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On the importance of an accurate representation of the initial state of the system in classical dynamics simulations

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A definition of a quantum-type phase-space distribution is proposed in order to represent the initial state of the system in a classical dynamics simulation. The central idea is to define an initial quantum phase-space state of the system as the direct product of the coordinate and momentum representations of the quantum initial state. The phase-space distribution is then obtained as the square modulus of this phase-space state. The resulting phase-space distribution closely resembles the quantum nature of the system initial state. The initial conditions are sampled with the distribution, using a grid technique in phase space. With this type of sampling the distribution of initial conditions reproduces more faithfully the shape of the original phase-space distribution. The method is applied to generate initial conditions describing the three-dimensional state of the Ar–HCl cluster prepared by ultraviolet excitation. The photodissociation dynamics is simulated by classical trajectories, and the results are compared with those of a wave packet calculation. The classical and quantum descriptions are found in good agreement for those dynamical events less subject to quantum effects. The classical result fails to reproduce the quantum mechanical one for the more strongly quantum features of the dynamics. The properties and applicability of the phase-space distribution and the sampling technique proposed are discussed. © 2000 American Institute of Physics. [S0021-9606(00)01118-1]

I. INTRODUCTION

Classical molecular dynamics (MD) has provided a useful tool to investigate a wide variety of dynamical processes in the field of chemical physics. The efficiency of the method allows one to study the dynamics of relatively large systems for which an exact quantum treatment is not feasible.^{1–10} However, due to the classical nature of the MD methodology, it is more suitable for those problems without strong quantum effects. Such a classical nature manifests itself also in the characterization of the initial state of the system in the MD treatment.

Same as the time-dependent Schrödinger equation (TDSE), the Hamilton (or Newton) equations which are solved in the MD method are initial value problems. Therefore an initial state must be specified prior to solve the equations of motion. In addition, in order to carry out a realistic calculation, the initial state should resemble, as closely as possible, the experimental conditions in which the system is prepared. In the case of the TDSE, the initial state consists of a wave packet (obtained variationally, for instance) represented in an N -dimensional coordinate space. In the classical MD formalism the initial state takes the form of a set of initial conditions in phase space (PS), each of them consisting of N coordinate positions and N conjugate momenta. Thus, while in the quantum-mechanical treatment the initial state is N -dimensional, the deterministic character of classical mechanics requires a $2N$ -dimensional PS representation of the system at $t=0$ (and actually at every time).

A classical method has been applied to generate a PS distribution of initial conditions. It consists of running for a long time a classical trajectory which is approximately con-

fined to the PS region corresponding to the energy of the initial state. At intermediate times of this long trajectory, sets of positions and momenta of the system are picked up, which constitute the different initial conditions.^{1,11} In a similar method¹² several trajectories are run for a given time (each one corresponding to a different initial condition), and the positions and momenta are picked up at the end of the trajectory. The long trajectory (or trajectories) would start at the classical turning points of the potential surface, assuming initially that all the momenta are zero. The advantages of this classical sampling of initial conditions are that it does not require the wave function of the initial state, and can be applied to systems with a large number of degrees of freedom. The main disadvantage is that the distribution of initial conditions obtained is purely classical. If the system is initially prepared in the ground or a low excited state, such a distribution becomes rather unrealistic. In addition, the confinement of the long trajectories in the initial PS region is achieved by removing some coupling terms from the Hamiltonian. As a consequence, the total energy of the initial conditions does not match that of the quantum initial state.

An alternative PS distribution to the above classical one can be generated from the quantum initial state. This type of distribution reflects more closely the quantum nature of the initial state in which the system is prepared. Obviously, the generation of this PS distribution is restricted to those system sizes for which it is possible to define previously a quantum initial state (either exactly or approximately). The problem is that the definition of a $2N$ -dimensional PS distribution from an N -dimensional state represented in coordinate space is not unique. In the early thirties Wigner proposed one such

distribution¹³ which has been extensively used.^{4(b),14} Other quantum-type distributions have been suggested and applied.^{15–17} All these distributions are models more or less advantageous (in terms of efficiency and simplicity) depending on the problem under study.

In this work an alternative model for a quantum-type PS distribution of initial conditions is suggested. The essential idea is to define the PS distribution as a direct product of the quantum distributions in coordinate and momentum space associated with the initial state. This definition of the PS distribution is simple and very efficient, and has the flexibility to adapt to a large variety of problems. The possible advantages of this PS distribution are investigated by generating initial conditions from which classical trajectories are propagated to simulate the ultraviolet photodissociation of the Ar–HCl cluster. The classical results are compared with those of an exact calculation.

The organization of the paper is the following: In Sec. II the procedure to generate the PS distribution and the sampling of initial conditions is described and discussed. The results of the classical dynamics simulation are shown and compared with exact quantum ones in Sec. III. Finally, conclusions are drawn in Sec. IV.

II. THE METHOD

A. Initial state

Prior to generating the PS distribution required to sample the initial conditions, the quantum initial state of the system has to be calculated. To this purpose the Ar–HCl cluster is represented in Jacobian coordinates (r, R, θ) , where r is the HCl distance, R is the separation between the Ar atom and the HCl center of mass, and θ is the angle between the vectors associated with r and R . Zero total angular momentum is assumed for the system. Thus the Hamiltonian can be expressed as

$$\hat{H}(r, R, \theta) = -\frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} + \left(\frac{1}{2\mu_r r^2} + \frac{1}{2\mu_R R^2} \right) \hat{j}^2 + V_{\text{H-Cl}}(r) + W(r, R, \theta), \quad (1)$$

being μ_r and μ_R the reduced masses associated with the r and R modes, respectively, and $W(r, R, \theta)$ the interaction potential of Ar with H and Cl. The potential surface where the initial state is calculated corresponds with the ground-electronic state $X^1\Sigma^+$ of Ar–HCl, and it has been described elsewhere.¹⁸

As in previous works^{18,19} on this system, the initial state [in its reduced form consistent with the Hamiltonian expressed as in Eq. (1)] is defined as

$$\Phi(r, R, \theta, t=0) = \chi_v(r) \varphi^{(v)}(R, \theta), \quad (2)$$

where $\chi_v(r)$ is the ground-vibrational state ($v=0$) of HCl, obtained as a solution of the equation

$$\left[-\frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} + V_{\text{H-Cl}}(r) \right] \chi_v(r) = E_v \chi_v(r),$$

and $\varphi^{(v)}(R, \theta)$ is calculated variationally, and also corresponds to the ground rovibrational state of the van der Waals

modes. For simplicity, the r dependence of the initial state of Eq. (2) has been separated in the framework of the vibrational diabatic approximation.²⁰ This separation of the HCl vibration is justified in the ground-electronic state of Ar–HCl, due to the large difference between the vibrational frequencies of HCl and the van der Waals modes.

B. Definition of the phase-space distribution

The main objective of a quantum-type PS distribution is to reflect the quantum nature of the initial state both in coordinate and in momentum space. Since the initial state already reflects that quantum nature in coordinate space, the problem becomes to define a quantum state (or distribution) in momentum space from the coordinate representation of the initial state. This is achieved by choosing a suitable basis set in momentum space, on which the initial state is projected out. Plane waves are convenient basis functions to transform the initial state in the radial coordinates to the corresponding momentum representation, through the Fourier transform. In the case of angular coordinates, Legendre polynomials, or in general spherical harmonics, can be used as basis functions to transform the initial state from coordinate to momentum space. Thus, for our present problem, the Ar–HCl cluster with $J=0$, given an initial state $\Phi(r, R, \theta)$, its momentum representation is obtained as

$$\tilde{\Phi}(p_r, p_R, j) = \frac{1}{2\pi\hbar} \int dr \int dR \int d\theta \sin\theta e^{-ip_r r/\hbar} \times e^{-ip_R R/\hbar} P_j(\cos\theta) \Phi(r, R, \theta), \quad (3)$$

where $P_j(\cos\theta)$ is a normalized Legendre polynomial. For a triatomic system with $J \neq 0$, $P_j(\cos\theta)$ should be replaced by a spherical harmonic $Y_l^m(\theta, \phi)$. For systems with more than three atoms one can also express the momentum representation of the initial state as a linear combination of basis functions composed of products of plane waves multiplied by two or more spherical harmonics. The above basis set has been chosen to transform the initial state to momentum space because the Fourier transform can be efficiently performed with the currently available fast Fourier transform (FFT) routines. We note, however, that other choices of the basis set in momentum space might be more convenient for specific problems.

Once we have obtained a quantum representation of the initial state both in coordinate $[\Phi(r, R, \theta)]$ and in momentum $[\tilde{\Phi}(p_r, p_R, j)]$ space, a “quantum phase-space state” is defined as the direct product $\Phi(r, R, \theta) \tilde{\Phi}(p_r, p_R, j)$. Then, the phase-space distribution is defined as the square modulus of such a phase-space state,

$$P(r, R, \theta, p_r, p_R, j) = |\Phi(r, R, \theta) \tilde{\Phi}(p_r, p_R, j)|^2, \quad (4)$$

or equivalently, since $\Phi(r, R, \theta)$ is a real function,

$$P(r, R, \theta, p_r, p_R, j) = |\Phi(r, R, \theta)|^2 |\tilde{\Phi}(p_r, p_R, j)|^2. \quad (5)$$

By applying the relation $p_\theta = [j(j+1)]^{1/2}\hbar$, we finally obtain the PS distribution in the coordinates and corresponding momenta, $P(r, R, \theta, p_r, p_R, p_\theta)$.

The quantum representation of the phase-space state is reflected in the properties of the distribution defined in Eqs. (4) or (5). So, the total energy of the system associated with $P(r, R, \theta, p_r, p_R, j)$ (or with the phase-space state) is exactly the same as that corresponding to the quantum initial state. This can be easily seen by averaging the Hamiltonian over the phase-space state,

$$\begin{aligned} \langle \Phi(r, R, \theta) \tilde{\Phi}(p_r, p_R, j) | \hat{H} | \Phi(r, R, \theta) \tilde{\Phi}(p_r, p_R, j) \rangle \\ = \langle \Phi(r, R, \theta) | \hat{H} | \Phi(r, R, \theta) \rangle \langle \tilde{\Phi}(p_r, p_R, j) | \tilde{\Phi}(p_r, p_R, j) \rangle \\ = E, \end{aligned}$$

where $\langle \tilde{\Phi}(p_r, p_R, j) | \tilde{\Phi}(p_r, p_R, j) \rangle = 1$, and $\langle \Phi(r, R, \theta) | \hat{H} | \Phi(r, R, \theta) \rangle = E$ is the quantum mechanical expectation value of the Hamiltonian operator. The quantum phase-space state $\Phi(r, R, \theta) \tilde{\Phi}(p_r, p_R, j)$ can be viewed as a coordinate-dependent wave function $\Phi(r, R, \theta)$ times a coordinate-independent phase $\tilde{\Phi}(p_r, p_R, j)$. Since the quantum mechanical Hamiltonian depends solely upon the coordinates and derivatives of the coordinates (but not upon the p_r, p_R , and j momenta), the above result for the expectation value of $\hat{H}$ becomes clear. The correct expectation values of other observables which are functions of the coordinates or the momenta are also reproduced. In addition, from Eq. (5) it is obvious that $P(r, R, \theta, p_r, p_R, j)$ gives the correct quantum distribution of the initial state, both in coordinate and in momentum space.

The above properties of $P(r, R, \theta, p_r, p_R, j)$ are also found in the Wigner distribution.¹³ However, the PS distribution defined in Eq. (5) presents some advantages over the Wigner function, which will be discussed in the following. It is well known that the Wigner distribution may take negative values at some phase-space points.^{13,14} By contrast, the PS distribution suggested here, obtained as the square modulus of the PS state, is real and positive in the whole region of phase space covered by the quantum initial state.

The definition of the Wigner distribution generates an intrinsic coupling between the coordinates and the momenta of the initial state. Such a coupling is also present in other quantum-type PS distributions like the Husimi distribution.^{15,16} This coordinate-momentum coupling is actually artificial, produced by the specific definition of the PS distribution. The definition of the PS distribution of Eq. (5) does not generate artificial couplings between the coordinate and momentum representations. In this sense the distribution proposed here is in closer correspondence with the physical properties of the system initial state. Figure 1 shows a comparison between the Wigner distribution $W(r, p_r)$ obtained for the vibrational state $\chi_{v=0}(r)$ of HCl,

$$W(r, p_r) = \frac{1}{2\pi\hbar} \int e^{ip_r s/\hbar} \chi_{v=0}^* \left(r + \frac{s}{2} \right) \chi_{v=0} \left(r - \frac{s}{2} \right) ds, \quad (6)$$

and the corresponding PS distribution $P(r, p_r) = |\chi_{v=0}(r)|^2 |\tilde{\chi}_{v=0}(p_r)|^2$. The two PS distributions show differences as a consequence of the coordinate-momentum coupling present in the Wigner distribution. When $W(r, p_r)$ is integrated either over p_r or over r (i.e., when the coordinate-momentum coupling disappears), the one-

FIG. 1. Phase-space distribution corresponding to the HCl vibrational wave function $\chi_{v=0}(r)$, calculated using (a) the Wigner definition of Eq. (6), and (b) the definition $|\chi_{v=0}(r)|^2 |\tilde{\chi}_{v=0}(p_r)|^2$.

dimensional distributions obtained (not shown) are graphically indistinguishable from $|\chi_{v=0}(r)|^2$ and $|\tilde{\chi}_{v=0}(p_r)|^2$, respectively.

The main disadvantage of the Wigner distribution is that its calculation becomes very expensive for initial states with two or more fully-coupled spatial degrees of freedom. The reason is that each spatial variable q_i in the initial state involves handling three coupled variables to calculate the Wigner distribution, q_i , p_i , and the dummy spatial variable s_i [see Eq. (6)]. In general, for an initial state with N coupled coordinates, the calculation of the $2N$ -dimensional Wigner distribution implies handling $3N$ coupled variables. As a result, the computational cost of the Wigner distribution is very high for $N=2$, and becomes prohibitive for $N>2$. The implication is that if a N -dimensional, fully-coupled initial state is available for a given system, it has to be factorized in order to obtain the corresponding Wigner distribution.

The definition of the PS distribution proposed in this work requires to transform the N -dimensional initial state from coordinate to momentum space. This transformation involves $2N$ coupled degrees of freedom, vs the $3N$ ones in the case of the Wigner distribution. In addition, the use of the FFT algorithm makes such a transformation more efficient. In practice, to transform a three-dimensional wave function like $\Phi(r, R, \theta)$ to momentum space [Eq. (3)] is very fast, and obtaining the momentum representation of initial states (usually localized in the interaction region) with $N=4$, or even $N=5$, is feasible. Thus the present definition of the PS distribution strongly reduces (or even makes unnecessary) the need to factorize the fully-coupled initial state. The result is a PS distribution of a better quality, where a large number of degrees of freedom remain coupled.

C. Sampling of the initial conditions

The distribution $P(r, R, \theta, p_r, p_R, j)$ [or $P(r, R, \theta, p_r, p_R, p_\theta)$] can now be used to sample a set of initial conditions in phase space, which will be the starting point of classical trajectories. A simple and efficient procedure, used with other quantum-type PS distributions, consists of sampling uniformly phase-space points, and checking their corresponding probability in the PS distribution. When this probability is higher than a pre-established quantity (e.g., a fraction of the maximum value of the distribution), the phase-space point is accepted as an initial condition. The new distribution of initial conditions generated in this way has a constant value in the region of phase space sampled. For an N -dimensional system this distribution (normalized to 1 in phase space) takes the value

$$P'(q_1, q_2, \dots, q_N, p_1, p_2, \dots, p_N) = \frac{1}{\Delta q_1 \Delta q_2 \cdots \Delta q_N \Delta p_1 \Delta p_2 \cdots \Delta p_N},$$

where Δq_i and Δp_i are the different intervals of the coordinates and momenta where the original PS distribution is higher than the preestablished value. Actually, the $P'(q_1, q_2, \dots, q_N, p_1, p_2, \dots, p_N)$ distribution approximates the original distribution in each degree of freedom q_i (or p_i) as a rectangle with a height $1/\Delta q_i$ (or $1/\Delta p_i$) and a basis Δq_i (or Δp_i). When the initial state of the system is the ground one, the original PS distribution has a Gaussian-type form in each degree of freedom. A rectangle-like distribution of the initial conditions will approach more the original distribution as long as the Gaussian-type functions are rather narrow. This is not usually the case when van der Waals modes are involved. If the initial state contains excitations in some of the system modes, the differences between the rectangle-like distribution and the original one become larger. As a major consequence, the distribution of initial conditions do not properly match the total energy associated with the original PS distribution (provided that it corresponds with the energy of the quantum initial state). For initial states of the system with a well-defined energy (like resonances, for instance), this fact may have important implications in the subsequent dynamics.

In order to reproduce more faithfully the original PS distribution in the sampling of the initial conditions, a somewhat different strategy has been adopted in this work. The distribution $P(r, R, \theta, p_r, p_R, j)$ is represented on a six-dimensional grid in phase space with a given density of points. This grid is the direct product of the two grids where $\Phi(r, R, \theta)$ and $\tilde{\Phi}(p_r, p_R, j)$ are represented. A new six-dimensional, more sparse PS grid is defined, such that the volume element dV of this new grid contains more than one volume element dv of the original grid. Each volume element dV acts like a "microgrid." Now the probability dP_i contained in each volume element dV_i is calculated,

$$dP_i = \int_{r_{in}^{(i)}}^{r_{fin}^{(i)}} dr \int_{R_{in}^{(i)}}^{R_{fin}^{(i)}} dR \int_{\theta_{in}^{(i)}}^{\theta_{fin}^{(i)}} d\theta \sin \theta \times \int_{p_{r_{in}}^{(i)}}^{p_{r_{fin}}^{(i)}} dp_r \int_{p_{R_{in}}^{(i)}}^{p_{R_{fin}}^{(i)}} dp_R \sum_{j_{in}^{(i)}}^{j_{fin}^{(i)}} P(r, R, \theta, p_r, p_R, j), \quad (7)$$

where the limits $r_{in}^{(i)}$, $r_{fin}^{(i)}$, $\dots$, $j_{in}^{(i)}$, and $j_{fin}^{(i)}$ depend on the specific volume element dV_i . If M is the total number of initial conditions to be generated, $M_i = \text{In}(M dP_i)$ (where In denotes the nearest integer) gives the number of initial conditions to be distributed in the phase-space volume element dV_i . These M_i initial conditions are uniformly distributed in dV_i .

Actually, what the present grid technique makes is to divide the single $2N$ -dimensional rectangle or box used in the cruder sampling method discussed above, into several smaller $2N$ -dimensional boxes (the volume elements dV_i). The grid technique allows one more flexibility to sample the initial conditions according to the real shape of the PS distribution. As a result, among other advantages, the total energy associated with the distribution of sampled initial conditions becomes closer to the true energy of the quantum initial state. By increasing the density of the sampling grid the correct value of the initial state energy is approached.

The density of the sampling grid has, however, a practical limit. On the one hand, increasing the density of the grid increases the computational cost of the sampling correspondingly. On the other hand, for a given number M of initial conditions, when the number of $2N$ -dimensional boxes of the grid increases, the probabilities dP_i , and therefore the numbers M_i of initial conditions to be distributed within each box decrease. This makes more difficult a uniform sampling of the initial conditions in each box (particularly for low M_i values). Increasing M proportionally to the increase of the grid density solves this problem, but increases the computational cost of the further dynamics simulation. In addition, the conversion of a real value like dP_i into an integer one like M_i has the effect that the number of initial conditions actually sampled is slightly smaller than the initially desired M . The reason is that for those grid boxes corresponding with the vanishing probability tails of the PS distribution, dP_i is very small and $M dP_i < 0.5$, which implies that $M_i = 0$. This causes the practical effect of a renormalization of the distribution of initial conditions with respect to the original PS distribution, where the very low-probability regions are slightly underestimated while the high-probability regions are slightly overestimated. Such an effect gets more pronounced as the size of the grid boxes decreases by increasing the grid density. Therefore, the sampling grid used should be the result of a compromise between reflecting properly the shape of the original PS distribution, and avoiding, as much as possible, the above negative effects of the sampling.

The six-dimensional grid chosen in the present work to sample the initial conditions of Ar-HCl is composed of $7 \times 15 \times 43 \times 7 \times 7 \times 5$ boxes in r, R, θ, p_r, p_R , and j , respectively, in the ranges $1.9 \text{ a.u.} \leq r \leq 3.0 \text{ a.u.}$, $6.6 \text{ a.u.} \leq R \leq 9.0 \text{ a.u.}$, $0 \leq \theta \leq \pi$, $-13.9 \text{ a.u.} \leq p_r \leq 13.9 \text{ a.u.}$, -7.4 a.u.

FIG. 2. One-dimensional probability density distributions in the coordinates r , R , and θ , obtained from the initial phase-space distribution $P(r, R, \theta, p_r, p_R, j)$ defined in Eq. (5). The solid curves are calculated by integrating $P(r, R, \theta, p_r, p_R, j)$ over the remaining degrees of freedom, while the histograms correspond to the distribution of initial conditions sampled with $P(r, R, \theta, p_r, p_R, j)$. In the case of the θ distribution the factor $\sin \theta$ has been included.

$\leq p_R \leq 7.4$ a.u., and $0 \leq j \leq 4$. Note that for the angular momentum j the sampling grid coincides with the grid of the $P(r, R, \theta, p_r, p_R, j)$ distribution. The number of initial conditions is taken to be $M=160\,075$, out of which $M'=150\,280$ initial conditions are actually sampled. There is a difference of 6% between M and M' . After renormalizing the distribution of sampled initial conditions, that 6% of intensity is transferred from the low to the high probability regions of $P(r, R, \theta, p_r, p_R, j)$, as discussed above. Figures 2 and 3 show a comparison between the different one-dimensional probability density distributions calculated from the original PS distribution $P(r, R, \theta, p_r, p_R, j)$ (solid curves), and from the distribution of sampled initial conditions (box histograms). It can be observed in the six histogram distributions that the intensity is slightly underestimated in the regions of the low-probability tails, and overestimated in the peaks of the distributions. The distribution associated with the angular coordinate θ (sampled with a higher grid density), is where the gradual transfer of intensity from the lower to the higher probability regions is more clearly appreciated. Despite this effect, the distribution of initial conditions reproduces closely the shape of the original PS distribution. Taking into account that the sampling grid used is relatively dense, the effect of renormalization is rather small.

The whole process of generating the PS distribution of Eq. (5) and sampling the 150 280 initial conditions with the above grid takes 38.5 CPU s in an Alpha station 500/400. Out of the 38.5 s, the cost of obtaining the PS distribution [essentially the transformation of $\Phi(r, R, \theta)$ to momentum

space] is only of 0.4 s, the remaining time being spent in the sampling of initial conditions. It is true that our initial state [Eq. (2)] is partially factorized, which makes more efficient to transform it to momentum space. If $\Phi(r, R, \theta)$ is treated as a fully-coupled, nonfactorized 3D wave function, the cost of generating the PS distribution increases from 0.4 to 13.2 s, which leaves the total time to obtain the initial conditions in 51.3 s. The sampling process is thus very efficient, particularly the obtention of the PS distribution.

III. DYNAMICS SIMULATIONS

Starting from the 150 280 initial conditions sampled in the above section, classical trajectories are propagated to simulate the photodissociation of Ar-HCl in the excited-electronic state $A^1\Pi$. The potential surface used in the calculations has been described previously.¹⁸ The results of the classical simulation are compared with those of an exact wave packet calculation.¹⁹ Both the classical and the quantum calculations simulate the photodissociation process for a total time of 80 fs. At this final time the classical and quantum one-dimensional probability density distributions are obtained and compared for the coordinate (Fig. 4) and momentum (Fig. 5) degrees of freedom. Although 150 280 trajectories have been integrated, it should be noted that essentially the same results are obtained with a smaller number of trajectories. However, since the classical simulation of the Ar-HCl photodissociation is very efficient (150 280 trajec-

FIG. 3. Same as Fig. 2 for the momenta p_r , p_R , and j .

FIG. 4. One-dimensional probability density distributions in the coordinates r , R , and θ , at the end of the dynamical simulations. The solid curves and the histograms correspond with the quantum and classical distributions, respectively. The distribution of initial conditions used in the classical calculation is that shown in Figs. 2 and 3, and sampled with Eq. (7). See the text for details. The factor $\sin \theta$ has been included in the θ distribution.

ries take less than 60 min. of CPU in an Alpha station 500/400), this number of trajectories ensures convergence of the results.

The classical distributions of Figs. 4 and 5 reproduce the main peaks of the quantum distributions at a semiquantitative level of accuracy. However, the low intensity tails of the quantum distributions are poorly described by classical mechanics, which only reproduces qualitatively part of these tails. The ultraviolet excitation of the Ar–HCl cluster deposits a large amount of energy (several eV) in the HCl bond. In previous quantum wave packet studies^{18,19,21,22} on the ultraviolet photodissociation of Ar–HCl it was found that the process occurs dominantly through direct or nearly-direct dissociation of the hydrogen fragment. The wave packet components associated with this dissociation mechanism give rise to the main peaks of the distributions of Figs. 4 and 5. Part of the initial wave packet prepares the cluster in excited-state resonances where the hydrogen is initially trapped in between the Ar and Cl atoms. In this case the dissociation of the hydrogen follows an indirect mechanism, through which the hydrogen collides with the heavier atoms, and transfers to them part of its initial excess energy. The indirect photodissociation mechanism manifests itself in the lower-probability tails of the quantum distributions displayed in Figs. 4 and 5. The direct photodissociation of the hot H fragment produced by the ultraviolet excitation of the cluster is expected to be a rather classical process. This explains the good agreement between the classical and the quantum descriptions in the regions of the distributions corresponding to direct photodissociation. By contrast, the mechanism of indirect photodissociation is subject to stronger quantum ef-

fects, such as resonances and interference effects. A pure classical treatment of the dynamics is expected to fail in describing quantitatively, or even semiquantitatively, this mechanism, as shown by the classical distributions of Figs. 4 and 5.

One of the quantum effects which are not reproduced by the classical dynamics is manifested in the zero intensity of the classical distribution associated with θ (Fig. 3) in the regions $\theta < 40^\circ$ and $\theta > 160^\circ$. The angle θ is defined in the calculations such that $\theta = 0$ corresponds with the collinear configuration of Ar–HCl, where the hydrogen points towards the Ar atom. The quantum distribution in the mode θ shows intensity at very small and very large angles, despite that these angular regions are blocked by the Ar and Cl atoms, respectively. Actually, this intensity is a manifestation of wave behavior of the quantum wave packet. When the wave packet reaches the “spheres” of the Ar and Cl atoms, part of the wave packet “go around” the spheres and produces intensity behind the spheres. Such a wave behavior is related to quantum interference between different components of the wave packet, and can be observed by monitoring the wave packet time evolution (see for instance Fig. 2 of Ref. 19). The classical trajectories cannot reproduce this wave behavior. A hydrogen atom described by a classical trajectory which collides with the hard sphere of an Ar or Cl atom cannot reach the region behind the sphere, and just bounces. The result is that the angular regions $\theta < 40^\circ$ and $\theta > 160^\circ$ are classically forbidden, and the corresponding intensity appears at intermediate angles ($60^\circ < \theta < 120^\circ$) in the classical distribution of Fig. 4.

In spite of the absence of quantum effects in the purely

FIG. 5. Same as Fig. 4 for the momenta p_r , p_R , and j .

FIG. 6. One-dimensional probability density distribution in the θ coordinate, $|\psi(\theta)|^2$, obtained from the $P(r, R, \theta, p_r, p_R, j)$ distribution of Eq. (5) (solid line), and the corresponding distribution of sampled initial conditions (histogram). The functions $|\psi(\theta)|^2 \sin \theta$ (dashed line) and $|\psi(\theta)|$ (dotted line) are also displayed for comparison. See the text for details.

classical treatment of the photodissociation dynamics, most of the intensity of the probability distributions is reproduced by classical dynamics in good agreement with the quantum description. Even the distribution tails, more affected by quantum effects, are reproduced classically, albeit qualitatively. The implication is that the main dynamical features of this photodissociation process are amenable to be described classically. However, the good level of agreement between the classical and the quantum dynamics is influenced, to a large extent, by the accurate characterization of the classical initial state, which closely resembles the quantum one.

The classical result for the probability distributions in the regions of the low-intensity tails deserves a more detailed analysis. While the quantum distributions exhibit long-extending tails, those of the classical distributions are clearly shorter in general (the only exception is the j distribution). In the above discussion, this qualitative result of the classical calculation has been explained in terms of the quantum effects present in the indirect photodissociation mechanism which produces the distribution tails. However, there is an additional factor, more technical in nature, which is partially responsible that the classical tails are shorter in extension than the quantum ones. This factor has to do with the specific form of the PS distribution used to sample the initial conditions.

The initial conditions are sampled according to the probability dP_i associated with each volume element dV_i in the sampling grid. The probabilities dP_i are calculated with Eq. (7), where the $\sin \theta$ factor appears in the volume element.²³ Actually, this is equivalent to sample the initial conditions according to a distribution $|\Phi(r, R, \theta)|^2 |\tilde{\Phi}(p_r, p_R, j)|^2 \sin \theta$, rather than with the distribution of Eq. (5). It should be noted that since the $\sin \theta$ factor has no dimensions, both the $|\Phi(r, R, \theta)|^2 |\tilde{\Phi}(p_r, p_R, j)|^2 \sin \theta$ and the $|\Phi(r, R, \theta)|^2 \times |\tilde{\Phi}(p_r, p_R, j)|^2$ distributions have the dimensions of a probability density. The $\sin \theta$ factor has the effect of killing the intensity of the distribution $|\Phi(r, R, \theta)|^2 |\tilde{\Phi}(p_r, p_R, j)|^2$

at very small and very large angles. This produces the initial θ distribution of Fig. 2, while the θ distribution obtained from $|\Phi(r, R, \theta)|^2 |\tilde{\Phi}(p_r, p_R, j)|^2$ has a maximum at $\theta = 0$, as well as the quantum initial state $\Phi(r, R, \theta)$. The initial orientations of the cluster corresponding with small θ angles are those for which the hydrogen is more blocked by Ar and Cl. For these initial configurations the hydrogen collides several times with the heavier atoms,^{11(b)} which is translated into a more effective energy transfer, and the long-extending tails of the quantum distributions. The lower intensity at small angles of the distribution of initial conditions of Fig. 2 is expected to produce shorter tails in the classical distributions with respect to the quantum result.

It is interesting to check the effect that including or not the $\sin \theta$ factor in the PS distribution has on the final classical probability distributions. To this purpose, a classical simulation has been carried out starting from initial conditions sampled with the PS distribution of Eq. (5), without including the $\sin \theta$ factor. In this case Eq. (7) cannot be used, and the initial conditions are sampled in a slightly different way than in the previous calculation. The same sampling grid as before is used. The basic difference is that, instead of the probability dP_i , what is now associated with each volume element dV_i is the average probability density,

$$\langle D \rangle_i = \frac{1}{K} \sum_{n=1}^K P_n^{(i)}(r, R, \theta, p_r, p_R, j), \quad (8)$$

where $P(r, R, \theta, p_r, p_R, j)$ is expressed as in Eq. (5), and the summation is carried out over the values of $P(r, R, \theta, p_r, p_R, j)$ at the K six-dimensional phase-space points constituting the microgrid of each volume element dV_i . The idea is to approximate the original PS distribution, represented on a more dense grid, by a probability density distribution represented on the more sparse sampling grid.

FIG. 7. Same as Fig. 4. In this case the distribution of initial conditions used in the classical simulation is sampled with Eq. (8). See the text for details.

Now the amount of initial conditions to be uniformly sampled within each volume element dV_i is obtained as $M_i = M\langle D \rangle_i$.

A distribution of 150 315 initial conditions is generated in this way, which resembles the original $P(r, R, \theta, p_r, p_R, j)$ distribution as closely as the previous one shown in Figs. 2 and 3 (this depends only on the density of the sampling grid). In fact, it should be noted that the two distributions of initial conditions are very similar in all the degrees of freedom, except in the angular coordinate. In Fig. 6 the initial probability distribution in the angle θ ,

$$|\psi(\theta)|^2 = \int dr \int dR \int dp_r \int dp_R \sum_j P(r, R, \theta, p_r, p_R, j),$$

is shown along with the corresponding distribution of initial conditions sampled. For the sake of comparison, the functions $|\psi(\theta)|^2 \sin \theta$ and $|\psi(\theta)|$ are also displayed in the figure.

After propagating the classical trajectories corresponding to the new distribution of initial conditions, one-dimensional probability density distributions are obtained and compared with the quantum ones in Figs. 7 and 8. Indeed, the new classical distributions exhibit tails more extended than the classical distributions of Figs. 4 and 5. Therefore, including or not the factor $\sin \theta$ in the distribution of initial conditions has an effect on the final outcome of the dynamics. However, the effect of excluding the $\sin \theta$ factor from the initial distribution is rather small in terms of the additional intensity produced in the tail regions where previously there was zero intensity. Thus one may conclude that still quantum effects play a major role in the description of the distribution tails.

The largest effect of the new distribution of initial conditions is observed in the main peaks of the classical distributions of Figs. 7 and 8, which now show a worse agreement with those of the quantum distributions. Part of the intensity of these peaks is moved towards the regions where the tails begin, and to a much lesser extent, towards the end of the tails. The result is a globally worse agreement between the classical and the quantum final distributions than in the case of the previous classical simulation shown in Figs. 4 and 5. The large difference between the results of the two classical simulations is caused by the difference in the shape of the two corresponding initial PS distributions in a single coordi-

nate, the angle θ . This bears on the general importance of an accurate characterization of the initial conditions in the MD simulations, particularly for the modes more relevant to the dynamics.

The differences between the classical distributions of Figs. 4 and 5 and those of Figs. 7 and 8 can be explained in terms of the curves shown in Fig. 6. The shape of this θ distribution is what actually differentiates the two initial distributions. The $|\psi(\theta)|^2$ distribution overestimates the initial configurations corresponding to small angles, while $|\psi(\theta)|^2 \sin \theta$ underestimates those configurations. The two distributions are very different for $\theta < 60^\circ$, and practically coincide for $\theta > 60^\circ$. The large intensity of $|\psi(\theta)|^2$ at low angles causes an artificial increase of the hydrogen blockage by Ar and Cl. This increased trapping of the H fragment is translated into a transfer of intensity from the main, direct dissociation peaks to the tails of the classical distributions of Figs. 7 and 8. The opposite behavior is caused by the $|\psi(\theta)|^2 \sin \theta$ distribution, which produces less extended tails in the classical distributions of Figs. 4 and 5. None of the distributions $|\psi(\theta)|^2$ or $|\psi(\theta)|^2 \sin \theta$ reproduces completely the quantum results, since the angular dependence of the initial wave packet, $|\psi(\theta)|$ [or $\psi(\theta)$], is in between the two of them (in the region $\theta < 50^\circ$ where most of the angular intensity is located). However, the function $|\psi(\theta)|$ appears to be somewhat closer to the distribution $|\psi(\theta)|^2 \sin \theta$ in the region around the maximum of the latter one. This would explain the better global agreement between the classical distributions of Figs. 4 and 5 and the quantum ones.

Quite different results can be obtained, therefore, depending on whether part of the volume element (actually the coordinate-dependent, adimensional part $\sin \theta$) is included or not in the initial PS distribution. More specifically, for the present problem a better agreement is found between the classical and the quantum results when the $\sin \theta$ factor is included in the initial distribution. It is not obvious *a priori* that this is the general trend. What seems to be clear is that in general the two types of distributions will have a different shape, and will produce different results. Thus the question arises about which of the two PS distributions is more justified from the conceptual point of view.

Classical trajectories are objects which have associated a real and positive distribution function at every time. Therefore, any model of a distribution used to sample initial con-

FIG. 8. Same as Fig. 7 for the momenta p_r , p_R , and j .

ditions for classical trajectories must fulfill that requirement. This is achieved by using as initial distributions probability densities, which are obtained by an squaring operation of the quantum initial state (which can be negative, or even complex in phase space), as in Eq. (5), or by a similar procedure. An exception is the Wigner distribution, which can be negative at some phase-space points, although usually it is real and positive in the relevant region of phase space. The conversion of the initial wave function into a probability density distribution implies a change in the shape of the initial state sampled for the classical trajectories, with respect to the one which is actually propagated quantum-mechanically. In other words, while quantum mechanics propagates a wave packet, classical mechanics propagates a probability density distribution. In this sense we believe there is no physical justification either to include or not a real, positive, and adimensional factor like $\sin \theta$ in the initial PS distribution.

There is a conceptual reason which leads to think that the PS distribution including the factor $\sin \theta$ is more correct. In the volume element $dv = \sin \theta dr dR d\theta dp_r dp_R$ the $\sin \theta$ function plays the role of a weighting function which determines the size of the volume element along the θ coordinate. For low and high angles the size of dv is small (or even zero at $\theta=0$ and $\theta=\pi$), while this size is maximum for $\theta = \pi/2$ and nearby angles. The probability associated with the different volume elements is correspondingly small or large, since it is already weighted by the size of the volume element. The initial conditions are sampled following the criterion of the probability of finding the system in a given region of phase space. The probability criterion implies that all the volume elements are implicitly treated as equally sized. When the initial distribution does not contain the weighting function $\sin \theta$, the sampling of initial conditions is performed assuming the above probability criterion, despite that the volume elements are actually of different size. By contrast, including the function $\sin \theta$ in the PS distribution is equivalent to redefine the volume element as $dv' = dr dR d\theta dp_r dp_R$, which now has a constant size in all regions of phase space.

The present results show that the outcome of a classical dynamics simulation may be strongly affected by the shape of the PS distribution used to sample the initial conditions. The present PS distribution is expected to be very similar in shape to that obtained with the Wigner definition (except for the coordinate-momentum couplings, which are probably small). Therefore, the results obtained using initially a

Wigner distribution are expected to be similar to those reported here. By contrast, rather different results are expected when using a classical PS distribution like the one described in the Introduction. This classical distribution in coordinate space presents maxima at the turning points of the coordinates, and a minimum at the equilibrium position, then having the opposite shape to the quantum distribution (which corresponds with a ground rovibrational state). Since the process studied in this work is mainly a direct photodissociation one, the dynamics is strongly influenced by the shape of the system initial state. Therefore, a much poorer agreement between the quantum and the classical results is expected for the present problem if a classical distribution of initial conditions is used.

As discussed above, the use of a probability density as a distribution function implies a somewhat different shape of the classical initial state sampled, as compared with the true quantum initial state. Such a difference in the shape of the initial states is expected to have a reflection in the results of the corresponding classical and quantum calculations. This suggests that using a sampling distribution closer in shape to the quantum initial state would produce classical results in better agreement with the quantum mechanical predictions. The definition of a quantum initial state in phase space, $\Phi(r, R, \theta) \tilde{\Phi}(p_r, p_R, j)$, suggested in this work, makes possible this alternative. Indeed, a distribution function of the type $|\Phi(r, R, \theta)| |\tilde{\Phi}(p_r, p_R, j)|$ can be defined, which is real and positive everywhere, and is closer in shape to the quantum initial state than the probability density $|\Phi(r, R, \theta)|^2 |\tilde{\Phi}(p_r, p_R, j)|^2 \sin \theta$. Classical simulations using the above initial PS distribution function are currently being performed.²⁴

IV. CONCLUSIONS

A quantum-type phase-space distribution to sample initial conditions for classical trajectories has been proposed in this work. An initial quantum phase-space state of the system is defined as the direct product of the coordinate and momentum representations of the quantum initial state. Then the phase-space distribution is defined as the square modulus of the above phase-space state. The suggested distribution presents the following properties: (i) It is real and positive everywhere in phase space; (ii) It gives the correct quantum

distributions both in coordinate and in momentum space; (iii) It matches the correct mean total energy of the quantum initial state; (iv) It does not assume any artificial coupling between coordinates and momenta generated by the definition itself of the distribution. The distribution, therefore, resembles very closely the quantum nature of the initial state of the system. The main advantage of the proposed distribution is that it is calculated very efficiently. This allows one to generate an initial phase-space distribution where the coupling between a larger number of degrees of freedom is retained.

A sampling grid technique is proposed in order to sample the initial conditions with the phase-space distribution. The technique consists of defining a $2N$ -dimensional grid in phase space (where N is the dimension of coordinate space), and calculating the probability of finding the system in each volume element of the grid. Then, a number of initial conditions is uniformly sampled on each volume element according to the corresponding probability. By using this grid technique the distribution of initial conditions sampled reproduces more closely the shape of the original phase-space distribution. As an illustration of the method, initial conditions are generated to describe the initial state of the Ar–HCl cluster prepared by ultraviolet excitation. The subsequent photodissociation dynamics is simulated by a classical trajectory calculation. Probability density distributions in the different coordinates and momenta are obtained at the end of the simulation, and compared with those of a quantum wave packet calculation. A good agreement between the classical and the quantum results is found in the regions of the distributions not affected by strong quantum effects (most of the intensity of the distributions). The classical description of the distribution intensity derived from a more strongly quantum dynamics is significantly poorer. The results show the importance of a faithful correspondence between the quantum initial state of the system and the initial conditions used in classical dynamics simulations.

The definition of a quantum phase-space distribution proposed here appears to be efficient, flexible, and easy to implement. Therefore its applicability to systems with more than three spatial degrees of freedom is envisioned. The complementary sampling grid technique is found promising as well, although its computational cost increases fastly with the number of degrees of freedom.

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