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Gaussian Weighted Trajectory Method. IV. No Rainbow Effect in Practice

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The Gaussian weighted trajectory method (GWTM) is a practical implementation of classical S matrix theory (CSMT) in the random phase approximation, CSMT being the first and simplest semi-classical approach of molecular collisions, developped in the early seventies. Though very close in spirit to the purely classical description, GWTM accounts to some extent for the quantization of the different degrees-of-freedom involved in the processes. While CSMT may give diverging final state distributions, in relation to the rainbow effect of elastic scattering theory, GWTM has never led to such a mathematical catastrophe. The goal of the present note is to explain this finding.

Key words: Gaussian weighted trajectory method, Classical S matrix theory, Rainbow effect

I. INTRODUCTION

For several decades, research in chemical reaction dynamics deepens our fundamental understanding of chemical reactivity. Nowadays, spatial and quantum state distributions of the final fragments of many molecular collisions are measured in highly sophisticated molecular beam experiments. Besides, these observables are predicted by accurate theoretical approaches, at least for the simplest processes. This synergy between experiment and theory allows to "shoot the movies" of the chemical encounters under scrutiny [1].

A routinely used theoretical approach is the quasi-classical trajectory method (QCTM) [2,3]. QCTM is indeed very friendly and no time consuming as compared to other approaches, in particular, exact quantum scattering (EQS) ones [4-11]. In addition to that, the applicability of EQS approaches turns out to be mainly limited to three-atom processes for the time being, even though a great deal of effort is made to go beyond the triatomic problem [12-15]. Therefore, QCTM should keep playing a central role for a long time, particularly in the case of polyatomic reactions for which more and more experimental data are available today [16-22].

Significant progress in the QCT method has been done in the last few years through the replacement of the standard binning (SB) or boxing procedure by the Gaussian weighting (GW) one [23-28]. This procedure consists in weighting each trajectory by a Gaussian-like coefficient such that the closer the final vibrational actions to integer values, the larger the coefficient. The Gaussian weighted trajectory method (GWTM) is particularly interesting in the very quantum situation where only a few vibrational and/or rotational levels of the final fragments can be populated. This approach might be an interesting alternative to existing classical treatments as far as the zero point energy leakage problem is concerned [29,30]. Last but not least, the adiabaticity correction recently added to the treatment seems to be promising, at least for indirect reactions [28].

Though initially proposed on the basis of rather intuitive arguments [23], the GW procedure can be shown to find its roots in classical S matrix theory (CSMT) [25,28], the former semi-classical approach of molecular collisions pioneered by Miller *et al.* in the early seventies [31-37]. GWTM is in fact a practical implementation of CSMT in the random phase approximation.

A well known drawback of CSMT is that, due to an effect analogous to the rainbow effect of elastic collision theory, it may lead to diverging S matrix elements and consequently, diverging final state distributions or state resolved integral cross sections (ICS). One might thus expect GWTM to also lead to such catastrophes, but as a matter of fact, this was never reported in the various GWTM calculations performed up to now [24,26-28,38-45]. In this work, this finding is justified.

II. DEVELOPMENTS

A. Classical S matrix theory

Consider the inelastic collision between an atom A and a diatom BC. The usual phase space coordinates employed to describe the previous process are (i) the distance R between A and the center of mass G of BC,

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(ii) its conjugate momentum P, (iii) the BC bond length r, (iv) its conjugate momentum p, (v) the orbital angular momentum l of A with respect to BC, (vi) its conjugate angle α_l, (vii) the rotational angular momentum j of BC, (viii) its conjugate angle α_j, (ix) the total angular momentum J, (x) its conjugate angle α, (xi) the projection M of the total angular momentum vector on a space-fixed axis, and (xii) its conjugate angle β. The angles belong to the range $[0, 2\pi]$. These variables are better defined in Ref.[46] and references therein. For the sake of simplicity, BC is supposed to be a harmonic oscillator (HO). The classical Hamiltonian of the system is then given by

$$H = \frac{P^2}{2\mu} + \frac{l^2}{2\mu R^2} + H_v + \frac{j^2}{2mr^2} + V_I(R, r, \theta) \quad (1)$$

with

$$H_v = \frac{p^2}{2m} + \frac{1}{2}m\omega^2(r - r_e)^2 \quad (2)$$

m and μ are respectively the reduced masses of BC and A with respect to BC, ω is the vibrational frequency of BC, r_e is its equilibrium distance, H_v is the vibrational energy of BC, θ is the angle between vectors $\mathbf{R}$ and $\mathbf{r}$, and $V_I(R, r, \theta)$ is the interaction potential energy between A and BC.

An alternative to the usual r and p coordinates, of importance for the following, is the set of angle-action coordinates (q, $\hbar x$) [33] related to the previous ones by

$$r = r_e + \sqrt{\frac{\hbar(2x+1)}{m\omega}} \sin q \quad (3)$$

and

$$p = m\sqrt{\hbar\omega(2x+1)} \cos q \quad (4)$$

H_v is now given by the well-known expression

$$H_v = \hbar\omega\Big(x + \frac{1}{2}\Big) \quad (5)$$

The dimensionless variable x is the classical equivalent to the vibrational quantum number. *Stricto-sensus*, x can only be termed action when $\hbar$ is kept at 1, as systematically supposed in the followings.

The fundamental quantities of quantum scattering theory are the S matrix elements or probability amplitudes to reach a given final quantum state when starting from a given initial one, the total energy being E. Calling (n_1, j_1, l_1) the initial quantum numbers and (n_2, j_2, l_2) the final ones, it is possible to show [33] that the S matrix element $S^J_{n_2 j_2 l_2, n_1 j_1 l_1}(E)$ satisfies the proportionality relation

$$S^J_{n_2 j_2 l_2, n_1 j_1 l_1}(E) \sim \int_0^\infty \mathrm{e}^{iEt}\mathrm{d}t\langle R_2 n_2 j_2 l_2|\mathrm{e}^{-i\hat{H}t}|R_1 n_1 j_1 l_1\rangle \quad (6)$$

where R_1 and R_2 are intended to be very large (infinite in principle) and $\hat{H}$ is the Hamiltonian operator, the exact expression of which is unnecessary here.

Replacing the propagator $\langle R_2 n_2 j_2 l_2|\mathrm{e}^{-i\hat{H}t}|R_1 n_1 j_1 l_1\rangle$ by a semi-classical expression of the van Vleck type and integrating over time within the stationary phase approximation led Miller to the central result of CSMT, also discovered at about the same time by Marcus within a WKB approach [31-37]:

$$S^J_{n_2 j_2 l_2, n_1 j_1 l_1}(E) = \sum_k \sqrt{\frac{1}{(2\pi)^3 \Delta_k}} \exp(i\phi_k) \quad (7)$$

The sum is over all the trajectories connecting (R_1, n_1, j_1, l_1) and (R_2, n_2, j_2, l_2) at the total energy E and the total angular momentum J. These trajectories correspond to the solutions of the equations $x(\bar{q}, \bar{\alpha}_j, \bar{\alpha}_l)$=$n_2$, $j(\bar{q}, \bar{\alpha}_j, \bar{\alpha}_l)$=$j_2$, and $l(\bar{q}, \bar{\alpha}_j, \bar{\alpha}_l)$=$l_2$, $\bar{q}, \bar{\alpha}_j$ and $\bar{\alpha}_l$ being the initial values of q, α_j and α_l at R=R_1, and $x(\bar{q}, \bar{\alpha}_j, \bar{\alpha}_l)$, $j(\bar{q}, \bar{\alpha}_j, \bar{\alpha}_l)$ and $l(\bar{q}, \bar{\alpha}_j, \bar{\alpha}_l)$ the final vibrational action, rotational angular momentum and orbital angular momentum at R=R_2. For the kth trajectory, the initial angles are denoted $(\bar{q}_k, \bar{\alpha}_{jk}, \bar{\alpha}_{lk})$. Δ_k is the Jacobian

$$\Delta = |det(M)| \quad (8)$$

with

$$M = \begin{pmatrix} \frac{\partial x}{\partial \bar{q}} & \frac{\partial x}{\partial \bar{\alpha}_j} & \frac{\partial x}{\partial \bar{\alpha}_l} \\ \frac{\partial j}{\partial \bar{q}} & \frac{\partial j}{\partial \bar{\alpha}_j} & \frac{\partial j}{\partial \bar{\alpha}_l} \\ \frac{\partial l}{\partial \bar{q}} & \frac{\partial l}{\partial \bar{\alpha}_j} & \frac{\partial l}{\partial \bar{\alpha}_l} \end{pmatrix} \quad (9)$$

for the kth trajectory and ϕ_k is the action

$$\phi = -\int_{-\infty}^{\infty} (R\dot{P} + q\dot{x} + \alpha_j\dot{j} + \alpha_l\dot{l})\mathrm{d}t' \quad (10)$$

along the same trajectory [47].

Squaring the modulus of $S^J_{n_2 j_2 l_2, n_1 j_1 l_1}(E)$ and assuming that the ϕ_ks are randomly distributed (random phase approximation) leads to the following population for the (n_2, j_2, l_2) state

$$P^J_{n_2 j_2 l_2, n_1 j_1 l_1}(E) = \sum_k \frac{1}{(2\pi)^3 \Delta_k} \quad (11)$$

The state resolved ICS for scattering from channel (n_1, j_1) to channel (n_2, j_2) is then given by

$$\sigma_{n_2 j_2, n_1 j_1}(E) = \frac{\pi}{(2j_1+1)k^2_{n_1 j_1}} \cdot \sum_{J, l_1, l_2} (2J+1) P^J_{n_2 j_2 l_2, n_1 j_1 l_1}(E) \quad (12)$$

where $k_{n_1 j_1}$ is the initial momentum consistent with E, n_1, and j_1.

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B. Expressing $P^J_{n_2j_2l_2,n_1j_1l_1}(E)$ in terms of Dirac distributions

We shall now prove that Eq.(11) can be rewritten as

$$P^J_{n_2j_2l_2,n_1j_1l_1}(E) = \frac{1}{(2\pi)^3}\int \mathrm{d}\bar{q}\ \mathrm{d}\bar{\alpha}_j\mathrm{d}\bar{\alpha}_l\delta_x\delta_j\delta_l \quad (13)$$

with

$$\delta_x = \delta[x(\bar{q},\bar{\alpha}_j,\bar{\alpha}_l)-n_2] \quad (14)$$
$$\delta_j = \delta[j(\bar{q},\bar{\alpha}_j,\bar{\alpha}_l)-j_2] \quad (15)$$
$$\delta_l = \delta[l(\bar{q},\bar{\alpha}_j,\bar{\alpha}_l)-l_2] \quad (16)$$

To this aim, let us consider the close neighborhood D_k of $(\bar{q}_k,\bar{\alpha}_{jk},\bar{\alpha}_{lk})$ in the three-dimensional space $(\bar{q},\bar{\alpha}_j,\bar{\alpha}_l)$. D_k is supposed to be sufficiently small for $x(\bar{q},\bar{\alpha}_j,\bar{\alpha}_l)$, $j(\bar{q},\bar{\alpha}_j,\bar{\alpha}_l)$, and $l(\bar{q},\bar{\alpha}_j,\bar{\alpha}_l)$ to be given inside it by their first order developments

$$x(\bar{q},\bar{\alpha}_j,\bar{\alpha}_l) = n_2 + Q_x \quad (17)$$
$$j(\bar{q},\bar{\alpha}_j,\bar{\alpha}_l) = j_2 + Q_j \quad (18)$$
$$l(\bar{q},\bar{\alpha}_j,\bar{\alpha}_l) = l_2 + Q_l \quad (19)$$

with

$$Q_x = \left.\frac{\partial x}{\partial\bar{q}}\right|_k(\bar{q}-\bar{q}_k) + \left.\frac{\partial x}{\partial\bar{\alpha}_j}\right|_k(\bar{\alpha}_j-\bar{\alpha}_{jk}) + \left.\frac{\partial x}{\partial\bar{\alpha}_l}\right|_k(\bar{\alpha}_l-\bar{\alpha}_{lk}) \quad (20)$$

$$Q_j = \left.\frac{\partial j}{\partial\bar{q}}\right|_k(\bar{q}-\bar{q}_k) + \left.\frac{\partial j}{\partial\bar{\alpha}_j}\right|_k(\bar{\alpha}_j-\bar{\alpha}_{jk}) + \left.\frac{\partial j}{\partial\bar{\alpha}_l}\right|_k(\bar{\alpha}_l-\bar{\alpha}_{lk}) \quad (21)$$

$$Q_l = \left.\frac{\partial l}{\partial\bar{q}}\right|_k(\bar{q}-\bar{q}_k) + \left.\frac{\partial l}{\partial\bar{\alpha}_j}\right|_k(\bar{\alpha}_j-\bar{\alpha}_{jk}) + \left.\frac{\partial l}{\partial\bar{\alpha}_l}\right|_k(\bar{\alpha}_l-\bar{\alpha}_{lk}) \quad (22)$$

Given that

$$\mathrm{d}Q_x\mathrm{d}Q_j\mathrm{d}Q_l = \Delta_k\mathrm{d}\bar{q}\mathrm{d}\bar{\alpha}_j\mathrm{d}\bar{\alpha}_l \quad (23)$$

we have from Eqs.(14)-(19)

$$\int_{D_k}\delta_x\delta_j\delta_l\mathrm{d}\bar{q}\mathrm{d}\bar{\alpha}_j\mathrm{d}\bar{\alpha}_l = \int_{D_k}\mathrm{d}Q_x\mathrm{d}Q_j\mathrm{d}Q_l\frac{1}{\Delta_k}\delta(Q_x)\delta(Q_j)\delta(Q_l) \quad (24)$$

leading immediately to

$$\int_{D_k}\mathrm{d}\bar{q}\mathrm{d}\bar{\alpha}_j\mathrm{d}\bar{\alpha}_l\delta_x\delta_j\delta_l = \frac{1}{\Delta_k} \quad (25)$$

Now, summing over k proves the equivalence between Eqs.(13) and (11).

C. SB-QCTM

QCTM within the SB procedure amounts to a Monte Carlo estimation of Eq.(13) with each Dirac distribution replaced by the square barrier function (SBF) $\Theta(u)$=1 if $|u|$ is lower than 1/2, and $\Theta(u)$=0 otherwise. Like the Delta distribution, the SBF is normalized to unity.

D. GWTM

GWTM amounts to a Monte Carlo estimation of Eq.(13) with the first Dirac distribution approximated by the Gaussian function

$$G(u) = \frac{\mathrm{e}^{-u^2/\epsilon^2}}{\pi^{1/2}\epsilon} \quad (26)$$

and the second and third Dirac distributions replaced by the SBF. ϵ is usually kept at 0.05. About ten times more trajectories than in SB-QCTM have then to be run in order to get the same accuracy [48].

The previous procedure supposes that at least ∼5 rotational levels are available to the products. In the contrary case, the second Dirac distribution may also be replaced by a Gaussian, though the calculations will then be about hundred times more time consuming than in SB-QCTM. However, most processes studied so far involve more than 10 final rotational levels and using a Gaussian or a SBF leads to the same result.

Any way, one notes that in GWTM, at least one of the Dirac distributions is replaced by a SBF.

E. No rainbow effect in practice

Assume that for the kth trajectory, Δ_k is zero, thus leading to an infinite value of $P^J_{n_2j_2l_2,n_1j_1l_1}(E)$ (see Eq.(11)). Since Δ_k is the product of the three eigenvalues of M, one of them is zero. The case where two eigenvalues are zero at the same time is expected to be so unlikely that we neglect such a possibility. One row of M (see Eq.(9)) can thus be written as a linear combination of the other two rows. We have thus

$$Q_l = \alpha Q_x + \beta Q_j \quad (27)$$

Last but not least, we do not consider up to the end of the present subsection the case where either Q_x or Q_j or Q_l is zero.

Let us now see the effect of replacing δ_l by the SBF

$$\Theta_l = \Theta[l(\bar{q},\bar{\alpha}_j,\bar{\alpha}_l)-l_2] \quad (28)$$

in Eq.(13), equivalent to Eq.(11).

To this aim, consider the matrix

$$M' = \begin{pmatrix} \frac{\partial x}{\partial\bar{q}} & \frac{\partial x}{\partial\bar{\alpha}_j} & \frac{\partial x}{\partial\bar{\alpha}_l} \\ \frac{\partial j}{\partial\bar{q}} & \frac{\partial j}{\partial\bar{\alpha}_j} & \frac{\partial j}{\partial\bar{\alpha}_l} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (29)$$

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where a_{31}, a_{32} and a_{33} are such that Δ'_k=$det(M')$ is different from zero. Defining Q'_l by

$$\Delta'_k Q'_l = a_{31}(\bar{q}-\bar{q}_k)+a_{32}(\bar{\alpha}_j-\bar{\alpha}_{jk})+ a_{33}(\bar{\alpha}_l-\bar{\alpha}_{lk}) \quad (30)$$

we have

$$\mathrm{d}Q_x\mathrm{d}Q_j\mathrm{d}Q'_l = \mathrm{d}\bar{q}\mathrm{d}\bar{\alpha}_j\mathrm{d}\bar{\alpha}_l \quad (31)$$

The contribution $P^{Jk}_{n_2j_2l_2,n_1j_1l_1}(E)$ to $P^{J}_{n_2j_2l_2,n_1j_1l_1}(E)$ due to the domain D_k can thus be written as

$$P^{Jk}_{n_2j_2l_2,n_1j_1l_1}(E) = \frac{1}{(2\pi)^3}\int_{D_k}\mathrm{d}Q_x\mathrm{d}Q_j\mathrm{d}Q'_l\delta_x\delta_j\delta_l \quad (32)$$

From Eqs.(14)-(19), we thus arrive at

$$P^{Jk}_{n_2j_2l_2,n_1j_1l_1}(E) = \frac{1}{(2\pi)^3}\cdot \int_{D_k}\mathrm{d}Q_x\mathrm{d}Q_j\mathrm{d}Q'_l\delta(Q_x)\delta(Q_j)\delta(\alpha Q_x+\beta Q_j) \quad (33)$$

It is quite clear that integration with respect to Q_x and Q_j makes the integrand equal to $\delta(0)$ which is infinite.

Now, if we replace δ_l by Θ_l (see Eq.(28)), we arrive at

$$P^{Jk}_{n_2j_2l_2,n_1j_1l_1}(E) = \frac{1}{(2\pi)^3}\int_{D_k}\mathrm{d}Q'_l \quad (34)$$

which has a finite value.

As a matter of fact, replacing one of the Dirac distributions by a SBF eliminates the possibility for $P^{Jk}_{n_2j_2l_2,n_1j_1l_1}(E)$, and thus $P^{J}_{n_2j_2l_2,n_1j_1l_1}(E)$, to diverge. This is precisely what is performed in GWTM, thereby justifying why no rainbow effect has been observed in the calculations carried out to date [24,26-28,38-45].

In the usual conditions of molecular beam experiments, j and l vary strongly during the collision, which is not necessarilly the case as far as x is concerned. Motion can be vibrationally adiabatic, at least partially, meaning that x=n_1 for a given volume of initial conditions $(\bar{q},\bar{\alpha}_j,\bar{\alpha}_l)$. Eq.(13) leads then to an infinite value of $P^{J}_{n_2j_2l_2,n_1j_1l_1}(E)$ when n_2=n_1. Eventhough replacing δ_x by a Gaussian in Eq.(13) will not make the previous population infinite in practice, its value will be much larger than 1. However, an adiabaticity correction is proposed elsewhere [28] to go round this difficulty. Within the framework of this correction, use of GWTM should exclude the possibility of any rainbow effect.

The present reasoning, developed in the case of inelastic collisions, can be straightforwardly extended to the case of reactive scattering.

III. CONCLUSION

So far, the possible rainbow effect of classical S matrix theory (CSMT) has never been observed in Gaussian weighted trajectory (GWT) calculations.

It has been shown in this work that the basic reason for the previous finding is that at least one Dirac distribution is replaced by a square barrier function in the derivation of the GWT method from CSMT.

In the case of vibrationally adiabatic processes, the rainbow effect should also not be observed in GWT calculations when the recently proposed adiabaticity correction is applied [28].

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[47] We intentionally forget the subtle problem of Morse-Maslov indices appearing in the developments when applying the stationary phase approximation. Though crucial for accurate semi-classical calculations, writing them explicitly is not necessary in the present work. For more details on these indices, see Ref.[37] and references therein.
[48] The populations obtained are unnormalized. For an alternative procedure leading to normalized populations, see Ref.[28].

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