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Statistical properties of quantum probability fluctuations in complex-forming chemical reactions

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Abstract

The energy dependence of quantum complex-forming reaction probabilities is well known to involve sharp fluctuations, but little seems to be known about their amplitudes. We develop here, for triatomic reactions, an analytical approach of their statistical distribution. This approach shows that the fluctuation amplitudes mainly depend on the numbers of available quantum states in the reagent and product channels. Its predictions appear to be in good quantitative agreement with quantum scattering calculations for the prototypical reaction $\text{H}^+ + \text{H}_2$.

1 Introduction

The rate constant of a three-atom exchange reaction at temperature T is given by¹

$$k(T) \propto \sum_{\mathbf{n}} \int dE \exp\left(-\frac{E}{k_B T}\right) \sigma_{\mathbf{n}}(E) \quad (1)$$

with

$$\sigma_{\mathbf{n}}(E) \propto \sum_J (2J + 1) P_{\mathbf{n}}^J(E) \quad (2)$$

and

$$P_{\mathbf{n}}^J(E) = \sum_{v'} P_{v'\mathbf{n}}^J(E). \quad (3)$$

E is the total energy, J the total angular momentum, $\mathbf{n}$ the reagent quantum state, v' the product vibrational state and k_B is Boltzmann's constant. $P_{\mathbf{n}}^J(E)$ and $P_{v'\mathbf{n}}^J(E)$ are the total and v' -resolved reaction probabilities consistent with $(E, J, \mathbf{n})$. $\sigma_{\mathbf{n}}(E)$ is the $\mathbf{n}$ -dependent integral cross section (ICS). $k(T)$ and $\sigma_{\mathbf{n}}(E)$ are measured in kinetics and molecular beam experiments, respectively. Since both quantities depend on $P_{\mathbf{n}}^J(E)$ and hence $P_{v'\mathbf{n}}^J(E)$, the latter are central quantities of both chemical kinetics and reaction dynamics. This is why they have been extensively studied by means of theoretical dynamical approaches over the last decades.²⁻²⁷

For direct reactions proceeding through a simple barrier, like the benchmark $\text{F} + \text{H}_2$ reaction,² quantum scattering calculations show that $P_{v'\mathbf{n}}^J(E)$ and thus $P_{\mathbf{n}}^J(E)$ are smooth functions of E .^{2,3} In contrast, analogous calculations for complex-forming chemical reactions show that these probabilities strongly fluctuate in terms of E . For $P_{\mathbf{n}}^J(E)$ and $P_{0\mathbf{n}}^J(E)$, the mean amplitude of the fluctuations decreases as E increases, while for $P_{v'\mathbf{n}}^J(E)$ with $v' > 0$, it first increases and then decreases. These findings date back to the early 1990s for atomic ion-diatom reactions,⁴⁻⁶ and the early 2000s for neutral atom-diatom reactions.^{7,28} Since then, many studies have confirmed the previous observations.⁹⁻²⁷

The origin of the sharp fluctuations is rather well understood. The study of Smith life-time matrix^{6,29,30} indeed reveals that fluctuations are resonance structures due to dense sets of metastable states above the dissociation limit of the intermediate complex. These structures are related to Ericson fluctuations,³¹ first seen in nuclear reaction cross sections.

On the other hand, little seems to be known about the energy dependence of fluctuation amplitudes. The goal of the present report is to fill this gap by developing an analytical approach of the statistical properties of fluctuation amplitudes. Its predictions are then compared with exact quantum scattering calculations on the benchmark complex-forming reaction $\text{H}^+ + \text{H}_2 \longrightarrow \text{H}_2 + \text{H}^+$.¹⁴

2 Theory

2.1 Distribution of state-to-state probabilities

We focus on triatomic heteronuclear complex-forming reactions of the type $\text{A} + \text{BC} \longrightarrow \text{A} + \text{BC}$ (inelastic and elastic channel α), $\text{AC} + \text{B}$ (reactive channel β), or $\text{AB} + \text{C}$ (reactive channel γ). Moreover, we assume that the classical dynamics is chaotic within the strong coupling region defining the complex. Consequently, statistical quantum methods (SQM)³²⁻³⁴ are expected to accurately describe the mean values of state-to-state probabilities.

Mean-potential phase space theory³⁵ (MPPST) replaces the exact potential energy in

channel α by its value averaged over the orientation of the reagents, with an analogous procedure in channels β and γ . Moreover, MPPST assumes, like the celebrated phase space theory,^{36,37} that in this new potential made isotropic in all channels, all available final states are equally likely. Since MPPST generally leads to predictions in very good agreement with SQM ones,^{15,32,33,35,38} we use in the following the former instead of the latter.

We call v , j and l the vibrational, rotational and orbital quantum numbers in channel α , and $(v''j''l'')$ and $(v'j'l')$ their analogs in channels β and γ , respectively. The MPPST probability to go from (v, j, l) to $(v'j'l')$ at the collision energy E and total angular momentum J reads

$$P_{v'j'l',vjl}^J = 1/N_E^{J,p}, \quad (4)$$

where $N_E^{J,p}$ is the number of quantum states available at E and J , and having the parity $p = (-1)^{l+j} = (-1)^{l'+j'} = (-1)^{l''+j''}$. Note that Eq. (4) implicitly requires that (j, l) and (j', l') have the same parity; in the contrary case, $P_{v'j'l',vjl}^J$ is 0.

Statistical methods tell nothing about the fluctuations of $P_{v'j'l',vjl}^J$ around its statistical expectation. On the other hand, classical S -matrix theory^{39–42} (CSMT) provides an answer, as we now show. First of all, a few definitions are in order. We call $\mathbf{a}$ the vector made of the vibrational, rotational and orbital actions of the reagents,⁴³ and $\mathbf{q}$ the vector made of the angles conjugate to these actions. The whole set of trajectories at E and J starting from the reagents with $\mathbf{a} = (v, j, l)$ is obtained by continuously varying the components of $\mathbf{q}$ between 0 and 2π . The CSMT probability amplitude to go from (v, j, l) to $(v'j'l')$ at E and J is expressed as

$$S_{v'j'l',vjl}^J = \sum_{k=1}^N \rho_k e^{i\Omega_k} \quad (5)$$

with the pre-exponential factor given by

$$\rho_k = \left[(2\pi)^3 \left| \frac{d\mathbf{a}'}{d\mathbf{q}} \right|_k \right]^{-1/2}. \quad (6)$$

The sum is over those trajectories, among the previously defined set, which end in the

products with $\mathbf{a}' = (v', j', l')$. Owing to the fractal dependence of $\mathbf{a}'$ on $\mathbf{q}$, typical of chaotic dynamics, these trajectories are endless. Hence, in Eq. (5), N must be seen as an infinitely large integer. $\frac{d\mathbf{a}'}{d\mathbf{q}}$ is the determinant of the partial derivatives of the components of $\mathbf{a}'$ with respect to the components of $\mathbf{q}$. The phase Ω_k is an action integral not necessary to detail here (more details on Eqs. (5) and (6) are given elsewhere^{44,45}). We only have to know that due to the chaotic dynamics of the long-lived complex, this quantity is on average much larger than π , and highly dependent on the initial conditions, just as ρ_k . Consequently, when E slightly varies, the ρ_k 's and Ω_k 's strongly vary and so does $S_{v'j'l'vjl}^J$, as illustrated in Fig. 1 for $N = 2$ and three random selections of the ρ_k 's and Ω_k 's. Our purpose is to determine an

Figure 1: Representation of $S_{v'j'l'vjl}^J$, given by Eq. (5), for $N = 2$ and three different sets of values of $(\rho_1, \Omega_1, \rho_2, \Omega_2)$ (only displayed in one case) corresponding to three slightly different values of E . $|S_{v'j'l'vjl}^J|$, given by the length of the solid segments, strongly fluctuates from one set to another.

analytical expression of the distribution of $|S_{v'j'l'vjl}^J|$. We assume that the latter is satisfyingly reproduced by (i) randomly selecting the Ω_k 's and (ii) replacing the ρ_k 's by their average

value $\bar{\rho}$. The problem is thus rigorously equivalent to that of the resultant of a large number of vibrations of the same pitch and of arbitrary phase, resolved by Rayleigh.^{46,47} Setting $|S_{v'j'l'vjl}^J| = S$ and using Rayleigh's results, we arrive at

$$\eta(S) = \frac{2S}{N\bar{\rho}^2} e^{-\left(\frac{S^2}{N\bar{\rho}^2}\right)}. \quad (7)$$

Moreover, setting $P_{v'j'l'vjl}^J = P = S^2$, the distribution $\psi(P)$ of P is found from $\eta(S)$ to be given by

$$\psi(P) = \frac{1}{N\bar{\rho}^2} e^{-\left(\frac{P}{N\bar{\rho}^2}\right)} \quad (8)$$

(we have used the fact that $\psi(P)dP = \eta(S)dS$). The mean value of P deduced from $\psi(P)$ is $N\bar{\rho}^2$. But we have previously seen that this value is also expected to be accurately predicted by MPPST, i.e., by the right-hand-side of Eq. (4). Therefore, one can replace $N\bar{\rho}^2$ in Eq. (8) by $1/N_E^{J,p}$, thus leading to the first key expression of this work, namely, the Poisson law:

$$\psi(P) = N_E^{J,p} e^{-N_E^{J,p}P}. \quad (9)$$

These developments generalize to some extent those of Sec. 2.2 in Ref.⁴⁵. They also support the conjecture of Blümel and Smilansky,⁴⁸ and corroborate the quantum scattering calculations of Launay and Honvault.⁴⁹ Such developments, recently implemented in the *Chaotic Dynamics Model*,⁵⁰ have already been used to rationalize the asymmetry of differential cross sections in complex-forming atom-diatom reactions.

2.2 Statistical properties of fluctuation amplitudes

2.2.1 Total reaction probability

For simplicity's sake, $N_E^{J,p}$ will be denoted by N . Moreover, the number of final quantum states available in channels α , β and γ will be called N_α , N_β and N_γ , respectively. We thus have $N_\alpha + N_\beta + N_\gamma = N$. P_k will represent the population of the k^{th} state, whose value

is distributed according to Eq. (9). The values of k lower or equal to N_α correspond to reagent states, the remaining values to product states. The distribution of the total reaction probability P_R reads

$$\chi(P_R) = \omega \int \Pi_{k=1}^N dP_k \Pi_{k=1}^N \psi(P_k) \delta \left(P_R - \sum_{k=N_\alpha+1}^N P_k \right) \delta \left(1 - \sum_{k=1}^N P_k \right). \quad (10)$$

$\Pi_{k=1}^N \psi(P_k)$ is the statistical weight of the N -uplet $(P_1, \dots, P_N)$. The first delta function implies

$$P_R = \sum_{k=N_\alpha+1}^N P_k, \quad (11)$$

which is correct since the sum is over those values of k corresponding to product states. The second delta function implies

$$\sum_{k=1}^N P_k = 1 \quad (12)$$

as it should be (selecting the P_k 's according to Eq. (9) does not rigorously ensure this if N is not infinite). Using Eq. (11), Eq. (12) can be rewritten as

$$\sum_{k=1}^{N_\alpha} P_k = 1 - P_R. \quad (13)$$

Since P_1 and P_N are positive (as all the P_k 's), Eqs. (11) and (13) imply the following inequalities:

$$\sum_{k=2}^{N_\alpha} P_k \leq 1 - P_R \quad (14)$$

and

$$\sum_{k=N_\alpha+1}^{N-1} P_k \leq P_R. \quad (15)$$

Using Eq. (9) (with N instead of $N_E^{J,p}$) and integrating with respect to P_1 and P_N leads to

$$\chi(P_R) = \omega N^N e^{-N} \int \Pi_{k=2}^{N_\alpha} dP_k \Theta(1 - P_R - \sum_{k=2}^{N_\alpha} P_k) \int \Pi_{k=N_\alpha+1}^{N-1} dP_k \Theta(P_R - \sum_{k=N_\alpha+1}^{N-1} P_k). \quad (16)$$

$\Theta(y)$ is the Heaviside function, equal to 1 (0) if y is positive (negative). The two Heaviside terms ensure that constraints (14) and (15) are satisfied. In order to simplify this expression, we need to know the analytical expression of the integral

$$I_n = \int dx_1 \dots dx_n \Theta(\Omega - x_1 \dots - x_n) \quad (17)$$

where the x_k 's are real positive. Direct integration leads to

$$I_n = \frac{\Omega^n}{n!}. \quad (18)$$

Using Eq. (18) and the fact that $N_\alpha + N_\beta + N_\gamma = N$, Eq. (16) leads to

$$\chi(P_R) = \frac{\omega N^N e^{-N} P_R^{N_\beta + N_\gamma - 1} (1 - P_R)^{N_\alpha - 1}}{(N_\beta + N_\gamma - 1)!(N_\alpha - 1)!}. \quad (19)$$

As previously stated, ω is such that integrating $\chi(P_R)$ between 0 and 1 gives 1. In order to deduce ω from this constraint, we use the fact that

$$I_{KL} = \int_0^1 dP P^K (1 - P)^L = \frac{K!L!}{(K + L + 1)!} \quad (20)$$

(this result is obtained using the integration by parts formula). The resulting expression of ω is then substituted to the latter in Eq. (19), thereby leading to the second key expression of this work:

$$\chi(P_R) = \frac{(N - 1)!}{(N_\beta + N_\gamma - 1)!(N_\alpha - 1)!} P_R^{N_\beta + N_\gamma - 1} (1 - P_R)^{N_\alpha - 1}. \quad (21)$$

Using again Eq. (19), one finds after some step of simple algebra that the mean values of P_R and P_R^2 are given by

$$\overline{P_R} = \frac{N_\beta + N_\gamma}{N} \quad (22)$$

and

$$\overline{P_R^2} = \frac{(N_\beta + N_\gamma)(N_\beta + N_\gamma + 1)}{N(N + 1)}, \quad (23)$$

respectively. We note that Eq. (22) is the statistical expectation, in line with the basic assumptions of our treatment. From the two previous expressions, we deduce the third key expression of this work, i.e., the root mean square deviation (RMSD)

$$\Delta = \left(\overline{P_R^2} - \overline{P_R}^2 \right)^{1/2} = \frac{1}{N} \left[\frac{N_\alpha(N_\beta + N_\gamma)}{N + 1} \right]^{1/2}. \quad (24)$$

Within our approach, the mean amplitude of the fluctuations is thus fully determined by the numbers of available states in each channel at the energy E .

2.2.2 Vibrational state-resolved reaction probability

Let $N_\beta^{v'}$ and $N_\gamma^{v'}$ be the numbers of product quantum states in channel β and γ , respectively, whose vibrational quantum number is equal to v' . The distribution of the probability $P_{v'}$ that the products are formed in vibrational state v' is straightforwardly deduced from $\chi(P_R)$ (see Eq. (21)) by replacing $N_\beta + N_\gamma$ by $N_\beta^{v'} + N_\gamma^{v'}$, and N_α by $N - N_\beta^{v'} - N_\gamma^{v'}$. We thus arrive at

$$\chi_{v'}(P_{v'}) = \frac{(N - 1)!}{(N_\beta^{v'} + N_\gamma^{v'} - 1)!(N - N_\beta^{v'} + N_\gamma^{v'} - 1)!} P_{v'}^{N_\beta^{v'} + N_\gamma^{v'} - 1} (1 - P_{v'})^{N - N_\beta^{v'} - N_\gamma^{v'} - 1} \quad (25)$$

for the distribution of $P_{v'}$. Analogously, the RMSD associated to this distribution is found from Eq. (24) to be given by

$$\Delta_{v'} = \frac{1}{N} \left[\frac{(N_\beta^{v'} + N_\gamma^{v'})(N - N_\beta^{v'} - N_\gamma^{v'})}{N + 1} \right]^{1/2}. \quad (26)$$

These two expressions will be useful when the B and C atoms are identical.

3 Application to the $\text{H}^+ + \text{H}_2$ reaction

We now apply the previous statistical analysis to the ion-molecule reaction between H^+ and H_2 in the rovibrational ground state ($v = 0, j = 0$). The collision energy will be denoted by E_c . Fig. 2 displays a comparison between the predictions of the Chaotic Dynamics Model (CDM) on one hand, and Exact Quantum Mechanics (EQM)¹⁴ on the other hand, for the total reaction probability at $J = 0$ as a function of E_c . Within the CDM, the value of the probability is randomly chosen following the distribution law of Eq. (21) at each collision energy. Both CDM and EQM data are plotted each 0.5 meV. The similarity between the two sets of fluctuation amplitudes is striking. The fluctuation amplitudes around the mean probability $\overline{P_R} = 2/3$ and their decrease with increasing collision energy is well captured. The average of $2/3$ comes from the fact that the three channels are similar and two of them lead to the products (see Eq. (22) with $N_\alpha = N_\beta = N_\gamma = N/3$). We note that the CDM probability fluctuates faster than the EQM one, in particular for the largest values of E_c . This is because our model does not take into account the link between probability fluctuations and the resonance lifetime of metastable states. However, this link has been previously investigated^{6,30} and we are primarily concerned with fluctuation amplitudes.

The RMSD obtained from the CDM is displayed in Fig. 3 (see the red curve). We recall that this quantity was deduced from the distribution $\chi(P_R)$ of the reaction probability at the energy E_c (see Eq. (21), where the number of states available in all channels depend on E_c). But for a real reaction simulated quantum mechanically on a given potential energy surface, and for a specific value of E_c , the reaction probability has a single value, not a distribution of values. Nevertheless, one may go round this difficulty by considering an energy range of width δE centered on E_c over which the probability involves a few fluctuations, and calculate the RMSD from the probabilities available within this range. It is clear from the lower panel

Figure 2: $\text{H}^+ + \text{H}_2(0,0)$ reaction probability as a function of collision energy E_c for $J = 0$ total angular momentum. Up: CDM. Down: EQM.¹⁴ E_c is in eV.

of Fig. 2 that the larger E_c , the smaller the frequency of fluctuations, and the larger δE should be for the same number of fluctuations. In line with these ideas, δE was taken at 15, 30 and 100 meV for $E_c < 0.4\text{eV}$, $0.4\text{eV} < E_c < 1\text{eV}$ and $E_c > 1\text{eV}$, respectively. The

Figure 3: RMSD from CDM (red, Eq. (24)) and EQM.¹⁴ E_c is in eV.

resulting RMSD is compared with the CDM one (Eq. (24)) in Fig. 3. The agreement is on average quite good, hence suggesting that the envelop of the fluctuations is satisfyingly captured by the CDM. However, regularity regions over the δE energy range used to compute the EQM RMSD leads to deviations from the CDM one. From Eq. (24) and the fact that $N_\alpha = N_\beta = N_\gamma = N/3$, the CDM RMSD reduces to

$$\Delta = \frac{1}{3} \left[\frac{2}{N+1} \right]^{1/2}. \quad (27)$$

Hence, the larger N , the smaller Δ . In other words, the larger the number of available states, the more efficiently the fluctuations of their populations compensate each other. The minimum value of N being 3 (for $E_c = 0$), the upper bound of Δ is $1/(3\sqrt{2}) \sim 0.24$.

The v' -resolved reaction probabilities, randomly chosen according to the distribution law

of Eq. (25), are given in Fig. 4. As previously stated, the fluctuation amplitudes decrease for $v' = 0$ whereas for $v' = 1$, they first increase until $\overline{P}_{v'=1}$ reaches a maximum, and then decrease. Again, the CDM and EQM results are in good agreement as far as the fluctuation amplitudes are concerned. The non monotonous behaviour of $P_{v'}$ can be explained from Eq. (26). Setting $N_{\beta}^{v'} + N_{\gamma}^{v'} = N_{v'}$ for the total number of v' -states, and using the fact that slightly above their energy threshold, there are many more N states available than $N_{v'}$ states, one may easily show that Eq. (26) reduces to $\Delta_{v'} \approx \sqrt{N_{v'}}/N$. $\Delta_{v'}$ is thus zero at threshold, and then increases. However, the excited states $v' + 1, v' + 2, \dots$, become available as E increases, and hence, N increases faster than $N_{v'}$. For $N \gg N_{v'}$, we again have $\Delta_{v'} \approx \sqrt{N_{v'}}/N$, so the larger N with respect to $N_{v'}$, the smaller $\Delta_{v'}$. This explains why the fluctuation amplitudes involve a maximum for excited vibrational states. For $v' = 2$, the agreement between CDM and EQM is more moderate than for the two previous states, but still satisfying.

4 Conclusion

The first exact quantum scattering calculations for complex-forming chemical reactions date back to the early 90's.⁴⁻⁶ Since that time, it was observed that the energy-dependence of quantum reaction probabilities involve sharp fluctuations whose amplitudes tend to decrease as the energy increases.⁹⁻²⁷ In the present work, we have proposed a statistical analysis of these fluctuations based in part on classical S -matrix theory,³⁹⁻⁴² and in part on a few assumptions, the main ones being a chaotic classical dynamics and the validity of MPPST³⁵ (a simple and yet, quite realistic statistical theory). These developments allow to recover the Poisson law for the distribution of state-to-state probabilities, supporting thereby the conjecture of Blümel and Smilansky,⁴⁸ corroborated by the quantum scattering calculations of Launay and Honvault.⁴⁹ Starting from the Poisson law, we have derived analytical distributions of fluctuation amplitudes as well as their standard deviations, and successfully applied

Figure 4: $\text{H}^+ + \text{H}_2(0,0)$ v' -resolved reaction probabilities as a function of collision energy E_c for $J = 0$ total angular momentum. Left: CDM (Eq. (21)). Right: EQM.¹⁴ E_c is in eV.

them to the benchmark $\text{H}^+ + \text{H}_2$ reaction.¹⁴ In conclusion, we believe that the statistical tools proposed in this paper should help analyzing future quantum scattering calculations on complex-forming chemical reactions and related processes.

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