO minimum; however, the energy of the reaction is above the barrier separating these minima, and so “isomerization” between these two minima undermines the correlation of a given minimum to a given reaction channel.

The exact CRP for each product was calculated [30, 47, 48, 49] using the wavepacket code of Gray and Balint-Kurti [52] for $J = 0$. These CRPs were obtained by summing initial state-selected reaction probabilities for HCl ($v = 0,j$) for j between 0 and 16. The resulting CRPs (for the two reaction products) are plotted versus the total energy in Fig. 5, where as seen the OH product dominates over the ClO by about a factor of 2.5. As seen the CRPs are oscillatory; this is a direct consequence of the complex dynamics in this reaction owing to the deep minima in the potential.

The effect of overall rotation on the reaction was determined by calculating the effective potentials for many values of J and K using the adiabatic rotation approximation, i.e., by Eqs. (12) and (13). The details of the calculations and contour plots of effective potentials are given elsewhere [30, 48, 49]. The resulting barriers are shown schematically, but realistically, in Fig. 6. Three barriers are indicated, but only two control the reaction dynamics, i.e., the entrance channel barrier controls the very exoergic reaction pathway to form OH + Cl and the ClO + H barrier controls the slightly exdoergic pathway for ClO + H.

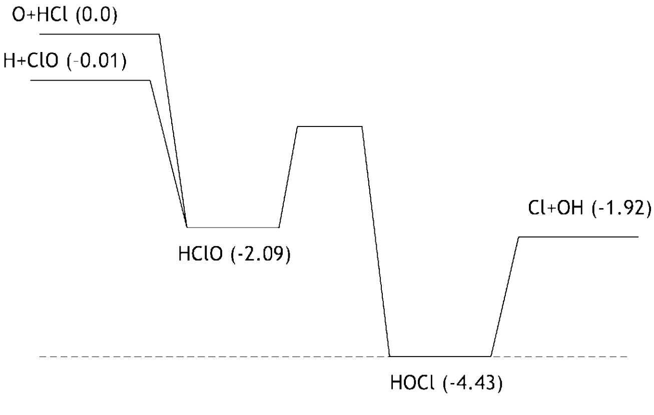

Fig. 4. Energetics (eV) for the O(^{1}D) + HCl reaction

As an example of using generalized *J*-shifting, the cross sections to form the two products for HCl ($v = j = 0$) were calculated using Eq. (15). These cross sections are not exact, and in order to make some assessment of their accuracy we also performed standard quasiclassical trajectory calculations (QCT) of these cross sections [49]. (Unfortunately exact quantum calculations of these cross sections are not feasible for us.) Of course QCT calculations are also not exact, and so some assessment of their accuracy is desirable. This can be done by comparing QCT and exact quantum

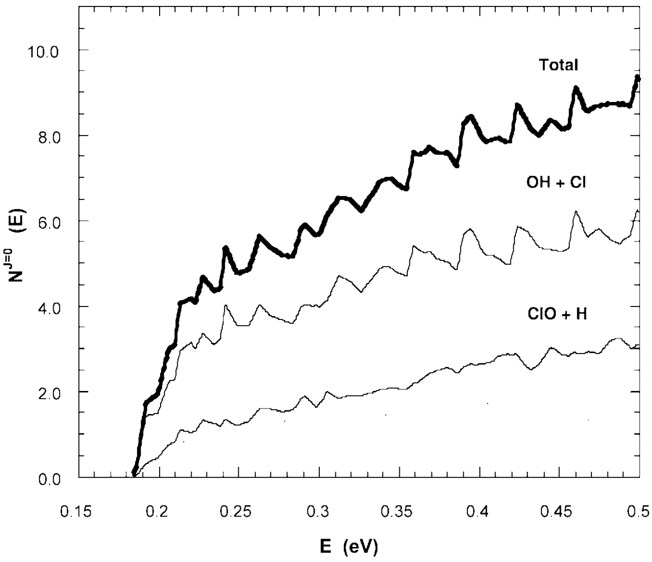

Fig. 5. Quantum cumulative reaction probabilities for zero total angular momentum for the O(^{1}D) + HCl reaction versus the total energy, E

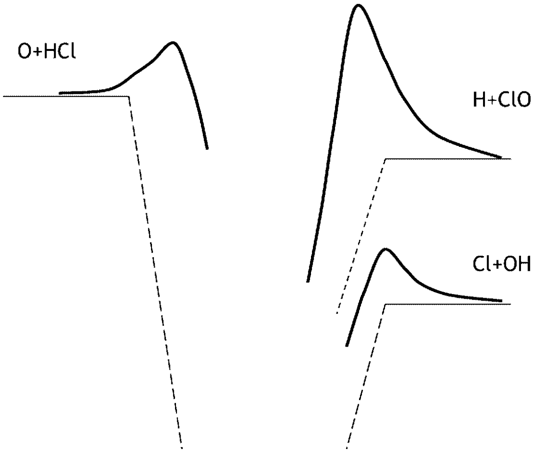

Fig. 6. Schematic of effective potentials for nonzero angular momentum for the O(^{1}D) + HCl reaction

calculations for $J = 0$. This is done in Fig. 7, where the reaction probabilities for HCl($v = j = 0$) to form each product are plotted against the initial relative translational energy. As seen, there is good agreement for the ClO channel; however, for the OH channel the two sets of probabilities are only in average agreement. Note especially that for $E_{\mathrm{trans}} = 0.20$ eV the QCT results are uniformly too large by 30 % or more. Keeping in mind the rigorous test of the accuracy of the QCT calculations for $J = 0$, consider the comparison of the QCT and approximate cross sections shown in Fg. 8. As seen, the qualitative behavior of the QCT and approximate quantum cross sections is very similar. For both products, the two sets of computed cross sections decrease with increasing translational energy, as expected for a reaction with no potential barrier. For the ClO channel the agreement between the QCT and approximate quantum cross sections is quite good; however, not as good as for the OH + Cl channel. This is consistent with the comparisons shown for $J = 0$, where the quantum calculations are exact. Thus, it appears that much of the disagreement between the approximate quantum and QCT cross sections for OH is due to errors in the QCT method. However, one must be cautious here since the *J–K*-shifting approximation introduces some errors as well.

To conclude this section, note that the rate constants for each product calculated with the *J–K*-shifting approximation are in good agreement with experiment, showing a very slight temperature dependence over the experimental range 200–400 K [30].

7 H + CH_4

To conclude the body of this overview, consider the H + $CH_4 \rightarrow H_2 + CH_3$ reaction. This is a direct reaction with 12 internal degrees of freedom and a large barrier to reaction. The first quantum calculations of this reaction were done using reduced dimensionality approaches for internal degrees of freedom. In brief, in this approach energy-shift approximations are made to obtain an approximate $J = 0$ CRP, $N^{J=0}(E)$. Thus if $N^{J=0,\mathrm{rd}}(E)$ denotes a reduced dimensionality CRP for $J = 0$, then the full dimensionality $J = 0$ CRP is given approximately by [8, 9]

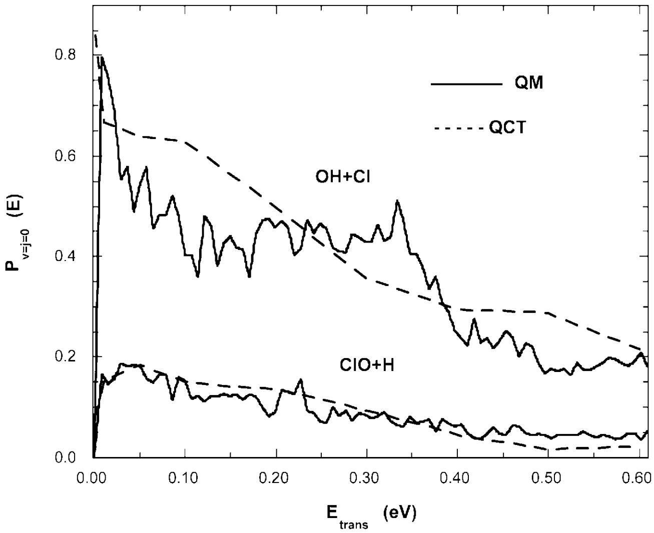

Fig. 7. Comparison of J = 0 quantum mechanical (*QM*) and quasiclassical trajectory (*QCT*) reaction probabilities for the O(^{1}D) + HCl ($v = j = 0$) reaction versus the initial relative translational energy, E_{trans}

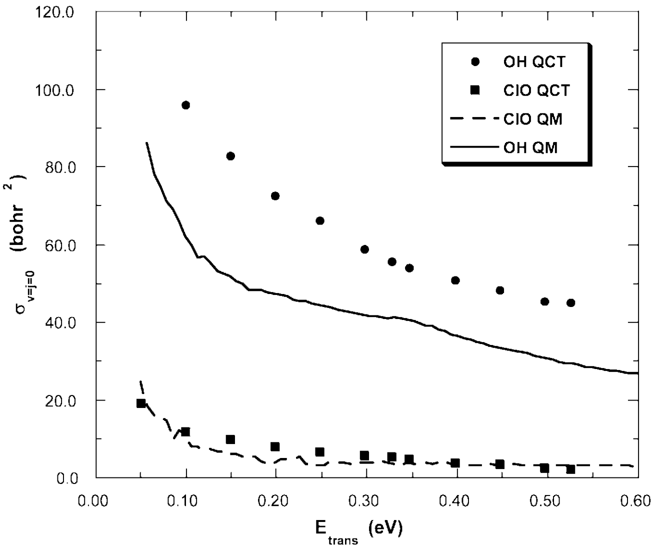

Fig. 8. Comparison of *J*-shifting QM and QCT cross sections for the O(^{1}D) + HCl ($v = j = 0$) reaction versus initial relative translational energy, E_{trans}

$$N^{J=0}(E) = \sum_{v'} N^{J=0,\mathrm{rd}}\left(E - E^{\ddagger}_{v'}\right), \qquad (16)$$

where v' represents vibrational quantum numbers of the degrees of freedom not included in the quantum calculation, and $E^{\ddagger}_{v'}$ are the TS vibrational energies corresponding to these degrees of freedom. (This procedure for H + CH_4 is discussed in more detail later.)

The first such reduced dimensionality quantum calculations of this reaction were done by Takayanagi [53], who considered three degrees of freedom, the CH stretch in CH_4, the initially unbound CH stretch, and a spectator coordinate representing the CH_4 umbrella mode. Subsequent to that calculation, Yu and Nyman [54] did quantum calculations with an additional degree of freedom, the local-mode CH bend in CH_4. The thermal rate constants obtained from these three and four-degrees-of-freedom reduced dimensionality calculations were generally in good agreement with each other, except at temperatures between 300 and 400 K, where the four-degrees-of-freedom calculation of the rate constant was above the three-degrees-of-freedom one by about a factor of 2.

Two time-dependent wavepacket calculations have been reported for this reaction. The first one, by Wang et al. [55], was done in four degrees of freedom using the semirigid vibrating rotor target model. These calculations were done for the ground rotational state of CH_4, and so the rate constant obtained cannot rigorously be directly compared to experiment, where the rate constant is thermally averaged over initial states. More recently we reported a six-degrees-of-freedom wavepacket calculation [56], using the atom–triatom scattering code of Zhang et al. [57]. This calculation used energy shifting for the remaining six degrees of freedom and *J*-shifting to obtain $k(T)$. The identification of the remaining modes is not necessarily straightforward. We were able to do this for H + CH_4 by comparing the eigenvectors of the normal modes of the full and reduced dimensionality TS[53].

All of these reduced dimensionality quantum calculations (except the ones by Zhang and coworkers) obtained the CRP by first calculating either state-to-state or initial state-selected reaction probabilities and then summing over these to obtain the CRP. A direct calculation of the $J = 0$ CRP was recently reported in full dimensionality by Huarte-Larranaga and Manthe [58]. This benchmark calculation allowed a direct test of the various approximate, reduced dimensionality methods, either at the level of a direct comparison of the $J = 0$ CRP or by a comparison of the thermal rate constant, where all methods used *J*-shifting. The comparison of rate constants was done by Huarte-Larranaga and Manthe [58], who found large differences between their rate constant and those from the three- and four-degrees-of-freedom calculations over the temperature range of their calculation, which was 200–500 K. In their calculation of $k(T)$ the normal-mode harmonic approximation for the vibrational partition function of CH_4 was used. Subsequently, it was pointed out that the exact full vibrational partition function should have been used, consistent with the exact treatment of the CRP [59, 60]. When this partition function is used instead of the harmonic one, the rate constant is reduced by factors of 1.5–3.0 over the previously mentioned temperature range, resulting in much improved agreement with the various reduced dimensionality calculations. For CH_4 the difference in the exact (for the potential used) and harmonic zero-point energy is −0.475 kcal/mol, which is much larger than *RT* over this temperature range. Thus, the importance of anharmonicity in the vibrational partition function, especially of larger molecules, must be taken into account, at least when doing "exact" calculations. (However, see later for further comments on this point for approximate calculations.)

The H + CH_4 reaction is perhaps the first one to focus clearly on the issue of anharmonicity of the reactant vibrational partition function in rigorous calculations of the rate constant. It also raised some subtle questions about what is the appropriate vibrational partition function to use in reduced dimensionality calculations. To summarize the discussion of this point and a tentative suggestion given in detail elsewhere [56], the issue revolves around what method is used to obtain the vibrational energies of the TS to be used in energy-shifting, see Eq. (16). If these energies are calculated in the usual normal-mode, harmonic approximation, then the corresponding vibrational energies of the reactant molecule should also be calculated using this approximation. This suggestion is at least a consistent one, and assumes that there will be some cancellation of errors by using the same approximation for the reactant and the TS. (Recall that in TST it is the difference in the vibrational energies of the TS and the reactant that matters.)

Having sorted out some of these issues between "exact" and reduced dimensionality calculations for this reaction, it should be noted that the various rate constants calculated are in good agreement with each other, but are not in agreement with experiment. This is clearly due to a deficiency in the global potential used [61]. Very recently Pu and Truhlar [62] reported a direct-dynamics calculation of the rate constant and obtained good agreement with experiment. They used a method that treats all degrees of freedom, except a multidimensional reaction coordinate, adiabatically, using a harmonic approximation for these energies and also for the CH_4 vibrational energies. They tested this method against the full dimensional calculations, which used anharmonic coupled CH_4 vibrational energies [59] and found very good agreement [63]. This is a verification of the consistency suggestion made earlier, i.e., that a harmonic treatment of reactive modes is consistent with using a harmonic treatment of the reactant vibrations.

8 Summary

I have reviewed several aspects of reduced dimensionality approaches to quantum reactive scattering. *J*-shifting and generalizations of it were focused on as these approximations apply to exact scattering calculations done for $J = 0$. Such calculations are now routine for general three-atom reactions (on a single potential-energy surface) and will soon be routine for direct calculations of the CRP for direct reactions of tetra-atomic reactions and even bigger reactions, such as H + CH_4, in favorable cases.

The *J*-shifting approximation was illustrated and tested for the direct $O(^3P)$ + HCl reaction and was found to be accurate for the thermal rate constant to within 30% over the temperature range 200–800 K. Interesting, low-energy resonances, due to van der Waals wells, were found in exact calculations. The wells were implicated in the failure of less exact reduced dimensionality calculations that assume adiabaticity in one or more internal degrees of freedom. This is an area for more research for these adiabatic-based theories.

Generalized *J*-shifting was applied to the complex, barrierless reaction $O(^1D)$ + HCl and one application of this approximation to the reaction cross sections to form the two products, OH and ClO, was presented along with quasiclassical trajectory results. Both sets of calculations predict the dominance of the OH product over ClO. However, the quantitative agreement between the approximate quantum and trajectory cross sections was only fair for the OH product, with the QCT results about 50% larger than the quantum ones. Better agreement was found for the ClO product.

The importance of treating the vibrational partition function of CH_4 in the H + CH_4 reaction consistent with the level of dimensionality reduction was discussed. This will be important for full and reduced dimensionality calculations of reactions with CH_4 [64, 65, 66, 67] and will become an increasingly important point as the field moves to the study of reactions involving polyatomic molecules.

Acknowledgements. I acknowledge the critical contributions of my coworkers, and thank the Department of Energy (DE-FG02-97ER14782) for financial support.

References

1. Lagana A, Riganelli A (1999) (eds) Reaction and molecular dynamics. Springer, Berlin Heidelberg New York
2. Bowman JM (1994) (ed) Advances in molecular vibrations. JAI, Greenwich
3. Bowman JM, Schatz GC (1995) Annu Rev Phys Chem 46: 169
4. Zhang DH, Zhang JZH (1996) In: Wyatt RE, Zhang JZH (eds) Dynamics of molecules and chemical reactions. Dekker, New York, pp 231–276
5. Skouteris D, Castillo JF, Manolopoulos DE (2000) Comput Phys Commun 133: 128
6. Peng T, Zhang DH, Wang DY, Li YM, Zhang JZH (2000) Comput Phys Commun 128: 492
7. Bowman JM (1985) Adv Chem Phys 61: 115
8. Bowman JM (1991) J Phys Chem 95: 4960
9. Bowman JM, Wang D-S (1994) In: Bowman JM (ed) Advances in molecular vibrations. JAI, Greenwich, p 189–223
10. Clary DC (1998) Science 279: 1879
11. Szichman H, Baer M, Nakamura H (1997) J Chem Phys 107: 3521
12. Bowman JM (2000) In: Lagana A, Riganelli A (eds) Reaction and molecular dynamics (Proceedings of the European School on Computational Chemistry, Perugia, Italy, July 1999). Springer, Berlin Heidelberg New York, pp 101–114
13. Miller WH (1998) J Phys Chem A 102: 793
14. Manthe U (1999) In: Lagana A, Riganelli A (eds) Reaction and molecular dynamics. Springer, Berlin Heidelberg New York, pp 130–149
15. Nobusada K, Nakamura H (1999) J Phys Chem A 103: 6715
16. Matzkies F, Manthe U (2000) J Chem Phys 112: 130
17. Bowman JM (1987) Chem Phys Lett 141: 545
18. Chatfield DC, Friedman RS, Schwenke DW, Truhlar DG (1992) J Phys Chem 96: 2414
19. Bowman JM, Shnider HM (1999) J Chem Phys 110: 4428
20. Carter S, Culik SJ, Bowman JM (1997) J Chem Phys 107: 10458
21. Carter S, Bowman JM, Handy NC (1998) Theor Chem Acc 100: 191
22. Schatz GC, Elgersma H (1980) Chem Phys Lett 73: 21
23. Mielke SL, Lynch BJ, Truhlar DG, Schwenke DW (1993) Chem Phys Lett 216: 441
24. Wang D, Bowman JM (1994) J Phys Chem 98: 7994
25. Zhang DH, Zhang JZH (1999) J Chem Phys 110: 7622
26. Baer T, Hase WL (1996) Unimolecular reaction dynamics. Oxford University Press, New York
27. Clary DC, Henshaw JP (1987) Faraday Discuss Chem Soc 84: 333
28. Rackham EJ, Huarte-Larranaga F, Manolopoulos DE (2001) Chem Phys Lett 343: 356
29. Gray SK, Petrongolo C, Drukker K, Schatz GC (1999) J Phys Chem A 103: 9448
30. Bittererova M, Bowman JM, Peterson K (2000) J Chem Phys 113: 6186
31. Bowman JM (1994) Chem Phys Lett 217: 36
32. Qi JX, Bowman JM (1997) J Chem Phys 107: 9960
33. Carter S, Bowman JM (1998) J Chem Phys 108: 4397
34. McCurdy CW, Miller WH, (1977) (eds) ACS symposium series 56. American Chemical Society, Washington, DC
35. Russell CL, Manolopoulos DE (1999) J Chem Phys 110: 177
36. De Fazio D, Castillo JF (1999) Phys Chem Chem Phys 1: 1165
37. Koizumi H, Schatz GC, Gordon MS (1991) J Chem Phys 95: 6421
38. Thompson WH, Miller WH (1997) J Chem Phys 106: 142
39. Poirier B (1998) J Chem Phys 108: 5216
40. Aoiz FJ, Banares L, Castillo JF, Menendez M, Verdasco JE (1999) Phys Chem Chem Phys 1: 1149
41. Skokov S, Tsuchida T, Nanbu S, Bowman JM, Gray SK (2000) J Chem Phys 113: 227
42. Nobusada K, Nakamura H, Lin YJ, Ramachandran B (2000) J Chem Phys 113: 1018
43. Ramachandran B, Schrader EA, Senekowitsch J, Wyatt RE (1999) J Chem Phys 111: 3862
44. Xie T, Wang D, Bowman JM, Manolopoulos DE (2002) J Chem Phys 116: 7461
45. Skodje RT, Skouteris D, Manolopoulos DE, Lee SH, Dong F, Liu K (2000) J Chem Phys 112: 4536
46. Skokov S, Zou S, Bowman JM, Allison TC, Truhlar DG, Lin Y, Ramachandran B, Garrett BC, Lynch BJ (2001) J Phys Chem A 105: 2298
47. Christoffel KM, Kim Y, Skokov S, Bowman JM, Gray SK (1999) Chem Phys Lett 315: 275
48. Bittererova M, Bowman JM (2000) J Chem Phys 113: 1
49. Christoffel KM, Bowman JM (2002) J Chem Phys 116: 4842
50. Piermarini V, Balint-Kurti GG, Gray SK, Gogtas F, Lagana A, Hernandez ML (2001) J Phys Chem A 105: 5743
51. Piermarini V, Lagana A, Balint-Kurti GG (2001) Phys Chem Chem Phys 3: 4515
52. Gray SK, Balint-Kurti GG (1998) J Chem Phys 108: 950
53. Takayanagi T (1996) J Chem Phys 104: 2237
54. Yu HG, Nyman G (1999) J Chem Phys 111: 3508
55. Wang ML, Li YM, Zhang JZH, Zhang DH (2000) J Chem Phys 113: 1802
56. Wang D, Bowman JM (2001) J Chem Phys 115: 2055
57. Zhang JZH, Dai JQ, Zhu W (1997) J Phys Chem A 101: 2746
58. Huarte-Larranaga F, Manthe U (2000) J Chem Phys 113: 5115
59. Bowman JM, Wang DY, Huang XC, Huarte-Larranaga F, Manthe U (2001) J Chem Phys 114: 9683
60. Huarte-Larranaga F, Manthe U (2001) J Phys Chem A 105: 2522
61. Jordan MJT, Gilbert RG (1995) J Chem Phys 102: 5669
62. Pu JZ, Truhlar, DG (2002) J Chem Phys 116: 1468
63. Pu J, Corchado, J.C., Truhlar, DG (2001) J Chem Phys 115: 6266
64. Skokov S, Bowman JM (2000) J Chem Phys 113: 4495
65. Palma J, Clary DC (2001) J Chem Phys 115: 2188
66. Yu HG, Nyman G (1999) J Chem Phys 110: 7233
67. Yu HG, Nyman G (2000) J Chem Phys 112: 238