

# Polyatomic Reaction Dynamics from the Barrier Top

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**Abstract.** Keck's idea of simulating a reaction by running trajectories from its transition state (TS) [Discuss. Faraday Soc. 33, 173 (1962)] is formally applied to polyatomic bimolecular reactions involving a barrier with the aim of estimating state-resolved integral cross sections. The two resulting approaches are rigorously equivalent to the conventional quasi-classical trajectory method, but are expected to substantially decrease the number of trajectories necessary to converge the calculations.

## 1 Introduction

The dynamics of polyatomic chemical reactions are commonly studied by means of the quasi-classical trajectory (QCT) method [1–3], for quantum scattering calculations [4–6] are very heavy, often prohibitive for such processes. However, one should not believe that conventional QCT calculations, within which trajectories are started from the reagent part of the phase space, are always easy to perform.

For barrier reactions, like for instance  $\text{OH} + \text{D}_2 \rightarrow \text{HOD} + \text{D}$  [7, 8] and  $\text{OH} + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{NH}_2$  [9], only a few percent of the trajectories appear to be reactive for common values of the collision energy (a few kcal/mol). This is because the incoming flux of trajectories through any surface located within the reagent channel is much larger than the minimum flux through the transition state (TS), located in the vicinity of the barrier top (for simplicity's sake, we do not consider processes involving multiple TSs up to the end of this work).

To circumvent this difficulty, J. C. Keck proposed to run trajectories from the TS forward and backward in time [10]. All these paths are reactive (and no reactive trajectory is potentially missed). The number of trajectories to run in order to calculate the rate constant is thus strongly minimized [10, 11].

The goal of this preliminary report is to build the formal framework corresponding to the application of Keck's idea to the estimation of state-resolved integral cross sections (ICS) for barrier polyatomic reactions. The two resulting approaches are strictly equivalent to the conventional QCT method, but are expected to be numerically more efficient.

Related developments have been performed by Frost and Smith for triatomic reactions [12] and by Hase and co-workers for polyatomic unimolecular fragmentations [13].

## 2 Theory

### 2.1 Molecular System

We consider the process  $A + B \rightarrow C + D$  where A, B, C and D are four non linear polyatomic molecules made of  $N_A$ ,  $N_B$ ,  $N_C$  and  $N_D$  atoms, respectively. In a first step, the transition state is supposed to be orthogonal to the reaction coordinate at the barrier saddle point.

The normal mode description of the vibration motion of A, B, C and D is assumed to be valid. Moreover, these species are supposed to be symmetric tops. The more complex asymmetric case will be considered in a future work.

In an ideal molecular beam experiment, A and B are in given quantum states specified in the next section. Their relative collision energy is denoted  $E_c$ , and their reduced mass,  $\mu$ .

The energy available with respect to the bottom of the reagent valley (an arbitrary choice which could be different) is denoted  $E$ .

### 2.2 Reagent and Product Quantum States

The quantum state of the reactants is specified by  $3N_A - 6$  vibrational normal mode quantum numbers forming vector  $\mathbf{n}_A$ ,  $3N_B - 6$  similar quantum numbers forming  $\mathbf{n}_B$ , and the eight quantized values  $J$ ,  $M$ ,  $L$ ,  $J_A$ ,  $J_B$ ,  $K$ ,  $K_A$  and  $K_B$  of, respectively, the total angular momentum ( $J$ ), its projection on the  $Z$ -axis of the laboratory frame ( $M$ ), the orbital angular momentum of A with respect to B ( $L$ ), the rotational angular momentum of A ( $J_A$ ), the rotational angular momentum of B ( $J_B$ ), the total rotational angular momentum ( $K$ ), and the two projections of the rotational angular momenta of A and B on one of their respective axes of inertia ( $K_A$  and  $K_B$ ).

All the previous quantum numbers but  $J$  and  $M$  form vector  $\mathbf{n}$ . Analogous numbers for the products form vector  $\mathbf{n}'$ .

### 2.3 Reagent and Product Action-Angle Coordinates

The classical analogues of the previous quantum numbers are the  $3N_A - 6$  and  $3N_B - 6$  vibrational actions forming vectors  $\mathbf{x}_A$  and  $\mathbf{x}_B$ , respectively, the total angular momentum  $j$ , its projection  $m$  on the  $Z$ -axis of the laboratory frame, the orbital angular momentum  $l$ , the rotational angular momenta  $j_A$  and  $j_B$  of A and B, respectively, the total rotational angular momentum  $k$ , and the projections  $k_A$  and  $k_B$  of the rotational angular momenta of A and B on one of their respective axes of inertia. The vibrational actions are expressed in  $\hbar$  unit while the momenta are in  $\hbar$  unit throughout this work.

All the previous actions but  $j$  and  $m$  form vector  $\mathbf{x}$ . Analogous numbers for the products form vector  $\mathbf{x}'$ .

To these actions correspond conjugate angles belonging to the range  $[0, 2\pi]$ . For  $j$  and  $m$ , these are  $\alpha$  and  $\beta$ . For the remaining actions, they are collectively denoted by  $\mathbf{q}$  for the reagents, and  $\mathbf{q}'$  for the products.

The dynamical state of the reagents is completely specified by  $\mathbf{x}$ ,  $\mathbf{q}$ ,  $j$ ,  $m$ ,  $\alpha$ ,  $\beta$ , the distance  $R$  between the mass centers of A and B, and its conjugate momentum  $P$ . The reagent phase space volume element is thus

$$d\Gamma = d\mathbf{x}d\mathbf{q}djdm\alpha d\beta dRdP. \quad (1)$$

Analogously, the dynamical state of the products is completely specified by  $\mathbf{x}'$ ,  $\mathbf{q}'$ ,  $j$ ,  $m$ ,  $\alpha$ ,  $\beta$ , the distance  $R'$  between the mass centers of C and D, and its conjugate momentum  $P'$ .

One may check that each phase space involves  $6N - 6$  coordinates, where  $N = N_A + N_B = N_C + N_D$ , as required within the center-of-mass system. Moreover, the total number of conjugate angles is  $3N - 6$ .

Such sets of phase space coordinates are discussed at length in ref. [14].

## 2.4 Action-Angle Coordinates at the TS

At the TS, there are  $3N - 7$  vibrational actions  $\mathbf{a}^\ddagger$  and the same number of conjugate angles  $\mathbf{q}_\mathbf{a}^\ddagger$ . The remaining phase space coordinates are  $j$ ,  $m$ ,  $\alpha$ ,  $\beta$ , the projection  $k^\ddagger$  of  $j$  on one of the axes of inertia of the TS, its conjugate angle  $\gamma^\ddagger$ , the reaction coordinate  $r^\ddagger$  and its conjugate momentum  $p^\ddagger$ , positive in the product direction. The TS is supposed to be defined by  $r^\ddagger = 0$ . Again, the total number of phase space coordinates is  $6N - 6$  (see, for instance, ref. [14] for more details).

$\mathbf{a}^\ddagger$  and  $k^\ddagger$  are collectively denoted by  $\mathbf{x}^\ddagger$  while  $\mathbf{q}_\mathbf{a}^\ddagger$  and  $\gamma^\ddagger$  are collectively denoted by  $\mathbf{q}^\ddagger$ . The phase space volume element at the TS is thus

$$d\Gamma^\ddagger = d\mathbf{x}^\ddagger d\mathbf{q}^\ddagger djdm\alpha d\beta dr^\ddagger dp^\ddagger. \quad (2)$$

## 2.5 State-resolved Integral Cross Section

The state-resolved ICS is given by

$$\sigma_{\mathbf{n}'\mathbf{n}} = \frac{1}{(2J_A + 1)(2J_B + 1)} \frac{\pi}{k_c^2} \sum_{JML'L} P_{\mathbf{n}'\mathbf{n}}^{JM} \quad (3)$$

with

$$k_c^2 = \frac{2\mu E_c}{\hbar^2}. \quad (4)$$

$P_{\mathbf{n}'\mathbf{n}}^{JM}$  is the probability of reaction from reagent state  $\mathbf{n}$  to product state  $\mathbf{n}'$  with  $J$  and  $M$  (and the collision energy  $E_c$ ).

## 2.6 Conventional Expression of State-to-State Probabilities

In the conventional QCT method [1–3], trajectories are run from the reagents onto the separated products (or reagents again). They are started at a large

initial value  $R_i$  of  $R$  such that A and B do not interact, with  $\mathbf{x} = \mathbf{n}$ ,  $j = J$ ,  $m = M$  and  $P$  determined by  $E_c$  and  $l = L$ . Formally, the ‘Bohr quantized’ version of  $P_{\mathbf{n}'\mathbf{n}}^{JM}$  is then given by

$$P_{\mathbf{n}'\mathbf{n}}^{JM} = \frac{1}{(2\pi)^{3N-6}} \int_{D_{\text{reac}}} d\mathbf{q} \delta(\mathbf{x}' - \mathbf{n}'), \quad (5)$$

where  $\mathbf{q}$  is integrated over the domain  $D_{\text{reac}}$  of initial angles leading to reactive trajectories, and  $\delta$  is the Dirac distribution.

This expression is the polyatomic analogue of the expression obtained for three-atom reactions from classical  $S$ -matrix theory [15] under the assumption of quenching of interference effects [3, 15–17]. Bohr quantization appears to be taken into account by building  $P_{\mathbf{n}'\mathbf{n}}^{JM}$  only from trajectories starting from integer values of reagent actions and finishing with integer values of product actions.

The weakness of Eq. (5) is that  $D_{\text{reac}}$  is *a-priori* unknown. Consequently, the smaller the measure of this region compared to the total volume  $(2\pi)^{3N-6}$  in the angle space, the less efficient the numerical calculation of  $P_{\mathbf{n}'\mathbf{n}}^{JM}$ .

## 2.7 TS Expression of State-to-State Probabilities

Eq. (5) can be rewritten as

$$P_{\mathbf{n}'\mathbf{n}}^{JM} = \frac{1}{(2\pi)^{3N-4}} \int_{D_{\text{reac}}} d\mathbf{x}d\mathbf{q}djdm d\alpha d\beta \delta(\mathbf{x} - \mathbf{n}) \delta(\mathbf{x}' - \mathbf{n}') \delta(j - J) \delta(m - M). \quad (6)$$

$\alpha$  and  $\beta$  are two Euler angles orienting the whole space (together with  $\cos^{-1}(M/J)$ ) [14]. Consequently,  $\mathbf{x}'$  does not depend on them. Integration over  $\alpha$  and  $\beta$  leads thus to  $(2\pi)^2$ . The remaining integrations over  $\mathbf{x}$ ,  $j$  and  $m$  remove the first, third and fourth delta functions. The equivalence between Eqs. (5) and (6) is thus proved.

Eq. (6) can in turn be transformed into

$$P_{\mathbf{n}'\mathbf{n}}^{JM} = \frac{1}{(2\pi)^{3N-4}} \int_{D_{\text{reac}}} d\mathbf{x}d\mathbf{q}djdm d\alpha d\beta dP \frac{|P|}{\mu} \Theta(-P) \Pi, \quad (7)$$

with

$$\Pi = \delta(H - E) \delta(\mathbf{x} - \mathbf{n}) \delta(\mathbf{x}' - \mathbf{n}') \delta(j - J) \delta(m - M). \quad (8)$$

$\Theta$  is the Heaviside function and the classical function of Hamilton of the system can be written as

$$H = \frac{P^2}{2\mu} + Q \quad (9)$$

( $Q$  is thus the sum of the potential energy and the rest of the kinetic energy). The equivalence between Eqs. (6) and (7) is straightforwardly proved by replacing

in Eq. (7),  $H$  by the right-hand-side of Eq. (9), and noting that  $dP|P|/\mu = dP^2/(2\mu)$ .

Now,  $d\mathbf{x}d\mathbf{q}djdm\alpha d\beta dP$  is, according to Eq. (1), equal to  $d\mathbf{\Gamma}/dR$ . It is thus the element of phase space surface orthogonal to the  $R$ -axis at  $R = R_i$ .  $d\mathbf{x}d\mathbf{q}djdm\alpha d\beta dP |P|/\mu \Theta(-P)$  is thus the elementary flux through the previous elementary area. Since this flux is conservative, one may substitute it in Eq. (7) by the analogous elementary flux  $d\mathbf{x}^\ddagger d\mathbf{q}^\ddagger djdm\alpha d\beta dp^\ddagger p^\ddagger \Theta(p^\ddagger)$  at the TS (the mass associated with  $p^\ddagger$  has been arbitrarily kept at one in the normal mode transformation). We thus arrive at

$$P_{\mathbf{n}'\mathbf{n}}^{JM} = \frac{1}{(2\pi)^{3N-4}} \int d\mathbf{x}^\ddagger d\mathbf{q}^\ddagger djdm\alpha d\beta dp^\ddagger p^\ddagger \Theta(p^\ddagger) \Pi. \tag{10}$$

No domain  $D_{reac}$  must be specified this time, since all the phase space states at the TS lie along reactive trajectories. Note that  $\mathbf{x}$  and  $\mathbf{x}'$  are now obtained by running trajectories from the TS backward and forward in time, respectively.

Since in terms of TS coordinates,  $H$  reads

$$H = \frac{p^\ddagger{}^2}{2} + Q^\ddagger, \tag{11}$$

subsequent integrations with respect to  $j, m, \alpha, \beta$  and  $p^\ddagger$  lead to

$$P_{\mathbf{n}'\mathbf{n}}^{JM} = \frac{1}{(2\pi)^{3N-6}} \int d\mathbf{x}^\ddagger d\mathbf{q}^\ddagger \delta(\mathbf{x} - \mathbf{n}) \delta(\mathbf{x}' - \mathbf{n}'). \tag{12}$$

Within the present approach,  $P_{\mathbf{n}'\mathbf{n}}^{JM}$  turns out to involve a microcanonical distribution of the phase space states at the TS.

For actual processes, however, the TS is never rigorously defined by  $r^\ddagger = 0$ , and other phase space bottlenecks along the reaction path may exist. The approximate TS (ATS) considered up to now is thus recrossed by part of the trajectories. Following Keck [10], the statistical weight  $\eta$  of a trajectory crossing the ATS with  $\mathbf{x}^\ddagger$  and  $\mathbf{q}^\ddagger$  is equal to (i) the inverse of the total number of crossings of the ATS towards the products along the entire trajectory if it is reactive or (ii) 0 if it is non reactive. Eq. (12) has thus to be modified as

$$P_{\mathbf{n}'\mathbf{n}}^{JM} = \frac{1}{(2\pi)^{3N-6}} \int d\mathbf{x}^\ddagger d\mathbf{q}^\ddagger \delta(\mathbf{x} - \mathbf{n}) \delta(\mathbf{x}' - \mathbf{n}') \eta. \tag{13}$$

This is the central expression of the first method proposed in this note.

In practice, the delta functions in the above expression can be replaced by Gaussian functions of the type

$$G(x) = \frac{1}{\pi^{1/2}\epsilon} \exp \left[ -\left(\frac{x}{\epsilon}\right)^2 \right], \tag{14}$$

for which the full width at half maximum (FWHM) is equal to  $2(\ln 2)^{1/2}\epsilon$ . This

procedure is called Gaussian binning (GB) [3, 16–18]. In a quantum spirit, i.e., to comply with Bohr quantization principle, one usually takes  $\epsilon$  at  $\sim 0.06$ , corresponding to a FWHM of  $\sim 10\%$ . However, it is known that for polyatomic reactions, calculations then scale like  $\sim 10^{N_v}$  where  $N_v$  is the total number of vibrational degrees-of-freedom involved in the process (within the present method,  $N_v = 3(N_A + N_B + N_C + N_D) - 12$ ). Consequently, GB turns out to be prohibitive for polyatomic reactions.

To go round this difficulty, one may use the 1GB procedure of Czako and Bowman [19, 20], which still deals with vibrational quantization to some extent, or simply, the standard binning (SB) procedure which replaces  $\delta(x)$  by 1 if  $|x| \leq 1/2$ , and 0 otherwise [3]. Note that GB with  $\epsilon$  at  $\sim 0.6$ , corresponding to a FWHM of  $\sim 100\%$ , is roughly equivalent to SB.

Finally,  $P_{\mathbf{n}'\mathbf{n}}^{JM}$  cannot depend on  $M$ , as the space is isotropic, and the sum over  $M$  in Eq. (3) leads thus to the common degeneracy factor  $2J+1$ . Moreover, one may transform the sum over  $L$  and  $L'$  in Eq. (3) into integrals, removing thereby the constraints on  $l$  and  $l'$  in Eq. (13), i.e.,  $\delta(l-L)$  and  $\delta(l'-L')$ .

## 2.8 Backward-Forward Method

A possible alternative to the previous method is as follows: (i) a relatively small number of phase space points (say, a few thousands) are selected at the TS according to a microcanonical distribution (see Eq. (12)); (ii) trajectories are run backward in time from these points, up to the reagents; (iii) the domain  $D_{\text{reac}}$  of angles  $\mathbf{q}$  leading to reaction is located from these trajectories; (iv) the conventional method (see Eq. (5)) is then used with a large number of trajectories run forward in time with  $\mathbf{q}$  randomly chosen within  $D_{\text{reac}}$ .

It is quite clear that ideally,  $D_{\text{reac}}$  should be a compact domain for the present approach to be efficient. This is expected to be the case if the dynamics between the reagents and the TS is direct, as is the case when there is no pre-barrier van der Waals well, for instance. In the contrary case, the numerical price to pay in order to locate  $D_{\text{reac}}$  might overcome the one to calculate Eq. (5) without backward step.

## 3 Conclusion

Two alternative and equivalent approaches to the conventional QCT method are proposed for the calculation of state-resolved ICS for polyatomic bimolecular reactions involving a barrier. Following J. C. Keck [10], both methods involve trajectories started from the TS in the direction of the products.

Within the first method, trajectories are run backward and forward in time until the reagents and the products are formed, respectively. Within the second approach, a relatively small number of trajectories are run backward in time in order to localize the initial phase space volume leading to reactive trajectories. A large number of paths is then run forward in time from this volume.

The codes necessary to apply these two methods to the processes mentioned in the introduction are under construction.

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