

# Stochastic dissociation of diatomic molecules

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The fragmentation of diatomic molecules under a stochastic force is investigated both classically and quantum mechanically, focusing on their dissociation probabilities. It is found that the quantum system is more robust than the classical one in the limit of a large number of kicks. The opposite behavior emerges for a small number of kicks. Quantum and classical dissociation probabilities do not coincide for any parameter combinations of the force. This can be attributed to a scaling property in the classical system which is broken quantum mechanically.

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## I. INTRODUCTION

The anharmonicity of molecular vibrations makes the dissociation of a molecule by irradiation of laser light a relatively difficult task.<sup>1</sup> Consequently, high intensity is required for dissociation, for instance,  $I > 10^{15}$  W/cm<sup>2</sup> for HF and  $I \geq 10^{14}$  W/cm<sup>2</sup> for HCl. At such intensities, however, the ionization process dominates and masks vibrational excitation and dissociation. Chelkowsky *et al.*<sup>2</sup> suggested that the dissociation threshold of a diatomic molecule can be lowered by two orders of magnitude using a frequency-chirped laser, and hence dissociation without ionization should be possible. In a similar spirit, circularly chirped pulses have been used by Kim *et al.*<sup>3</sup> for the dissociation of diatomic molecules. They found that the threshold laser intensity is sufficiently reduced, to achieve dissociation without ionization.

Here, we investigate the possibility for dissociation of diatomic molecules under a stochastic force, which could eventually be chosen such that ionization is minimal. A second motivation for our work is the question, if stochastic driving destroys quantum coherence and eventually brings the quantum and classical evolution close to each other.

We model the force as a sequence of pulses (kicks) at random times, each kick carrying an independent weight.<sup>4</sup> This type of force, similar to white shot noise, has been used to model the passage of ions through carbon foils before.<sup>5</sup> Its average strength  $\gamma$  and the average number of kicks  $\langle \Delta t \rangle$  determine the dynamics of the system which is taken as a Morse oscillator<sup>6</sup> with parameters corresponding to hydrogen fluoride (HF) and hydrogen chloride (HCl) molecules. The classical and quantum evolutions of the system are conveniently compared by using the Wigner transform of the initial wave function as initial phase-space distribution in the classical evolution.

We begin the main text of this paper in Sec. II with a brief description of the stochastic Hamiltonian. In Sec. III we explain the classical and quantum methods with which we

solve the stochastic dynamics, which is the Langevin equation with test particle discretization and Monte Carlo sampling in the classical case and the direct solution of the stochastic Schrödinger equation with a standard fast Fourier transform (FFT) split-operator method with absorbing boundary conditions in the quantum case. Results, particularly for the dissociation probability will be presented and discussed in Sec. IV, while Sec. V concludes the paper.

## II. DESCRIPTION OF THE MODEL

The one-dimensional stochastic Hamiltonian of our system reads (atomic units are used unless stated otherwise)

$$H(t) = H_0 - xF(t) \equiv \frac{p^2}{2m} + V(x) - xF(t), \quad (1)$$

where the molecular dipole gradient<sup>2</sup> has been absorbed into the stochastic force  $F(t)$ . The Hamiltonian  $H_0$  describes vibrational motion of the molecule in the Morse potential,<sup>6</sup>

$$V(x) = -D_e + D_e(1 - \exp(-\beta x))^2, \quad (2)$$

with well depth  $D_e$  and length scale  $\beta$ . The eigenenergies  $E_n$  of the Morse oscillator  $H_0$  are given by

$$E_n = \hbar\omega_e(n + 1/2)[1 - B(n + 1/2)/2], \quad 0 \leq n \leq [j], \quad (3)$$

where  $\omega_e$  is the harmonic frequency,  $n_b = [j] + 1$  is the number of bound states with

$$j = 1/B - 1/2, \quad B = \hbar\beta(2mD_e)^{-1/2}, \quad \hbar\omega_e = 2BD_e. \quad (4)$$

The parameters specific to HCl and HF are given in Table I. The stochastic force  $F(t)$  (Refs. 4 and 8) in Eq. (1),

$$F(t) = \sum_{i=1}^{N_t} \gamma_i \delta(t - t_i), \quad (5)$$

stands for a series of random impulses of strength  $\gamma_i$  at times  $t_i$ , i.e.,  $F(t)$  is a kind of white shot noise<sup>7</sup> responsible for multiple  $\delta$  kicks undergone by the molecule, where  $N_t$  is the number of kicks up to time  $t$  controlled by the Poisson count-

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TABLE I. Parameters of the HF and HCl molecules, for the Morse potential.

Molecule	$B$	$D_e$ (eV)	$\beta$ ( $a_0^{-1}$ )	$N_b$	$\omega_e$ (Hz)
HCl	$4.07 \times 10^{-2}$	4.40	0.9780	25	$8.66 \times 10^{13}$
HF	$4.19 \times 10^{-2}$	6.125	1.1741	24	$12.38 \times 10^{13}$

ing process  $N_r$ . It is characterized by the average kicking interval  $\langle \Delta t \rangle \equiv \lambda^{-1}$  about which the actual interval  $\Delta t_i = t_i - t_{i-1}$  are exponentially distributed, similarly as the actual kicking strengths  $\gamma_i$  about their mean  $\gamma$ ,

$$P(\Delta t_i) = \lambda \exp(-\lambda \Delta t_i), \quad P(\gamma_i) = \gamma^{-1} \exp(-\gamma_i/\gamma). \quad (6)$$

We restrict our analysis to positive  $\gamma_i$  and assume that  $\gamma_i$  and  $t_i$  are mutually uncorrelated random variables generated by the distributions functions of Eq. (6). The determination of  $F(t)$  reduces to the construction of a stochastic sequence  $(\gamma_i, t_i)$  which can be done assuming that the random times  $t_i$  form a Poisson sequence of points leading to a delta-correlated process.<sup>4</sup> It is easy to show<sup>8</sup> that the constructed stochastic force has the following properties:

$$\begin{aligned} \langle F(t) \rangle &= \gamma \lambda, \\ \langle F(t)F(s) \rangle &= 2\gamma^2 \lambda \delta(t-s) + \gamma^2 \lambda^2. \end{aligned} \quad (7)$$

The corresponding power spectrum, i.e., the Fourier transform of  $\langle F(t)F(s) \rangle$ , is given by

$$S(\omega) = 4 \frac{\gamma^2 \lambda}{\sqrt{2\pi}} + \gamma^2 \lambda^2 \sqrt{2\pi} \delta(\omega). \quad (8)$$

These properties reveal the difference between the present stochastic force (white shot noise) and a pure white noise which is delta correlated with *zero mean*.

### III. DYNAMICS

#### A. Time evolution

Our system as described is nondeterministic due to the stochastic nature of its Hamiltonian but closed. This is consistent with a regime of high effective temperature and no dissipation. Specifically speaking, the system is a simple anharmonic particle which is not coupled to any environment (zero dissipation and no diffusion) but subject to an external force.<sup>9</sup> A perturbative solution for this system is in general not possible, because the field strengths applied significantly distort the system. We are interested in the formulation of the dynamics which is applicable for the quantum as well as for the classical treatments. This can be done in an elegant way by propagating the Wigner transform  $W$  of the density matrix  $\rho(t) = |\psi(t)\rangle\langle\psi(t)|$  with a (quantum) master equation<sup>10</sup>

$$i\hbar \frac{\partial W}{\partial t} = L_{cl}W + L_qW + \hat{O}W,$$

$$L_{cl} = -\frac{p}{m} \frac{\partial}{\partial x} + \frac{\partial V}{\partial x} \frac{\partial}{\partial p},$$

$$L_q = \sum_{n(\text{odd}) \geq 3}^{\infty} \frac{1}{n!} \left( \frac{\hbar}{2i} \right)^{n-1} \frac{\partial^n V}{\partial x^n} \frac{\partial^n}{\partial p^n}.$$

Here,  $L_{cl}$  and  $L_q$  represent the classical and quantum Liouville operators, respectively, while  $\hat{O}$  stands for the superoperator resulting from the random kicks undergone by the molecule. Unfortunately, solving the master equation and constructing  $\hat{O}$  is a complicated task. It is much easier to solve the equations of motion derived from Eq. (1) directly.

The classical time evolution obeys the Langevin equation,

$$\frac{dp}{dt} = -\frac{\partial V}{\partial x} + F(t), \quad (9)$$

while the quantum evolution can be obtained from the stochastic Schrödinger equation,

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = H(t)|\psi(t)\rangle. \quad (10)$$

Both formulations have in common that they must be solved over a larger number of realizations  $N_r$  of the stochastic force. Only the average over all realizations produces the solution of the classical Langevin and the stochastic Schrödinger equations, respectively.

#### B. Initial state

The molecule is considered to be initially in the ground vibrational state  $|\psi_0\rangle \equiv |0\rangle$  with energy  $E_0$  [Eq. (3)]. For the classical propagation we take the Wigner distribution of the ground state as initial phase-space distribution. Analytically, the initial phase-space density is given by

$$W_0(x(\xi), p) = \frac{2}{\pi \hbar \Gamma(2j)} \xi^{2j} K_{-2ip/\hbar, \beta}(\xi), \quad (11)$$

where  $\xi(x) = (2/B)\exp(-\beta x)$  and  $K_\alpha$  is the modified Bessel function of the third kind.<sup>11</sup>

#### C. Classical approach

The stochastic Langevin equation (9) can be solved numerically with test particles (“test particle discretization”) so that the Wigner function is given by

$$W(x, p, t) = N_{\text{test}}^{-1} \sum_{k=1}^{N_{\text{test}}} \delta(x - x_k(t)) \delta(p - p_k(t)), \quad (12)$$

where  $N_{\text{test}}$  is the number of test particles and the  $(x_k(t), p_k(t))$  are the classically evolved trajectories of the test particles. Their initial conditions  $(x_k(0), p_k(0))$  are Monte Carlo sampled by dividing the phase space into small bins  $S_{lm}$ .<sup>12</sup> In each  $S_{lm}$  the initial conditions for  $n_{lm}$  test particles are randomly chosen where  $n_{lm}$  is determined by the value of

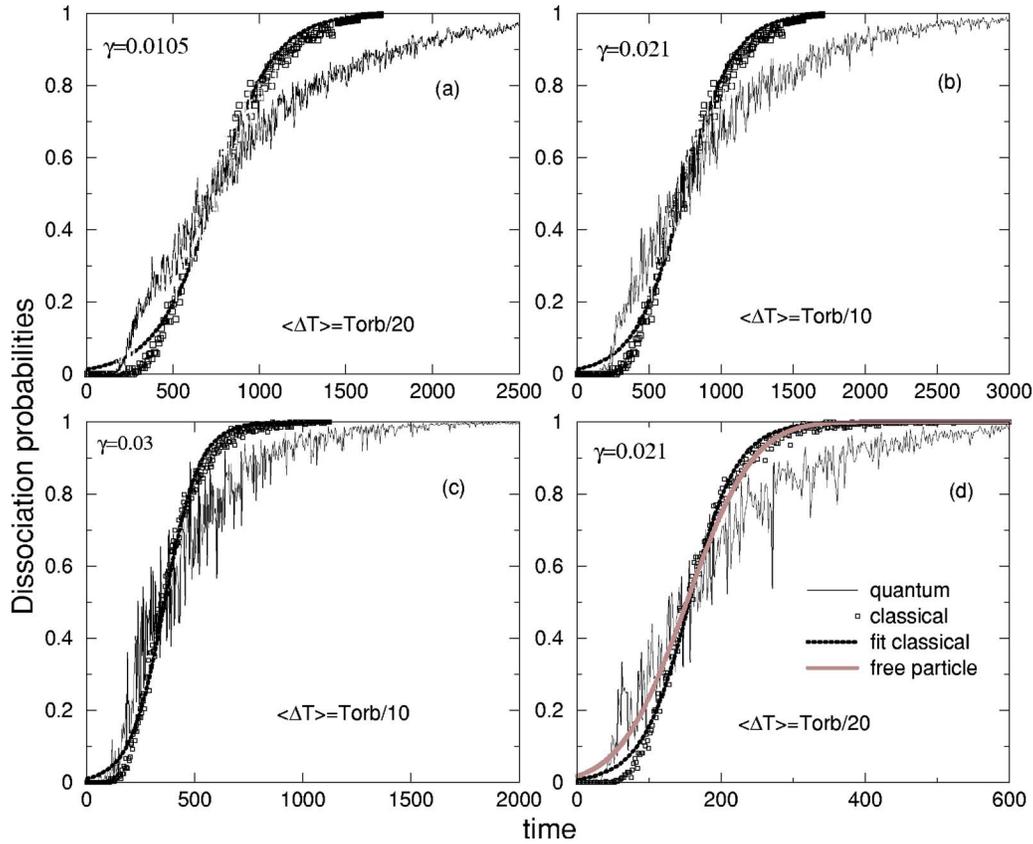


FIG. 1. Quantum and classical dissociation probabilities of HF for  $\gamma$  and  $\langle \Delta t \rangle$  as labeled on each panel, where  $T_{\text{orb}}=0.085$ . Squares denote the classical dissociation probabilities fit with (19). The red (grey) line is a free-particle model, see text. Results obtained for HCl are qualitatively similar.

the Wigner function  $W(x, p)$  attached to the respective phase-space bin,

$$n_{lm} = W(x_l, p_m) S_{lm} N_{\text{test}}, \quad (13)$$

with  $S_{lm} = (x_{l+1} - x_l)(p_{m+1} - p_m)$ .

For each realization  $r$  of the stochastic force Eq. (12) yields the propagated Wigner function  $W_r(x, p, t)$  which must be averaged over the  $N_r$  realizations to obtain the final result  $W(x, p, t)$ .

#### D. Quantum approach

For a given realization  $r$ , the solution of the stochastic Schrödinger equation (10) amounts to solve the standard time-dependent Schrödinger equation,

$$|\psi_r(t)\rangle = U_r(t, t_0) |\psi(t_0)\rangle, \quad (14)$$

where  $U_r(t, t_0)$  is the evolution operator and  $|\psi(t_0)\rangle = |0\rangle$ . Since the stochastic force consists of instantaneous kicks,  $U_r(t, t_0)$  can be written as

$$U_r(t, t_0) = U_0(t, t_N) \prod_{i=0}^{n_r-1} \exp\left(\frac{i}{\hbar} x \gamma_i\right) U_0(t_{i+1}, t_i), \quad (15)$$

with  $n_r$  kicks for the realization  $r$  and

$$U_0(t_{i+1}, t_i) = \exp\left(-\frac{i}{\hbar} (t_{i+1} - t_i) H_0\right). \quad (16)$$

This representation illustrates how the stochastic driving operates. Between two kicks at  $t_i$  and  $t_{i+1}$  the molecule evolves

freely with  $U_0$  according to the Hamiltonian  $H_0$  [Eq. (16)]. At each kicking time  $t_i$  the stochastic force induces a phase shift by  $\exp((i/\hbar)x\gamma_i)$ . In practice, however, it is easier to compute  $|\psi_r(t)\rangle$  directly using the standard FFT split-operator algorithm<sup>13</sup> with absorbing boundary conditions.

#### E. Dissociation probability

The observable we are interested in is the quantum dissociation probability, which is the amount of population in the continuum states. However, it is easier to calculate the complement, i.e., the population of all bound states  $\psi_\nu$ . It reads for a given realization  $r$

$$P_\nu^r(t) = |\langle \psi_\nu | \psi_r(t) \rangle|^2. \quad (17)$$

The dissociation probability for the realization  $r$  is then given by

$$P_d^r(t) = 1 - \sum_{\nu=0}^{N_b-1} P_\nu^r(t). \quad (18)$$

Classically,  $P_{d;\text{cl}}^r(t)$  is given in terms of trajectories  $N_+(t)$  which have positive energy  $E(t) > 0$  at time  $t$ . The physical result is obtained by averaging Eq. (18) over the  $N_r$  realizations. For the results we will present we chose  $N_r=100$  and  $N_{\text{test}}=1000$  which was sufficient to achieve convergence.

## IV. RESULTS AND DISCUSSIONS

### A. Quantum and classical dissociation probabilities

An overview over the results is given in Fig. 1. As a general trend one sees that quantum and classical dissociation probabilities do not coincide, in neither limit of the stochastic force (small and large  $\gamma$  and  $\langle\Delta t\rangle$ ). Furthermore, for all parameter combinations, the classical dissociation takes off later but increases faster eventually overtaking the quantum dissociation and going into saturation earlier than in the quantum case. The more abrupt classical dissociation can be parameterized with

$$P_{d;cl} \simeq \frac{1}{2} \tanh(at + b) + \frac{1}{2}, \quad (19)$$

which fits quite well the classical dissociation. The fact, that the discrepancy between the quantum and the classical curves prevails even in the parameter limits for the stochastic force, can be partially attributed to a scaling invariance. This invariance with respect to the ratio  $\gamma/\langle\Delta t\rangle = \langle F(t) \rangle$  is obeyed by the classical dynamics but not by the quantum dynamics. The scaling invariance means that for equal average stochastic force  $\langle F(t) \rangle$  [compare Eq. (7)], the classical dynamics is the same, yet on different effective time scales. This can be seen by transforming the dynamics to a dimensionless time variable  $\tau = t/\langle\Delta t\rangle$ . The effective Hamiltonian in the new time variable  $\tau$ ,  $(H-E)dt/d\tau$ , remains invariant against changes of  $\langle F(t) \rangle = \gamma/\langle\Delta t\rangle$ .

While the classical dynamics gives qualitatively the same picture as the quantum dynamics it does not approach the quantum result, not even in the limit of a large number of kicks. This is different from a Coulomb system under stochastic driving.<sup>5</sup> Since it becomes classical close to  $E=0$  (which corresponds formally to the dissociation threshold here) one can show that the Coulomb system itself behaves almost classical, and therefore the classical scaling under the stochastic force also applies to the quantum Coulomb system close to  $E=0$ . The molecular system behaves nonclassically, even close to the dissociation threshold, which prevents it to approach the classical scaling under the stochastic force. Interestingly, the nature of stochastic driving, namely the cancellation of interferences, does not help to approach classical behavior. The reason is that the dynamics in the Morse potential without stochastic force differs classically and quantum mechanically, particularly for higher energies, where the nonlinearity of the potential is strong. Consequently, one may ask if under a very strong stochastic force, i.e., without a potential, classical and quantum dynamics become similar.

### B. The free-particle limit under stochastic driving

If  $V=0$  in Eq. (1), i.e.,  $H_0 = p^2/2m$ , one sees immediately with the help of Ehrenfest's theorem that classical and quantum observables should agree since Eq. (1) only contains linear and quadratic operators. Therefore, the state  $|\psi(t)\rangle$  time evolved under the stochastic driving from an initial momentum  $|\psi(0)\rangle = |p\rangle$  is simply given by  $|\psi(t)\rangle = |p(t)\rangle$  where  $p(t)$  is defined by the classical time evolution, starting from the initial momentum  $p_i$  at time  $t_0$ ,

$$p_i = \lambda \gamma(t - t_0) + p_i. \quad (20)$$

We can define a formal analog to the dissociation probability, namely the probability to find a particle after time  $t$  with positive momentum

$$P_d(t) \equiv \int_0^\infty dp_i W(p_i(p_i)), \quad (21)$$

where  $p_i(p_i)$  can be obtained from Eq. (20) and  $W(p)$  is the initial momentum distribution which we assume for simplicity to be Gaussian,

$$W(p_i) = (\alpha/\sqrt{\pi}) \exp(-\alpha^2 p_i^2). \quad (22)$$

Inserting Eqs. (22) and (20) into Eq. (21) leads to an incomplete Gaussian integral with the analytical solution

$$P_d(t) = \frac{1}{2} \operatorname{erfc}[-\alpha \lambda \gamma(t - t_0)]. \quad (23)$$

We may use this analytical expression  $P_d(t)$  with the two parameters  $\alpha$  and  $t_0$  to fit and interpret the dissociation probabilities in Fig. 1. At some time  $t_0 > 0$  after a number of kicks the systems will have a distribution (with width  $\alpha$ ) of energies and the mean energy may be considered to be high enough to approximate the dynamics with a free-particle Hamiltonian under stochastic driving without a potential. As one can see in Fig. 1, this approximation becomes increasingly better for larger time in comparison to the *classical* response, while the quantum response remains different. In Fig. 1(d)  $P_d(t)$  is plotted for  $\gamma=0.021$ ,  $\lambda=\langle\Delta T\rangle^{-1}=235.301$ ,  $m=1782.83$ ,  $\alpha=0.02135$ , and  $t_0=150$ .

## V. CONCLUSIONS

We have proposed and discussed the possibility of dissociating diatomic molecules by a stochastic force. This problem has been explored as function of the characteristic parameters of the stochastic force, namely the average strength of kicks  $\gamma$  and the average time between kicks  $\langle\Delta t\rangle$ . In view of the effectivity of the stochastic force to dissociate the molecule with typical  $\langle\Delta t\rangle$  much longer than electronic time scales we expect the stochastic force to be an efficient way to dissociate a molecule. In contrast to Coulomb dynamics there is no parameter limit of the stochastic force where classical and quantum results coincide. The reason is the classical scaling of the dynamics under the stochastic force which is broken by the quantum dynamics. We recall that the present system is a closed one, not coupled to an environment and therefore not subject to dissipation and diffusion. For the latter case of an open system the classical-quantum correspondence has been investigated systematically, with the general tendency that strong decoherence makes the quantum system to behave more classically. In contrast, little is known about the quantum-classical correspondence in the present case of a closed system exposed to a stochastic force.

We hope that our results will stimulate efforts to achieve the experimental dissociation of diatomic molecules using white shot noise. Experiments, using a stochastic force similar to the present one, have been successfully performed by Milner *et al.*<sup>14</sup> on the dynamics of rotors.

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<sup>12</sup>We use a fixed grid for all times with 2048 points in  $x \in [-L/50, 49L/50]$  and 201 points in  $p \in [-10, 10]$ , where  $L=500$ . Each phase space bin  $S_{im}$  is a constant area defined by  $(x_{i+1} - x_i)(p_{m+1} - p_m)$ .

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