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Semiclassical Wigner theory of photodissociation in three dimensions: Shedding light on its basis

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The semiclassical Wigner theory (SCWT) of photodissociation dynamics, initially proposed by Brown and Heller [J. Chem. Phys. **75**, 186 (1981)] in order to describe state distributions in the products of direct collinear photodissociations, was recently extended to realistic three-dimensional triatomic processes of the same type [Arbelo-González *et al.*, Phys. Chem. Chem. Phys. **15**, 9994 (2013)]. The resulting approach, which takes into account rotational motions in addition to vibrational and translational ones, was applied to a triatomic-like model of methyl iodide photodissociation and its predictions were found to be in nearly quantitative agreement with rigorous quantum results, but at a much lower computational cost, making thereby SCWT a potential tool for the study of polyatomic reaction dynamics. Here, we analyse the main reasons for this agreement by means of an elementary model of fragmentation explicitly dealing with the rotational motion only. We show that our formulation of SCWT makes it a semiclassical approximation to an approximate planar quantum treatment of the dynamics, both of sufficient quality for the whole treatment to be satisfying. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4916646>]

I. INTRODUCTION

Current molecular beam and laser techniques, in particular the fast-developing velocity map imaging method, make possible the measurement of the distribution of the translational energy between photodissociation products with an impressive accuracy, even for polyatomic reactions which are thus more and more studied.^{1–5}

Theoretical models are hence necessary to accurately predict product state populations⁶ from which the translational energy distribution is straightforwardly deduced.⁷ These models can then be used to analyse the reaction mechanism and find the key factors controlling the process.⁶ Besides, they can also serve to predict the outcomes of photofragmentations playing major roles in planetary atmospheres⁸ or interstellar clouds.⁹

Assuming the electronic problem of a process under scrutiny has been solved by the usual methods of quantum chemistry^{10–12} and the potential energy surfaces (PESs) involved in the process are available as well as their possible nonadiabatic couplings, state-of-the-art descriptions of its dynamics are performed within the framework of rigorous quantum treatments of nuclear motions.^{13–26} More often than not, however, these treatments can hardly be applied to polyatomic processes involving more than three atoms, for the basis sizes necessary to converge the calculations may either be prohibitive, or require computation times of several months.

As technically viable alternatives, two main classical dynamical methods are available, which allow to decrease computation times down to a few hours or days for polyatomic reactions. The most popular by far is the standard approach proposed on a mostly intuitive basis by Goursaud and Sizun in the mid-seventies^{27,28} for triatomic negative ion fragmentations with frozen rotational motions. The latter were later included in the treatment by Schinke²⁹ (see also chapter 5 of Ref. 6 for a detailed review on the subject). This method involves three steps: (i) the initial conditions of the trajectories are selected according to the Wigner distribution associated with the quantum state of the molecule before the optical excitation; (ii) the resulting swarm of phase space points is classically propagated in the excited electronic state onto the separated products; and (iii) the standard or Gaussian binning procedures are used to estimate the final state populations.⁷ This approach will simply be referred to as the *classical trajectory method* (CTM) in the following. The second approach, quite marginal compared to CTM, was introduced by Brown and Heller³⁰ a few years after Goursaud and Sizun, based on previous seminal and illuminating semiclassical developments by Heller^{31,32} in which, among other things, the approach of Goursaud and Sizun was put on firmer theoretical grounds. The two first steps of this method are the same as previously. On the other hand, the Wigner distributions associated with the product quantum states are used to weight trajectories. We call this second method *semiclassical Wigner theory* (SCWT) from now on. Just like Goursaud and Sizun, Brown and Heller derived SCWT assuming inactive rotational motions. In addition to mixing the quantum and classical descriptions in a very natural way, SCWT leads to

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calculations nearly as simple to perform as CTM. Moreover, Brown and Heller showed that for a collinear model of cyanogen iodide (ICN) fragmentation, SCWT expectations are in better agreement with approximate quantum or accurate semiclassical predictions than CTM ones.³⁰

Encouraged by this result, we recently decided to apply SCWT to the photodissociation of methyl iodide, a benchmark polyatomic reaction^{6,22,23,33} for which CTM is not always accurate. We realized, however, that contrary to CTM, SCWT had not been extended to realistic three-dimensional processes involving rotational motions since its original derivation.^{30,34} We thus spent some efforts in order to formally take into account these motions in SCWT, starting with the triatomic case for simplicity's sake. We then applied the resulting approach to a realistic three-atom like model of methyl iodide fragmentation.³⁵ After several unfruitful attempts, we eventually arrived at SCWT predictions in quantitative agreement with exact quantum results for the majority of the final state distributions considered, contrary to CTM. In addition, the semiclassical calculations were found to be far less demanding than the quantum ones, an important result as far as polyatomic reactions are concerned. Reference 35 will be called Part I in the following.

Somehow surprised by the quality of the previous agreement, unusual for a semiclassical description of non-collinear processes within curvilinear coordinates, we worked at identifying its causes. The goal of the present paper is to report this study which was mainly performed after the publication of Part I. We shall also give some important additional details on the calculations of Part I for the reader potentially interested in reproducing them.

It should be clear that the processes of interest here are direct dissociations proceeding through strongly repulsive excited electronic states such that no isolated resonance can be seen in the absorption spectrum.⁶ SCWT cannot deal with the interference effects associated with such resonances. Note that for unimolecular fragmentations which involve a very large number of resonances, efficient statistical-dynamical methods are available.^{7,36,37}

The paper is organized as follows. The three-dimensional version of SCWT proposed in Part I is summarized in Sec. II. A simple model of dissociation only involving the rotational motion is proposed in Sec. III in order to reduce as far as possible the complexity of the system while keeping it realistic. The study of the legitimacy of SCWT is then performed within the framework of this model. In Sec. IV, the case of methyl iodide photodissociation is considered in the light of the main findings of Sec. III. Section V concludes.

II. SUMMARY OF SCWT IN THREE DIMENSIONS

Though our ultimate goal is the application of SCWT to polyatomic species involving at least four atoms, we have for simplicity's sake limited up to now our developments to the triatomic case. Nevertheless, we plan to extend SCWT to larger systems in a near future. We first define the system of interest, second, present the key expressions of the method, and third, apply them to methyl iodide photodissociation.

A. System

A triatomic ABC molecule is optically excited by a photon of energy $h\nu$ from its rovibronic ground state at energy E_0 up to a given repulsive excited electronic state. The future products, AB and C, strongly repel each other immediately after the photon absorption and are formed in a few tens of femtoseconds. The total energy of ABC is $E = E_0 + h\nu$. The optical excitation is supposed not to excite the rotational motion of ABC, a standard and quite reasonable approximation. The Jacobi coordinates used throughout this work are (i) the modulus R of the vector $\mathbf{R}$ going from the center-of-mass (CM) G of AB to C, (ii) the modulus r of the vector $\mathbf{r}$ going from A to B, and (iii) the angle θ between $\mathbf{R}$ and $\mathbf{r}$. P , p , and P_θ are the momenta conjugate to R , r , and θ , respectively. V_g and V_e are the potential energies in the ground and excited electronic states, respectively. The zero of energy is defined as the minimum of V_e in the separated products. m is the reduced mass of AB and μ the one of C with respect to AB. $d(R, r, \theta)$ is the modulus of the transition dipole vector responsible for the electronic transition.⁶ The final quantum state of AB is denoted (n, j) , where n and j are the vibrational and rotational quantum numbers. τ denotes the running time.

The approach will be applied in Sec. II C to a triatomic-like model of methyl iodide photodissociation. The specificities of this model as compared to the present ABC system will then be specified.

B. Formulation

The next developments summarize those presented in Sec. II A of Part I. However, a few more details are provided which are useful, in particular for practical calculations.

The population of state (n, j) is given by³⁵

$$P_{nj} = \frac{\sigma_E^{nj}}{\sum_{nj} \sigma_E^{nj}}, \quad (1)$$

with

$$\sigma_E^{nj} = \left| \int_{-\infty}^{+\infty} dR \int_{-\infty}^{+\infty} dr \int_0^\pi d\theta \sin \theta \left[\frac{\mu}{2\pi\hbar^2 k_{nj}} \right]^{1/2} \times e^{-ik_{nj}R} \chi_n(r) Y_j^0(\theta) \Phi_t(R, r, \theta) \right|^2. \quad (2)$$

σ_E^{nj} is proportional to the state-resolved absorption cross section. k_{nj} is the wavenumber associated with AB in state (n, j) (see Eq. (15) in Part I). $\chi_n(r)$ is the n th excited vibrational state of AB. $Y_j^0(\theta)$ is the j th spherical harmonic (see Eq. (16) in Part I). $\Phi_t(R, r, \theta)$ is the time-evolved wavepacket in the excited electronic state at t when starting from

$$\Phi_0(R, r, \theta) = d(R, r, \theta) \phi_0(R, r, \theta) \quad (3)$$

at the instant 0 of the optical excitation. $\phi_0(R, r, \theta)$ is the internal ground state of the reagent molecule in the electronic ground state, i.e., prior to the optical excitation. t may, in principle, be any time for which $\Phi_t(R, r, \theta)$ entirely lies within the product channel. In the following, however, t will be identified as the minimum time for which this is the case.

This choice will minimize the duration of the dynamical calculations (there is obviously some arbitrariness in this choice). $\phi_0(R, r, \theta)$ is the solution of the time-independent Schrödinger equation

$$[\hat{T}_{3D} + \hat{V}_g]\phi_0 = E_0\phi_0, \quad (4)$$

with

$$\hat{T}_{3D} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2I \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta}. \quad (5)$$

$\hat{V}_g$ is the operator corresponding to V_g and I is the reduced moment of inertia of the system (see Eq. (A12) in Part I). $\hat{T}_{3D}$ is the kinetic energy operator for a zero total angular momentum (see Part I and references therein). The subscript 3D of the previous operator will prove meaningful in Sec. III. $\Phi_t(R, r, \theta)$ is the value at t of $\Phi_\tau(R, r, \theta)$, solution of the time-dependent

Schrödinger equation

$$i\hbar \frac{d\Phi_\tau}{d\tau} = [\hat{T}_{3D} + \hat{V}_e]\Phi_\tau, \quad (6)$$

where $\hat{V}_e$ is the operator corresponding to V_e . Though θ is limited to the range $[0, \pi]$ in Eq. (2), both $Y_j^0(\theta)$ and $\Phi_t(R, r, \theta)$ are mathematically defined for any positive or negative value of θ .

A strictly equivalent phase space integral expression of σ_E^{nj} (see Eq. (2)) is

$$\sigma_E^{nj} = (2\pi\hbar)^3 \int d\Gamma \rho_t(\Gamma) \rho_{tr}(R, P) \rho_n(r, p) \rho_j(\theta, P_\theta), \quad (7)$$

with $\Gamma = (R, r, \theta, P, p, P_\theta)$. $\rho_t(\Gamma)$ is the Wigner density related to $\Phi_t(R, r, \theta)$ by

$$\rho_t(\Gamma) = \frac{1}{(\pi\hbar)^3} \int_{-\infty}^{+\infty} ds_R \int_{-\infty}^{+\infty} ds_r \int_{s_-(\theta)}^{s_+(\theta)} ds_\theta e^{2i(Ps_R + ps_r + P_\theta s_\theta)/\hbar} \Phi_t^*(R + s_R, r + s_r, \theta + s_\theta) \Phi_t(R - s_R, r - s_r, \theta - s_\theta), \quad (8)$$

where for θ within the range $[-\pi, \pi]$,

$$s_-(\theta) = \max[-(\pi + \theta), \theta - \pi] \quad (9)$$

and

$$s_+(\theta) = \min[\pi + \theta, \pi - \theta], \quad (10)$$

while for $|\theta| > \pi$,

$$s_-(\theta) = s_+(\theta) = 0 \quad (11)$$

($\rho_t(\Gamma)$ is thus zero in the second case). These boundaries are represented in Fig. 1. Though they were not specified in Part I, they were taken into account in the calculations. Note that $\theta \pm s_\theta$ in Eq. (8) can take negative values, which is not a problem as we have previously seen that $\Phi_t(R, r, \theta)$ is mathematically defined for any real value of θ .

The translational and vibrational Wigner distributions $\rho_{tr}(R, P)$ and $\rho_n(r, p)$ are given by Eqs. (19) and (20) in Part I, respectively, and the rotational one is given by

$$\begin{aligned} \rho_j(\theta, P_\theta) &= \frac{1}{\pi\hbar} \int_{s_-(\theta)}^{s_+(\theta)} ds e^{2iP_\theta s/\hbar} \sin(\theta + s) \\ &\times Y_j^0(\theta + s) \sin(\theta - s) Y_j^0(\theta - s), \end{aligned} \quad (12)$$

where for θ within the range $[0, \pi]$,

$$s_-(\theta) = \max[-\theta, \theta - \pi] \quad (13)$$

and

$$s_+(\theta) = \min[\theta, \pi - \theta], \quad (14)$$

and for $\theta < 0$ or $\theta > \pi$, $s_-(\theta)$ and $s_+(\theta)$ satisfy Eq. (11) (thus making $\rho_j(\theta, P_\theta)$ zero). These boundaries are represented in Fig. 2. Note they are different from those displayed in Fig. 1. Again, $\theta \pm s$ in Eq. (12) can take negative values, which is not a problem as we have previously seen that $Y_j^0(\theta)$ is mathematically defined for any real value of θ .

We now introduce in the previous rigorous quantum formulation the following classical ingredient: we assume that $\rho_\tau^C(\Gamma)$, obtained by propagating $\rho_0(\Gamma)$ from $\tau = 0$ to $\tau = t$ according to Liouville equation,³⁸ is a satisfying approximation of $\rho_\tau(\Gamma)$. Consequently, we may rewrite Eq. (7) as

$$\sigma_E^{nj} \approx (2\pi\hbar)^3 \int d\Gamma \rho_t^C(\Gamma) \rho_{tr}(R, P) \rho_n(r, p) \rho_j(\theta, P_\theta). \quad (15)$$

Now, $\rho_t^C(\Gamma)$ satisfies the identity

$$\rho_t^C(\Gamma) d\Gamma = \rho_0(\Gamma_0) d\Gamma_0 \quad (16)$$

FIG. 1. Lower and upper bounds $s_-(\theta)$ and $s_+(\theta)$ of s_θ in Eq. (8). The green area corresponds to the relatively small values of $|\theta|$. For such values, it is clear that $s_-(\theta)$ is slightly larger than $-\pi$ while $s_+(\theta)$ is slightly lower than π .

FIG. 2. Lower and upper bounds $s_-(\theta)$ and $s_+(\theta)$ of s in Eq. (12).

in which $\mathbf{\Gamma}$ and $d\mathbf{\Gamma}$ should, respectively, be understood as the dynamical state of ABC and the volume element reached at time t when starting from state $\mathbf{\Gamma}_0$ and the volume element $d\mathbf{\Gamma}_0$ at time 0. Equation (16) expresses a basic property of classical mechanics, namely, the fact that the probability to lie within $d\mathbf{\Gamma}$ does not depend on t . For clarity's sake, the components of $\mathbf{\Gamma}$ will be called $(R_t, r_t, \theta_t, P_t, p_t, P_{\theta_t})$ in the following. They are determined by solving Hamilton equations⁶

$$\frac{du}{d\tau} = \frac{dH_e}{dp_u} \quad (17)$$

and

$$\frac{dp_u}{d\tau} = -\frac{dH_e}{du}, \quad (18)$$

with $(u, p_u) = (R, P)$, (r, p) , or (θ, P_θ) and H_e is the classical function of Hamilton (see Eq. (24) in Part I). Equations (15) and (16) finally lead to a semiclassical Wigner expression analogous to the one of Brown and Heller^{30,34}

$$\sigma_E^{nj} = (2\pi\hbar)^3 \int d\mathbf{\Gamma}_0 \rho_0(\mathbf{\Gamma}_0) \rho_r(R_t, P_t) \times \rho_n(r_t, p_t) \rho_j(\theta_t, P_{\theta_t}), \quad (19)$$

the only difference being that the rotational motion of AB is now taken into account. In Part I, we replaced the calculation of the cross sections at t by the analogous calculation at a given value of the distance R roughly defining the frontier between the reagent molecule and the free products. As shown below, however, such a replacement does not seem to be necessary.

C. Application to the photodissociation of methyl iodide

The triatomic-like model used in this work is the same as in Part I and has thus been detailed there and in references therein. Hence, we only briefly redefine it here. Nevertheless, we take the opportunity of this work to give some important additional details omitted in Part I.

The CH_3I molecule is considered as a CXI pseudo-triatomic molecule, the pseudoatom $X = \text{H}_3$ being located at the CM of the three H atoms. $\mathbf{R}$ is the vector going from the CM of CX to I, and $\mathbf{r}$ is the vector going from X to C. Its modulus r represents the umbrella bend of the CH_3 group. The C_{3v} symmetry of CH_3 is assumed to be preserved throughout the whole fragmentation (see Fig. 1 in Part I). CH_3I is assumed to be dissociated upon optical excitation at 266 nm (A band) from the $\tilde{X}^1A_1$ electronic ground state to the 3Q_0 and 1Q_1 electronic excited states. The $\tilde{X}^1A_1$ and 1Q_1 electronic surfaces correlate asymptotically with the $\text{CH}_3 + \text{I}(^2P_{3/2})$ products, while the 3Q_0 surface correlates with the $\text{CH}_3 + \text{I}^*(^2P_{1/2})$ products. The origin of the PESs and the transition dipole moments used in the calculations is detailed in Part I. The 3Q_0 and 1Q_1 states are nonadiabatically coupled. For simplicity's sake, however, we ignored this fact, focusing our attention on SCWT for fragmentations taking place adiabatically on single excited electronic states. SCWT, however, can be straightforwardly extended to processes involving nonadiabatic transitions by using several approaches, like the Landau-Zener-Stueckelberg model,³⁹ its extension by Zhu and Nakamura,⁴⁰ or the surface hopping method of Tully^{41,42} (this is not an exhaustive list).

Upon optical excitation at 266 nm, the energies available to the final products in the 3Q_0 and 1Q_1 states are $11\,258.53\text{ cm}^{-1}$ and $18\,862.09\text{ cm}^{-1}$, respectively. The reduced moment of inertia I is given by Eq. (A12) in Part I with mr^2 replaced by the moment of inertia I_{CH_3} of CH_3 , given by Eqs. (3) and (4) of Ref. 22. The initial state $\phi_0(R, r, \theta)$ of CH_3I , the vibrational eigenstates χ_n of CH_3 and their corresponding eigenenergies E_n were determined by variational approaches.²² The energy of the final state (n, j) of CH_3 is approximated by

$$E_{nj} = E_n + \frac{\hbar^2 j(j+1)}{2I_{\text{CH}_3}^e}, \quad (20)$$

where $I_{\text{CH}_3}^e$ is the value of I_{CH_3} at the planar equilibrium geometry of CH_3 , corresponding to $r = 0$. E_{nj} leads to the wave number k_{nj} (see Eq. (15) in Part I) from which the translational Wigner distribution (see Eq. (19) in Part I) depends. The wavepacket $\Phi_0(R, r, \theta) = d(R, r, \theta)\phi_0(R, r, \theta)$ at time 0 was found to be very well fitted by the product of three Gaussians

$$\Phi_0(R, r, \theta) = \eta \exp \left[-\alpha_R(R - \bar{R})^2 - \alpha_r(r - \bar{r})^2 - \alpha_\theta\theta^2 \right], \quad (21)$$

where η is a normalization factor not necessary to specify. The resulting Wigner density $\rho_0(\mathbf{\Gamma})$, given by Eq. (8), appears to be accurately approximated by

$$\rho_0(\mathbf{\Gamma}) = \frac{1}{\pi^3} \rho_1(R, P_R) \rho_2(r, p_r) \rho_3(\theta, P_\theta), \quad (22)$$

with

$$\rho_1(R, P_R) = \exp \left[-2\alpha_R(R - \bar{R})^2 - P_R^2/(2\alpha_R) \right], \quad (23)$$

$$\rho_2(r, p_r) = \exp \left[-2\alpha_r(r - \bar{r})^2 - p_r^2/(2\alpha_r) \right], \quad (24)$$

and

$$\rho_3(\theta, P_\theta) = \exp \left[-2\alpha_\theta\theta^2 - P_\theta^2/(2\alpha_\theta) \right]. \quad (25)$$

For the 1Q_1 state, $\alpha_R = 28.2467$, $\alpha_r = 12.7204$, $\alpha_\theta = 9.3612$, $\bar{R} = 4.117$, and $\bar{r} = 0.689$. These values are in atomic units (a.u.). For the 3Q_0 state, the values of α_R , α_r , and α_θ are unchanged, but $\bar{R} = 4.167$ and $\bar{r} = 0.666$. The previous expression of $\rho_0(\Gamma)$ was then used to generate the initial conditions Γ_0 (see Eq. (19)) of 10^6 trajectories in each electronic state. In practice, Γ_0 was randomly chosen within a hypercubic volume such that $\rho_0(\Gamma)$ is negligible at the limits of this volume. Then, a random number was selected and the initial conditions were accepted when $\pi^3\rho_0(\Gamma)$, at most equal to 1, was found larger than the random number. Otherwise, they were rejected. Trajectories were run according to Eqs. (17) and (18) by means of the fourth-order Runge-Kutta integrator⁴³ up to $t = 4100$ and 2500 a.u. (about 100 and 60 fs) in the 3Q_0 and 1Q_1 states, respectively. These durations are necessary for the swarm of trajectories to definitely have left the interaction region. The time step was set at 4 a.u. ≈ 0.1 fs, a standard choice for classical simulations of gas-phase chemical reactions. From their final conditions, trajectories were assigned the statistical weights equal to the product of the translational, vibrational, and rotational Wigner densities (see Eqs. (19) and (20) in Part I and Eq. (12) in the present work).⁴⁴ These weights were finally added in order to get a number proportional to σ_E^{nj} (see Eq. (19)) from which P_{nj} was deduced (see Eq. (1)).

The vibrational state distributions obtained from exact quantum mechanical (QM) calculations (see Ref. 35 and

references therein for the technical details) and SCWT are represented in Fig. 3 while the rotational state distributions for given vibrational states are shown in Fig. 4. The semiclassical results are found to be in close agreement with the quantum ones, just like in Part I. We thus note that, as previously outlined, stopping the trajectories at a given time rather than at a given radial distance leads to similar predictions. Both criteria seem to minimize in roughly the same way the degrading effect which progressively alters state distributions on the way to infinitely separated products.^{34,45}

Last but not least, running 1.5×10^5 and 10^5 trajectories for the 3Q_0 and 1Q_1 states, respectively, is enough to recover the SCWT rotational state distributions displayed in Fig. 4. Even less trajectories (2×10^4 per electronic state) suffice for the vibrational state distributions shown in Fig. 3. The real times necessary to run these trajectories are ~ 13 min (rotational state distributions) and ~ 2 min (vibrational state distributions) on a single processor, against ~ 47 min for parallelized QM calculations on 31 processors. The small numerical cost of SCWT is an encouraging result as regards the treatment of polyatomic reactions.

The whole information given in the present paper and in Part I should allow the interested reader to reproduce our calculations. In addition, our codes are available on demand. Note that the codes used to get the SCWT results presented here and in Part I have, respectively, been constructed by L.B. and W.A.-G. in an independent manner. The close agreement found between their predictions (as it should be) strengthens their reliability.

III. JUSTIFICATION OF THE TREATMENT OF ROTATIONAL MOTIONS IN THE PREVIOUS FORMULATION

Here, we propose a simple fragmentation model with the aim of justifying the treatment of rotational motions merely presented as a recipe in Sec. II. In order to reduce as much as possible the complexity of the study, the model ignores the vibrational motion of the nascent diatom while the translational motion is implicitly taken into account. The model is presented in Sec. III A. Sections III B–III D are preparatory steps necessary for the final derivation of SCWT, performed in Sec. III E.

A. Model system

We consider an asymmetric linear rigid rotor whose center-of-mass belongs to a space-fixed z-axis, and an atom recoiling from the rotor along the previous axis. θ is the polar angle between the (oriented) rotor and the z-axis and ψ is the azimuth of the rotor with respect to the x-axis.

We shall use the acronym 3D as subscript or superscript in the rest of the developments in order to indicate that an operator, a state, or a density refers to the rotor in the three-dimensional space. The purpose of this notation is to differentiate this case from the one introduced further below in which the rotor is constrained to lie within a space-fixed plane, and to which the acronym 2D will refer.

FIG. 3. Vibrational state distributions in the 3Q_0 (upper panel) and 1Q_1 (lower panel) electronic states, found by means of QM (red curves) and SCWT (blue dashed curves).

FIG. 4. Vibrationaly resolved rotational state distributions in the 3Q_0 (left panels) and 1Q_1 (right panels) electronic states, found by means of QM (red curves) and SCWT (blue dashed curves).

The kinetic energy operator is given here by

$$\hat{T}_{3D} = -\frac{\hbar^2}{2I} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \psi^2} \right), \quad (26)$$

where, again, I is the moment of inertia of the rotor. The interaction between the rotor and the atom, however, is supposed not to depend on ψ . Moreover, the azimuthal quantum number is supposed to be 0. Therefore, the state of the rotor will be developed on the spherical harmonics Y_j^0 , which only depend on θ . The last term in Eq. (26) is thus useless and the effective kinetic operator reads

$$\hat{T}_{3D} = -\frac{\hbar^2}{2I \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta}. \quad (27)$$

When the atom is close to the rotor, its rotation is strongly hindered, but as time goes on, the rotor rotates more and more freely. A time-dependent potential corresponding to this system is

$$V_\tau(\theta) = 2c \sin^2(\theta/2) e^{-\lambda\tau}. \quad (28)$$

This expression was chosen in order to mimic the excited state dynamics following the optical excitation of CH_3I , as will be reflected by the final rotational state distribution. The values of the parameters c and λ as well as those introduced later below will be taken accordingly. At time 0, the state of the rotor is denoted by $\Phi_0(\theta)$ while $\Phi_\tau^{3D}(\theta)$ represents the time-evolved wavepacket. The final rotational state distribution is given by

$$P_j^{3D} = \left| \int_0^\pi d\theta \, 2\pi \sin \theta Y_j^0(\theta) \Phi_\tau^{3D}(\theta) \right|^2, \quad (29)$$

where t is sufficiently large for $V_t(\theta)$ to be vanishingly small whatever the value of θ . As in Sec. II B, we assume in the following that t is the minimum time satisfying the previous requirement. Moreover, the wavepacket is again defined for any real value of θ , so we shall not limit its representation to the range $[0, \pi]$ in the following. The initial state of the rotor is chosen to be

$$\Phi_0(\theta) = \eta e^{-\alpha\theta^2}, \quad (30)$$

with $\eta = 2.5337$ and $\alpha = 10$. This state is comparable to the angular part of $\Phi_0(R, r, \theta)$ for CH_3I . It is normalized to unity as follows:

$$\int_0^\pi d\theta \, 2\pi \sin \theta |\Phi_0(\theta)|^2 = 1. \quad (31)$$

The norm being a conserved quantity, $\Phi_t^{3D}(\theta)$ also satisfies the above relation. $\Phi_\tau^{3D}(\theta)$ can generally be expressed as

$$\Phi_\tau^{3D}(\theta) = \sum_{j=0}^N c_j(\tau) Y_j^0(\theta) e^{-iE_j\tau/\hbar}, \quad (32)$$

with

$$E_j = \frac{\hbar^2 j(j+1)}{2I}. \quad (33)$$

We found that taking N at 20 is enough for converging the calculations. $c_j(\tau)$ is a complex number and it is clear from Eqs. (29) and (32) and the fact that $Y_j^0(\theta)$ satisfies Eq. (31), that

$$P_j^{3D} = |c_j(t)|^2. \quad (34)$$

FIG. 5. Red curve: $|\Phi_t^{3D}(\theta)|^2$, obtained from Eq. (6) with $\hat{T}_{3D}$ given by Eq. (27); blue curve: $|\Phi_{t+\delta_t}^{2D}(\theta)|^2$, obtained from Eq. (6) with $\hat{T}_{3D}$ replaced by $\hat{T}_{2D}$, given by Eq. (36), and Eq. (38). $t = 3500$ and $\delta_t = 700$, in a.u. The remaining magenta and green curves are defined within the figure.

From Eqs. (6) and (32), we arrived at a set of coupled differential equations satisfied by the real and imaginary parts of the coefficients $c_j(\tau)$, which can simply be solved by using standard integrators. These equations are summarized in Appendix A. We performed calculations for the following set of parameters: $c = 0.17$, $\lambda = 0.0022$, and $I = 11585$ (the value of $I_{CH_3}^e$), in a.u. c is such that $V_0(\theta)$ fits the true potential $V_e(\bar{R}, \bar{r}, \theta)$ in the 3Q_0 state. λ was chosen in order to make P_j^{3D} resemble P_{0j} for CH_3I in the 3Q_0 electronic state (see the left upper panel in Fig. 4). The angular dependence of $V_r(\theta)$ turns out to be negligible for τ larger than $t = 3500$, beyond which the fragmentation is considered as finished. A fourth-order Runge-Kutta integrator⁴³ was used with a time step of 0.1 a.u. Such a small value was necessary to keep the norm of the wavepacket at roughly one to one part in thousand during the propagation. In Fig. 5, the probability densities $|\Phi_0(\theta)|^2$ and $|\Phi_t^{3D}(\theta)|^2$ are represented by the magenta and red curves, respectively, within the range $[-\pi, \pi]$. Since the maximum of $|\Phi_0(\theta)|^2$ is much larger than the one of $|\Phi_t^{3D}(\theta)|^2$, only the base of $|\Phi_0(\theta)|^2$ is shown. As a matter of fact, the Gaussian shape of the initial state (see Eq. (30)) is preserved by the spreading of the wavepacket. The green curve represents $V_0(\theta)$. Its relative shape is conserved as time increases (see Eq. (28)). The width of $|\Phi_t^{3D}(\theta)|^2$ turns out to be sufficiently small as compared to 2π for $|\Phi_t^{3D}(\theta)|^2$ to be negligible at $\pm\pi$. $V_r(\theta)$ turns out to be nearly quadratic over the range where $|\Phi_t^{3D}(\theta)|^2$ is nonzero up to $\tau = t$. These two facts will have important consequences in the following. The rotational state distribution is represented by the red solid curve in Fig. 6. As previously stated, this distribution closely resembles the one displayed in the left-upper panel of Fig. 4.

B. Approximate planar quantum treatment

We shall now show that the rotational state distribution is very satisfyingly reproduced when constraining the rotational motion within a space-fixed plane containing the z -axis. We

FIG. 6. Rotational state distributions found by exact quantum (red solid curve), approximate quantum (blue dashed curve), and semiclassical Wigner (turquoise dashed-dotted curve) calculations.

shall in fact demonstrate further in this work that SCWT is a close approximation to the quantum dynamics in such a plane, explaining thereby the accuracy of the SCWT rotational state distribution (see Secs. III C–III E).

As stated above, we artificially limit the motion of the rotor to the (x, z) plane (we could have chosen (y, z) as well, or any other plane containing the z -axis). In this case, the angular momentum operator reads

$$\hat{j} = \frac{\hbar}{i} \frac{\partial}{\partial \theta}. \quad (35)$$

The kinetic energy operator is thus

$$\hat{T}_{2D} = \frac{\hat{j}^2}{2I} = -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \theta^2}. \quad (36)$$

$\hat{T}_{3D}$ (see Eq. (27)) can then be rewritten as

$$\hat{T}_{3D} = \hat{T}_{2D} - \frac{\hbar^2}{2I} \cot \theta \frac{\partial}{\partial \theta}. \quad (37)$$

The right-most term in Eq. (37) plays a minor role as compared to $\hat{T}_{2D}$ within the neighborhood of $\pi/2$, but a major role at the poles.

We repeated the previous calculations with $\hat{T}_{2D}$ instead of $\hat{T}_{3D}$, calling $\Phi_t^{2D}(\theta)$ the resulting wavepacket. A summary of the developments corresponding to these calculations is given in Appendix B. At time t , we found that $|\Phi_t^{2D}(\theta)|^2$ still had a Gaussian shape, but with a width smaller than the one of $|\Phi_t^{3D}(\theta)|^2$. We thus kept propagating $\Phi_t^{2D}(\theta)$ beyond $\tau = t$ until the spreading of the wavepacket made the width of the 2D density equal to the 3D one. The time at which this happened was $t' = 4200$ a.u. The time-delay $\delta_t = t' - t$ was thus found equal to $4200 - 3500 = 700$ a.u. In addition, we observed that $\Phi_{t+\delta_t}^{2D}(\theta)$ was not normalized like $\Phi_t^{3D}(\theta)$, i.e., its norm calculated according to Eq. (31) was not equal to 1. The reason is that $\hat{T}_{2D}$ confers on θ the status of a Cartesian coordinate for which the definition of the norm of a wavefunction does not involve the $\sin \theta$ factor. The norm such as defined by the left-hand-side of Eq. (31) has thus no reason to be conserved by the 2D propagation. The norm of $\Phi_t^{3D}(\theta)$ is equal to 1 at time 0, but

FIG. 7. Real and imaginary parts of $\Phi_t^{3D}(\theta)$ and $\bar{\Phi}_{t+\delta_t}^{2D}(\theta)$.

is generally different from 1 at later times. We thus considered

$$|\bar{\Phi}_{\tau+\delta_\tau}^{2D}(\theta)|^2 = \frac{|\Phi_{\tau+\delta_\tau}^{2D}(\theta)|^2}{\int_0^\pi d\theta \, 2\pi \sin \theta |\Phi_{\tau+\delta_\tau}^{2D}(\theta)|^2}, \quad (38)$$

which obviously complies with the 3D normalization rule, and compared it with $|\Phi_t^{3D}(\theta)|^2$ in Fig. 5 (blue curve against red one). Both densities are in close agreement.

We then decided to compare the real and imaginary parts of $\bar{\Phi}_{\tau+\delta_\tau}^{2D}(\theta)$ with the ones of $\Phi_t^{3D}(\theta)$. Since only the modulus of the former can be deduced from Eq. (38), we considered the expression

$$\bar{\Phi}_{\tau+\delta_\tau}^{2D}(\theta) = \frac{e^{-i\varphi_\tau} \Phi_{\tau+\delta_\tau}^{2D}(\theta)}{\left[\int_0^\pi d\theta \, 2\pi \sin \theta |\Phi_{\tau+\delta_\tau}^{2D}(\theta)|^2 \right]^{1/2}} \quad (39)$$

and varied the phase shift φ_τ so as to maximize the agreement between $\bar{\Phi}_{\tau+\delta_\tau}^{2D}(\theta)$ and $\Phi_t^{3D}(\theta)$. With $\varphi_t = 1.64$, we arrived at the blue curves in Fig. 7, to be compared with the red curves. We repeated the same calculations at $\tau = 1000, 1500$, and 2000 with $(\varphi_{1000}, \delta_{1000}) = (1.35, 18)$, $(\varphi_{1500}, \delta_{1500}) = (1.48, 30)$, and $(\varphi_{2000}, \delta_{2000}) = (1.56, 200)$, and obtained the same level of agreement (these times have nothing particular; we could have chosen any other ones between 0 and 3500). As a conclusion,

$$\Phi_\tau^{3D}(\theta) \approx \bar{\Phi}_{\tau+\delta_\tau}^{2D}(\theta), \quad (40)$$

which formalizes the fact that, despite the differences between $\hat{T}_{2D}$ and $\hat{T}_{3D}$, the planar wavepacket dynamics bear strong similarities with the exact 3D ones.

Since $\Phi_{t+\delta_t}^{2D}(\theta)$ is proportional to $\Phi_t^{3D}(\theta)$ (see the last two equations),

$$P_j^{2D} = \left| \int_0^\pi d\theta \, 2\pi \sin \theta Y_j^0(\theta) \Phi_{t+\delta_t}^{2D}(\theta) \right|^2 \quad (41)$$

is necessarily proportional to P_j^{3D} . This is illustrated in Fig. 6, where

$$\bar{P}_j^{2D} = \frac{P_j^{2D}}{\sum_j P_j^{2D}} \quad (42)$$

is represented by the blue dashed curve. Since $\Phi_{t+\delta_t}^{2D}(\theta)$ is not normalized to unity, we had to renormalize P_j^{2D} to 1 in order to make its comparison with P_j^{3D} relevant. $\bar{P}_j^{2D}$ appears to be in very good agreement with P_j^{3D} . We shall see that this is one of the two reasons why our formulation of SCWT³⁵ may be accurate. Note that we could have calculated P_j^{2D} at t , instead of $t + \delta_t$. Beyond t , the potential is indeed negligible and $\Phi_\tau^{2D}(\theta)$ is the state of a free rotor whose rotational state distribution is time-independent.

The similarities between the 3D and 2D quantum dynamics are expected to be even stronger in the case where the equilibrium angle is at $\pi/2$ and the initial Gaussian state is centered at this value, for we have previously seen that the right-most term in Eq. (37) plays a minor role as compared to $\hat{T}_{2D}$ within the neighborhood of $\pi/2$, making thereby $\hat{T}_{2D}$ roughly equivalent to $\hat{T}_{3D}$. The triatomic systems corresponding to this situation are T-shaped.

C. P_j^{3D} and P_j^{2D} in terms of Wigner densities

It is shown in Appendix C that P_j^{3D} and P_j^{2D} (see Eqs. (29) and (41), respectively) can be re-expressed in terms of Wigner densities as follows:

$$P_j^{\Lambda D} = (2\pi)^3 \hbar \int_0^\pi d\theta \int_{-\infty}^\infty dP_\theta \, \rho_j(\theta, P_\theta) \rho_t^{\Lambda D}(\theta, P_\theta), \quad (43)$$

with $\Lambda = 2, 3$. $\rho_j(\theta, P_\theta)$ is given by Eq. (12) and

$$\begin{aligned} \rho_t^{\Lambda D}(\theta, P_\theta) &= \frac{1}{\pi \hbar} \int_{S_-(\theta)}^{S_+(\theta)} ds \, e^{2iP_\theta s/\hbar} \Phi_t^{\Lambda D*}(\theta + s) \Phi_t^{\Lambda D}(\theta - s), \end{aligned} \quad (44)$$

where for θ within the range $[\theta_a, \theta_b]$,

$$S_-(\theta) = \max[\theta_a - \theta, \theta - \theta_b] \quad (45)$$

and

$$S_+(\theta) = \min[\theta - \theta_a, \theta_b - \theta], \quad (46)$$

while for θ out of the previous range, $S_-(\theta)$ and $S_+(\theta)$ satisfy Eq. (11) (thus making $\rho_t^{\Lambda D}(\theta, P_\theta)$ zero). Apart from the constraints $\theta_a \leq 0$ and $\theta_b \geq \pi$, θ_a and θ_b are arbitrary. The available region in the plane (s, θ) defined by Eqs. (45) and (46) is represented by the yellow plus grey areas in Fig. 8.

D. Ability of classical mechanics to propagate ρ_t^{2D}

It is proved in Appendix D that the quantum transport equation satisfied by ρ_τ^{2D} (see Eq. (44)) tends to Liouville equation in the classical limit. This is also true in the quantum regime when the angular dependence of the potential is nearly quadratic, as is the case in our model system, and quite often in photodissociations. To illustrate this statement, ρ_t^{2D} is compared in Fig. 9 with ρ_t^C , obtained by classically propagating ρ_0^{2D} a period of time t (here, $t = 4200$ a.u.). Some details on the classical propagation are given in Appendix E. θ_a and θ_b have been kept at $-\pi$ and π , respectively (it is shown in Appendix D that these values make ρ_τ^{2D} satisfy

FIG. 8. The region of the plane (s, θ) contributing to $\rho_t^{AD}(\theta, P_\theta)$ is made of the union of the yellow area and the grey square. See text for the mathematical details.

FIG. 9. Contour level representation of the quantum density ρ_t^{2D} and the classical density ρ_t^C .

Liouville equation in the classical limit). In line with the demonstration of Appendix D, the two densities ρ_t^{2D} and ρ_t^C appear to be in excellent agreement (this agreement may be lost for inappropriate values of θ_a and θ_b ; in this case, the planar SCWT derived below loses its accuracy).

E. SCW formula for the planar motion

Since ρ_t^{2D} and ρ_t^C are nearly equal, P_j^{2D} (see Eq. (43)) is closely approximated by

$$P_j^{SCW} = (2\pi)^3 \hbar \int d\theta dP_\theta \rho_t^C(\theta, P_\theta) \rho_j(\theta, P_\theta). \quad (47)$$

Moreover, ρ_t^C rigorously satisfies the identity

$$\rho_t^C(\theta, P_\theta) d\theta dP_\theta = \rho_0^{2D}(\theta_0, P_{\theta_0}) d\theta_0 dP_{\theta_0}, \quad (48)$$

in which (θ, P_θ) and $d\theta dP_\theta$ should, respectively, be understood as the dynamical state and the volume element reached at time t when starting from state (θ_0, P_{θ_0}) and the volume element $d\theta_0 dP_{\theta_0}$ at time 0 (see also Eq. (16)). From the two previous equations, we have

$$P_j^{SCW} = (2\pi)^3 \hbar \int d\theta_0 dP_{\theta_0} \rho_0^{2D}(\theta_0, P_{\theta_0}) \rho_j(\theta_t, P_{\theta_t}), \quad (49)$$

where the subscript t has been added to the arguments of ρ_j in order to emphasize that these variables are those obtained at time t when starting from θ_0 and P_{θ_0} at time 0.

Equation (D12), the expression of $\rho_0^{2D}(\theta_0, P_{\theta_0})$ associated with the initial state $\Phi_0(\theta)$ (see Appendix D for more details), was used to generate the initial conditions (θ_0, P_{θ_0}) of 10 000 trajectories which were propagated up to $t = 4200$. Trajectories were then assigned the statistical weight $\rho_j(\theta_t, P_{\theta_t})$. The renormalized distribution

$$\bar{P}_j^{SCW} = \frac{P_j^{SCW}}{\sum_j P_j^{SCW}} \quad (50)$$

is represented by the turquoise dashed-dotted curve in Fig. 6. Like the densities ρ_t^{2D} and ρ_t^C (see Fig. 9), the distributions $\bar{P}_j^{SCW}$ and $\bar{P}_j^{2D}$ are in close agreement (turquoise and blue curves in Fig. 6), as it should be given that the planar quantum transport equation is closely approximated by Liouville equation (see Appendix D). Moreover, we have seen in Sec. III B that $\bar{P}_j^{2D}$ is in very good agreement with $\bar{P}_j^{3D}$ (red curve in Fig. 6). Consequently, the planar SCWT represents a very satisfying alternative to the exact quantum dynamics.

Before this analysis, we had no clear idea about the reasons why our extension of SCWT could work. Now, we know that within the framework of our model system, our extension of SCWT is a close approximation to the planar quantum dynamics because we have proved it from first principles. Moreover, empirical evidence points to a clear ability of the planar quantum dynamics to nearly reproduce (after renormalization) the exact final quantum state populations, which completes the justification of the good accuracy of SCWT (also after renormalization). Of course, it would have been preferable to analytically establish from first principles the link between the 2D and 3D dynamics, ideally

FIG. 10. Contour level representation of the projection of the Wigner density (8) onto the (θ, P_θ) plane for the fragmentation of CH_3I in the 3Q_0 and 1Q_1 electronic states. ρ_t is the quantum density while $\bar{\rho}_t^c$ is the renormalized classical one. $t = 100$ and 60 fs in the 3Q_0 and 1Q_1 states, respectively.

by deriving expressions in the same spirit as Eqs. (39) and (40). This task, however, does not seem to be simple.

F. Inability of classical mechanics to propagate ρ_t^{3D}

One may wonder whether following the same strategy as in Secs. III C–III E with ρ_t^{3D} instead of ρ_t^{2D} would not lead to a 3D SCWT in even better agreement with the exact 3D quantum dynamics than the planar SCWT. The answer, however, is negative for the following reasons.

Soon after the publication of Part I, a paper by Fischer *et al.*, entitled “Wigner function for the orientation state” came to our attention,⁴⁷ followed some time after by its generalization to any curved configuration space.⁴⁸ A major implication of these works regarding SCWT is that ρ_t^{3D} as defined by Eq. (44) cannot satisfy Liouville equation in the classical limit. Hence, when trying to redo the developments of Appendix D within the 3D model, one gets lost in very heavy and lengthy expressions that do not simplify in such a way that one can recover Liouville equation. An alternative definition of ρ_t^{3D} is required (in particular, the integrand in Eq. (44) has to be multiplied by $|\sin(\theta + s)\sin(\theta - s)|^{1/2}$ ^{47,48}).

We thus rederived SCWT by using this alternative definition. Unfortunately, when applied to our model system, the resulting approach leads to a rotational state distribution that shows seemingly erratic fluctuations around the exact values (given by the red curve in Fig. 6). It seems that

within the energy regime common to fragmentations, classical mechanics strongly fails at correctly propagating the rotational Wigner density of Refs. 47 and 48. The energy available to the system might have to be much larger for the classical propagation to be realistic, contrary to what we have found with density (44).⁵¹ For the present time, this limitation prevents from developing an accurate 3D SCWT of photodissociation, at least in curvilinear coordinates. Fortunately, however, ρ_t^{3D} is proportional to $\rho_{t+\delta t}^{2D}$ (see Eqs. (39), (40), and (44)) and thus, also to $\rho_{t+\delta t}^c$, ensuring thereby the accuracy of the (renormalized) planar SCWT.

IV. BACK TO METHYL IODIDE

An analogous route as in Sec. III can be followed for CH_3I . According to Kuppermann *et al.*,⁵² the Schrödinger equation in a space-fixed plane for zero total angular momentum is given by Eq. (6) with $\hat{T}_{3D}$ (see Eq. (5)) replaced by⁵³

$$\hat{T}_{2D} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2I} \frac{\partial^2}{\partial \theta^2}. \quad (51)$$

Consequently, the transformation of the angular part of the kinetic operator when going from the 3D space to the space-fixed plane is the same as in Sec. III (compare Eqs. (5) and (51) with Eqs. (27) and (36)). Here again, the exact quantum dynamics is thus expected to be satisfyingly reproduced by the planar dynamics.

Moreover, the dependence of I (see Sec. II C) on R and r is usually very weak, so that one may consider I as a constant of motion throughout the dissociation. $\hat{T}_{2D}$ has, thus, the quadratic structure of a kinetic energy operator expressed in Cartesian coordinates. Following the derivation of Eq. (8) in Ref. 49 and the developments of Appendix D, it is then possible to show that the planar quantum transport equation deduced from Eq. (51) is equal to Liouville equation for the same planar motion (implied by Eqs. (17) and (18) in this work and Eq. (24) in Part I) plus a quantum correction related to the anharmonicities of the potential $V_e(R, r, \theta)$. SCWT as formulated in Part I and Sec. II of this work ignores this quantum correction and hence, replaces the quantum propagation of the planar time-evolved Wigner density by its classical propagation. One thus arrives at Eq. (15) which, using Eq. (16), finally leads to Eq. (19).

We wish to emphasize that the replacement of $\rho_\tau(\Gamma)$ by $\rho_\tau^C(\Gamma)$ in Eq. (7), leading to Eq. (15), is thus justifiable from first principles only within the quantum planar dynamics. We erroneously thought that the previous substitution was valid within the exact quantum dynamics when we proposed our formulation of SCWT and were lucky enough that the planar quantum dynamics bear strong similarities with the exact ones, as can be inferred from the very good agreement between SCWT and exact quantum state distributions observed in Figs. 3 and 4. Note that the above-mentioned anharmonicities are sufficiently small for the quantum correction to Liouville equation to be nearly negligible in the case of methyl iodide, owing to the good accuracy of the SCWT predictions.

We can corroborate the previous statements by checking that the exact 3D quantum and classical Wigner densities for the photodissociation of CH_3I are in good agreement and that their main features are quite similar to those of the previously discussed densities. The projection onto the (θ, P_θ) plane of $\rho_t(\Gamma)$, given by Eq. (8), is obtained by

$$\rho_t(\theta, P_\theta) = \int dR dP_R dr dp_r \rho_t(\Gamma). \quad (52)$$

From Eqs. (8) and (52), we arrive at

$$\begin{aligned} \rho_t(\theta, P_\theta) = & \frac{1}{\pi\hbar} \int dR dr ds_\theta e^{2iP_\theta s_\theta/\hbar} \Phi_t^*(R, r, \theta + s_\theta) \\ & \times \Phi_t(R, r, \theta - s_\theta) \end{aligned} \quad (53)$$

(see Eqs. (9)–(11) for the boundaries of s_θ). This density, deduced from the exact propagation of Φ_t (see Ref. 35 and references therein for the technical details) and a numerical evaluation of the above integral, is represented in the upper panels of Fig. 10 for the 3Q_0 and 1Q_1 electronic states at $t = 100$ and 60 fs, respectively. The renormalized classical density $\bar{\rho}_t^C$ is represented in the lower panels at the same times. Both sets of densities are in good agreement.⁵⁴ Furthermore, the topological features of the present densities are very similar to those of the densities displayed in Fig. 9. The present comparison, together with the similarity of the rotational state distributions presented in Figs. 4 (left-upper panel) and 6, supports the validity of the model system of Sec. III and gives credit to its main conclusions.

V. CONCLUSION

In the early 1980s, Brown and Heller proposed the SCWT of photodissociation dynamics, which allows the accurate prediction of product state distributions for direct collinear reactions.³⁰ At the heart of this treatment is the idea that the classical propagation of the Wigner distribution corresponding to the time-evolved wavepacket is relatively accurate for sufficiently brief fragmentations (between ~50 and ~150 fs). This is the only approximation that Brown and Heller introduce in their approach which, apart from that, is exact.

In a recent paper,³⁵ we extended SCWT to three-dimensional triatomic processes and applied the resulting approach to a realistic three-atom like model of methyl iodide dissociation. We obtained final state distributions in (nearly) quantitative agreement with exact quantum results, but at a much lower numerical cost. The difficult step of this extension of SCWT was the introduction of new rotational Wigner distributions that we had to modify several times by trial and error induction before arriving at satisfying results.

The goal of the present work was to shed light on the basic reasons why our formulation of SCWT may work. In order to reduce the complexity of the problem, we have considered a simplified model of photodissociation explicitly dealing with the rotational motion only, and involving a bending force vanishing in the course of time in a similar way as for CH_3I .

The conclusions of our analysis as regards triatomic reactions are the following: first, empirical evidence points to a clear ability of the planar quantum dynamics to nearly reproduce the exact final quantum state populations after *ad-hoc* renormalization. Second, we have demonstrated from first principles that our formulation of SCWT is a close approximation to the planar quantum dynamics, leading thereby to final state distributions in good agreement with exact quantum ones (also after renormalization). In other words, our formulation of SCWT makes it a semiclassical approximation to an approximate planar quantum treatment of the dynamics, both of sufficient quality for the whole treatment to be satisfying. Clearly, it would have been preferable to analytically establish the link between the planar and exact quantum dynamics, rather than empirically, i.e., through numerical calculations. This task, however, seems to be non-trivial.

We only considered the case where the reaction path corresponds to linear configurations. However, the planar dynamics are in even closer agreement with the exact ones for T-shaped reaction paths (see Sec. III B), so SCWT is expected to work satisfyingly whatever the topology of the interaction is provided that the reaction is direct. Last but not least, we plan to extend our method to nontriatomic-like polyatomic fragmentations, hoping that the quality of its predictions will be maintained.

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APPENDIX A: WAVEPACKET PROPAGATION WITH $\hat{T}_{3D}$

Replacing in Schrödinger Eq. (6) $\Phi_\tau^{3D}(\theta)$ by the right-hand-side of Eq. (32), using the fact that

$$\hat{T}_{3D} Y_j^0 = E_j Y_j^0, \quad (A1)$$

with E_j given by Eq. (33), multiplying on the left by $2\pi \sin \theta$, and integrating over θ , leads to

$$i\hbar \frac{dc_k}{d\tau} = \sum_{j=0}^N V_{kj} c_j \exp[i(E_k - E_j)\tau/\hbar], \quad (A2)$$

with

$$V_{kj} = 2\pi \int_0^\pi d\theta \sin \theta Y_k^0(\theta) V_\tau(\theta) Y_j^0(\theta). \quad (A3)$$

Setting $c_k = c_k^{re} + ic_k^{im}$, Eq. (A2) leads to the coupled differential equations satisfied by c_k^{re} and c_k^{im} , $k = 1, \dots, N$. The values of these coefficients at time 0 are deduced from

$$c_j(0) = 2\pi \int_0^\pi d\theta \sin \theta Y_j^0(\theta) \Phi_0(\theta). \quad (A4)$$

Since $\Phi_0(\theta)$ is a real function (see Eq. (30)), their imaginary parts are 0.

APPENDIX B: WAVEPACKET PROPAGATION WITH $\hat{T}_{2D}$

$\Phi_\tau^{2D}(\theta)$ can generally be expressed as

$$\Phi_\tau^{2D}(\theta) = \sum_{j=-N}^N c_j(\tau) \phi_j(\theta) e^{-iE_j\tau/\hbar}, \quad (B1)$$

with

$$\phi_j(\theta) = \frac{1}{(2\pi)^{1/2}} e^{ij\theta} \quad (B2)$$

and

$$E_j = \frac{\hbar^2 j^2}{2I}. \quad (B3)$$

The plane wave $\phi_j(\theta)$ is indeed an eigenstate of $\hat{T}_{2D}$ of energy E_j ,

$$\hat{T}_{2D} \phi_j = E_j \phi_j. \quad (B4)$$

Following the same reasoning as in Appendix A, the coefficients $c_j(\tau)$ are found to satisfy

$$i\hbar \frac{dc_k}{d\tau} = \sum_{j=-N}^N V_{kj} c_j \exp[i(E_k - E_j)\tau/\hbar], \quad (B5)$$

with

$$V_{kj} = \int_{-\pi}^\pi d\theta \phi_k^*(\theta) V_\tau(\theta) \phi_j(\theta). \quad (B6)$$

Setting $c_k = c_k^{re} + ic_k^{im}$, Eq. (B5) leads to the coupled differential equations satisfied by c_k^{re} and c_k^{im} , $k = -N, \dots, N$. The

values of these coefficients at time 0 are deduced from

$$c_j(0) = \int_{-\pi}^\pi d\theta \phi_j^*(\theta) \Phi_0(\theta). \quad (B7)$$

APPENDIX C: ROTATIONAL STATE DISTRIBUTION IN TERMS OF WIGNER DENSITIES

The proof of the equivalence between Eqs. (29) and (41) on one hand, and Eq. (43) on the other hand, is as follows. From Eqs. (12), (43), and (44) and using the identity

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^\infty dk e^{ikx}, \quad (C1)$$

one arrives through integration over P_θ in Eq. (43) at

$$P_j^{\Lambda D} = 8\pi^2 \int_0^\pi d\theta \int_{S_-(\theta)}^{S_+(\theta)} ds \sin(\theta + s) Y_j^0(\theta + s) \times \Phi_t^{\Lambda D}(\theta + s) \sin(\theta - s) Y_j^0(\theta - s) \Phi_t^{\Lambda D*}(\theta - s). \quad (C2)$$

We now make the change of variable $u = \theta + s$ and $v = \theta - s$, implying $dudv = 2d\theta ds$. The u and v axes are drawn in Fig. 8. Within the (u, v) plane, the available area is the grey square of π side length lying on the u -axis with its left lower corner at the origin of the frame.⁴⁶ Consequently, both u and v take any value within the range $[0, \pi]$ and

$$P_j^{\Lambda D} = (2\pi)^2 \int_0^\pi du \int_0^\pi dv \sin u Y_j^0(u) \Phi_t^{\Lambda D}(u) \times \sin v Y_j^0(v) \Phi_t^{\Lambda D*}(v). \quad (C3)$$

Equation (29) and its 2D version (41) have thus been recovered, thereby proving the validity of Eq. (43).

The strict equivalence between Eqs. (2) and (7) can be proved by means of the previous method.

APPENDIX D: DERIVATION OF THE QUANTUM TRANSPORT EQUATION AND ITS CLASSICAL LIMIT

Equation (44) being close to the original definition of the Wigner density⁴⁹ and θ having in the planar case the status of a Cartesian coordinate (also because the moment of inertia I is here a constant of motion), the demonstration mainly follows the original demonstration of Wigner.⁴⁹

From definition (44) of ρ_τ^{2D} and Schrödinger equation (6) with $\hat{T}_{3D}$ replaced by $\hat{T}_{2D}$ (see Eq. (36)) and $\hat{V}_e$ replaced by the operator associated with $V_\tau(\theta)$, one arrives at

$$\frac{\partial \rho_\tau^{2D}}{\partial \tau} = O_1 + O_2 + O_3, \quad (D1)$$

with

$$O_1 = \frac{1}{2\pi I i} \int_{S_-(\theta)}^{S_+(\theta)} ds e^{2iP_\theta s/\hbar} \frac{\partial^2 \Phi_\tau^{2D*}(\theta + s)}{\partial \theta^2} \Phi_\tau^{2D}(\theta - s), \quad (D2)$$

$$O_2 = -\frac{1}{2\pi I i} \int_{S_-(\theta)}^{S_+(\theta)} ds e^{2iP_\theta s/\hbar} \Phi_\tau^{2D*}(\theta + s) \frac{\partial^2 \Phi_\tau^{2D}(\theta - s)}{\partial \theta^2}, \quad (D3)$$

and

$$O_3 = \frac{1}{\hbar^2 \pi i} \int_{S_-(\theta)}^{S_+(\theta)} ds e^{2iP_\theta s/\hbar} [V_\tau(\theta - s) - V_\tau(\theta + s)] \times \Phi_\tau^{2D*}(\theta + s) \Phi_\tau^{2D}(\theta - s). \quad (D4)$$

Using the fact that

$$\frac{\partial^2 \Phi_\tau^{2D}(\theta \pm s)}{\partial \theta^2} = \frac{\partial^2 \Phi_\tau^{2D}(\theta \pm s)}{\partial s^2} \quad (D5)$$

and

$$\frac{\partial \Phi_\tau^{2D}(\theta \pm s)}{\partial \theta} = \pm \frac{\partial \Phi_\tau^{2D}(\theta \pm s)}{\partial s}, \quad (D6)$$

it is shown after lengthy but standard developments involving integration by part that

$$\frac{\partial \rho_\tau^{2D}}{\partial \tau} = Q_1 + Q_2 + Q_3, \quad (D7)$$

with

$$Q_1 = -\frac{P_\theta}{I} \frac{1}{\pi \hbar} \int_{S_-(\theta)}^{S_+(\theta)} ds e^{2iP_\theta s/\hbar} f_\theta(s), \quad (D8)$$

$$Q_2 = \frac{1}{2\pi I i} [e^{2iP_\theta s/\hbar} f_\theta(s)]_{S_-(\theta)}^{S_+(\theta)}, \quad (D9)$$

$$f_\theta(s) = \frac{\partial}{\partial \theta} [\Phi_\tau^{2D*}(\theta + s) \Phi_\tau^{2D}(\theta - s)], \quad (D10)$$

and

$$Q_3 = \sum_{n=0}^{\infty} \frac{1}{(2n+1)!} \left(\frac{\hbar}{2i} \right)^{2n} \frac{\partial^{2n+1} V_\tau}{\partial \theta^{2n+1}} \frac{\partial^{2n+1} \rho_\tau^{2D}}{\partial P_\theta^{2n+1}} \quad (D11)$$

(O_3 easily transforms into Q_3 when considering the Taylor series expansion of $V_\tau(\theta - s)$ and $V_\tau(\theta + s)$).

Now, we wish to demonstrate that in the classical limit, Liouville equation is a close approximation to the previous transport equation. A necessary condition, however, will appear to be that $|\Phi_\tau^{2D}(\theta)|^2$ takes negligible values around θ_a and θ_b . For the system at hand, this is the case if $\theta_a = -\pi$ and $\theta_b = \pi$, as can be seen from the blue curve in Fig. 5 (this curve represents $|\Phi_{\tau+\delta\tau}^{2D}(\theta)|^2$, proportional to $|\Phi_{t+\delta t}^{2D}(\theta)|^2$ (see Eq. (39)) which, due to the spreading of the wavepacket, is even broader than $|\Phi_t^{2D}(\theta)|^2$). We thus assume that $\theta_a = -\pi$ and $\theta_b = \pi$ in the following.

In such a case, Eqs. (45) and (46) reduce to Eqs. (9) and (10), respectively, and we are in the situation depicted in Fig. 1. Also, $\rho_0^{2D}(\theta, P_\theta)$, deduced from Eqs. (30) and (44)-(46), appears to be accurately approximated by

$$\rho_0^{2D}(\theta, P_\theta) \propto \exp[-2\alpha\theta^2 - P_\theta^2/(2\alpha)]. \quad (D12)$$

The proportionality factor does not need to be specified. We can now proceed with the demonstration. As outlined at the end of Sec. III A, $V_\tau(\theta)$ is nearly harmonic over the range where $|\Phi_\tau^{2D}(\theta)|^2$ is nonzero (see Fig. 5). As is well known, a wavepacket which is initially Gaussian remains Gaussian in a harmonic potential⁵⁰ (this is an exact result only in Cartesian coordinates, which is the case of θ here). Since $\Phi_0^{2D}(\theta) = \Phi_0(\theta)$ is Gaussian (see Eq. (30)), we have

$$\Phi_\tau^{2D}(\theta) \propto e^{-(\alpha_\tau + i\beta_\tau)\theta^2}, \quad (D13)$$

where α_τ and β_τ are time-dependent real numbers and α_τ has a positive value decreasing with τ . This last condition is necessary for ensuring the spreading of $|\Phi_\tau^{2D}(\theta)|^2$ as time goes on. Whenever $V_\tau(\theta)$ involves anharmonicities, Eq. (D13) is still qualitatively reasonable provided that these are not too strong. Using this expression, one gets from Eq. (D10)

$$f_\theta(s) \propto e^{-2\alpha_\tau(\theta^2 + s^2)}. \quad (D14)$$

In other words, $f_\theta(s)$ is proportional to $|\Phi_\tau^{2D}(\theta)|^2 |\Phi_\tau^{2D}(s)|^2$. But it is clear from Fig. 5 that $|\Phi_\tau^{2D}(\theta)|^2$ is negligible around $\theta = \pm\pi$. Consequently, $f_\theta(s)$ can be significantly different from zero for small values of $|\theta|$ only. For such values, however, it is clear from Fig. 1 that $S_-(\theta)$ is slightly larger than $-\pi$ while $S_+(\theta)$ is slightly lower than π . Since $f_\theta(s)$ is proportional to $|\Phi_\tau^{2D}(s)|^2$ (see Eq. (D14)), which is negligible at $\pm\pi$, and $S_\pm(\theta)$ is close to $\pm\pi$, $f_\theta(S_\pm(\theta)) \approx 0$. Consequently, $f_\theta(S_\pm(\theta))$ can be considered as 0 whatever the value of θ and so does Q_2 (see Eq. (D9)) which can thus be canceled from Eq. (D7).

In addition to that, we have from Eqs. (44) and (D10)

$$\frac{\partial \rho_\tau^{2D}}{\partial \theta} = \frac{1}{\pi \hbar} \int_{S_-(\theta)}^{S_+(\theta)} ds e^{2iP_\theta s/\hbar} f_\theta(s) + Q_4 + Q_5, \quad (D15)$$

with

$$Q_4 = \frac{1}{\pi \hbar} e^{2iP_\theta S_+(\theta)/\hbar} \Phi_\tau^{2D*}(\theta + S_+(\theta)) \Phi_\tau^{2D}(\theta - S_+(\theta)) \frac{\partial S_+(\theta)}{\partial \theta} \quad (D16)$$

and

$$Q_5 = \frac{1}{\pi \hbar} e^{2iP_\theta S_-(\theta)/\hbar} \Phi_\tau^{2D*}(\theta + S_-(\theta)) \Phi_\tau^{2D}(\theta - S_-(\theta)) \frac{\partial S_-(\theta)}{\partial \theta}. \quad (D17)$$

Using Eq. (D13), we find

$$\Phi_\tau^{2D*}(\theta + s) \Phi_\tau^{2D}(\theta - s) \propto e^{-2\alpha_\tau(\theta^2 + s^2)}. \quad (D18)$$

$\Phi_\tau^{2D*}(\theta + s) \Phi_\tau^{2D}(\theta - s)$ is thus proportional to $f_\theta(s)$ (see Eq. (D14)). As a result, $\Phi_\tau^{2D*}(\theta + S_\pm(\theta)) \Phi_\tau^{2D}(\theta - S_\pm(\theta))$, just like $f_\theta(S_\pm(\theta))$, is negligible and

$$Q_4 \approx 0 \approx Q_5. \quad (D19)$$

Equations (D8), (D15), and (D19) lead to

$$Q_1 = -\frac{P_\theta}{I} \frac{\partial \rho_\tau^{2D}}{\partial \theta}. \quad (D20)$$

From Eqs. (D7), (D11), and (D20) and the fact that $Q_2 \approx 0$, we finally arrive in the limit where $\hbar$ tends to 0 at

$$\frac{\partial \rho_\tau^{2D}}{\partial \tau} = -\frac{P_\theta}{I} \frac{\partial \rho_\tau^{2D}}{\partial \theta} + \frac{\partial V_\tau}{\partial \theta} \frac{\partial \rho_\tau^{2D}}{\partial P_\theta}. \quad (D21)$$

From Eqs. (17) and (18) with $(u, p_u) = (\theta, P_\theta)$ and the classical function of Hamilton H equal here to $P_\theta^2/(2I) + V_\tau(\theta)$, Eq. (D21) can be rewritten as

$$\frac{\partial \rho_\tau^{2D}}{\partial \tau} = -\dot{\theta} \frac{\partial \rho_\tau^{2D}}{\partial \theta} - \dot{P}_\theta \frac{\partial \rho_\tau^{2D}}{\partial P_\theta} = \{H, \rho_\tau^{2D}\}, \quad (D22)$$

which is recognized to be Liouville equation.

Within the present model system, $V_\tau(\theta)$ can be considered as nearly quadratic and therefore, Q_3 reduces to the rightmost term in Eq. (D21), even when $\hbar$ is not kept at 0. In the harmonic case, Liouville equation is thus also valid in the quantum regime, a well known result for standard Cartesian coordinates (θ is “accidentally” Cartesian here; in the 3D case, or for I depending on the bond length, θ is curvilinear). More generally, however, the relatively short time of interaction between nascent products in direct reactions (between ~ 50 and ~ 150 fs) is expected to minimize the spreading of the wavepacket, and hence the effect of anharmonicities, making thereby the classical propagation of the wavepacket relatively accurate.

APPENDIX E: CLASSICAL PROPAGATION OF THE WIGNER DENSITY

As far as the calculation of $\rho_{t+\delta_t}^C$ is concerned, we have used the following method: we considered at time $t + \delta_t = 4200$ a regular grid of 200×200 points of coordinates $(\theta_{t+\delta_t}, P_{\theta_{t+\delta_t}})$, with $\theta_{t+\delta_t}$ in the range $[-\pi, \pi]$ and $P_{\theta_{t+\delta_t}}$ in the range $[-15, 15]$. These points served as initial conditions of trajectories run backward in time during 4200 a.u. For some trajectories, θ becomes larger (lower) than π ($-\pi$) as τ decreases. The sign of P_θ is then inverted in order to maintain θ in the range $[-\pi, \pi]$, as required. The values of (θ_0, P_{θ_0}) obtained at the end of the propagation, i.e., at time 0, were used to calculate $\rho_0^{2D}(\theta_0, P_{\theta_0})$ from Eq. (D12). According to Liouville equation, the density is conserved along trajectories and thus, $\rho_{t+\delta_t}^C(\theta_{t+\delta_t}, P_{\theta_{t+\delta_t}}) = \rho_0^{2D}(\theta_0, P_{\theta_0})$. This method was found to be much more efficient than selecting the initial conditions of a batch of trajectories according to ρ_0^{2D} , running them forward in time for 4200 a.u., and using 200×200 boxes centered at the points $(\theta_{t+\delta_t}, P_{\theta_{t+\delta_t}})$ of the previous grid to calculate $\rho_{t+\delta_t}^C(\theta_{t+\delta_t}, P_{\theta_{t+\delta_t}})$ by means of the usual binning procedure (requiring far more than 200×200 trajectories).

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⁵³Equation (51) in the present work is deduced from Eq. (2.14) in Ref. 52. In reality, $\partial^2/\partial\theta^2$ in Eq. (51) should be replaced by $(\partial^2/\partial\theta^2 + 1/4)$ for $\hat{T}_{2D}$ to be exact (the $1/4$ term was forgotten in Eq. (2.14) of Ref. 52, but not in Eq. (3.6) of the same work). However, we are dealing with processes for which j^2 is on average much larger than $1/4$, implying thereby that the latter can reasonably be neglected with respect to $\partial^2/\partial\theta^2$.

⁵⁴The time delay δ_t observed between the 3D and 2D wavepackets in Sec. III B is not seen between the 3D quantum Wigner density and the classical Wigner density, assumed to closely approximate the 2D quantum one. However, we have seen before that δ_t is a diverging function of t ; hence, the times at which the Wigner densities are considered are presumably too short for the divergence to show up.