



Effects of oscillatory behavior of the dipole function on the dissociation dynamics of the classical driven Morse oscillator

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ABSTRACT

The role of the spatial dependence of dipole coupling on the dissociation dynamics of the classical driven Morse oscillator is investigated, in particular, the effects of oscillatory behavior of the dipole function are considered. The initial conditions for the calculations are chosen to correspond to highly excited vibrational states, which are close to the Morse potential separatrix. It is shown that the oscillatory form of the dipole function influences the splitting of the separatrix and accordingly the dissociation dynamics. Specifically, the dipole oscillatory behavior can prevent trajectories from escaping the potential well and consequently inhibiting the dissociation mechanism. It is found that this inhibition of dissociation is related to the change of sign of the dipole function.

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1. Introduction

Investigations of simple model systems involving the motion of classical particles in one-dimension potentials and driven by external time-dependent fields have proved to be important to gain physical insights into microscopic processes [1,2]. For instance, 1D classical model systems have been used to interpret the experimentally observed shifts of the ionization threshold of hydrogen atoms driven by bichromatic fields and to give an explanation for the frequency dependence in the microwave ionization of excited hydrogen atoms [3,4]. Another example is the study of the dissociation of diatomic molecules by infrared laser fields, which is often modeled by the classical driven Morse oscillator [5,6]. In these model systems, the coupling between the unperturbed part representing the atom or the molecule and the external field is usually given in the dipole approximation. The coupling term is then constituted by the product of a time-dependent external field with a position-dependent dipole function. Although much effort has been made to understand the role of the time-dependent external field on the system dynamics, the same attention has not been given to the spatial dependence of the dipole function.

Here, we consider the dissociation dynamics modeled by the classical one-dimension driven Morse oscillator [7–15]. It has been

widely recognized that the laser-driven classical dissociation of the Morse oscillator occurs through chaotic routes. For weak fields, the phase space is dominated by Kolmogorov–Arnold–Moser (KAM) tori and the chaotic layers cover a relative small part of the phase space. As the intensity of the drive increases, resonance islands grow and overlap each other, while most of the KAM tori vanish. The phase space becomes dominated by a chaotic sea, leading to dissociation. Such chaotic behavior has stimulated several quantum–classical comparisons within the Morse model and correspondences between the two theories have been found in some regimes [16–25]. The precise system dynamics, however, depends on the spatial dependence of dipole function considered [26]. Furthermore, diatomic molecules possess varied shapes of the dipole function and the dipole of some molecules presents oscillatory behavior [27–30]. Thus, understanding the specific role of the dipole function on the dissociation dynamics of the Morse oscillator may help to comprehend subtleties of the dissociation dynamics of distinct diatomic molecules.

The goal of this paper is to investigate the effects of oscillatory behavior of the dipole function on the classical dissociation dynamics of the Morse oscillator. The oscillatory behavior of the dipole function is obtained through the introduction of a continuous parameter. For low values of this parameter, the dipole function is not oscillatory and resembles the dipole function of the HF molecule, which is used as a reference. Oscillations of the dipole function are obtained increasing the value of this parameter. Section 2 begins with a description of the Morse model system, which is followed by the parametrization of the dipole function. In Section 3, we present and discuss the results of the numerical calculations. Finally, conclusions are drawn in Section 4.

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2. Model system

2.1. Classical dissociation in the driven Morse oscillator

The classical driven Morse oscillator is commonly used as a model for the dissociation of a diatomic molecule under a linearly polarized laser field [8,7,9,10,6]. The Hamiltonian of the system can be written in two parts, one stands for the free molecule $\mathcal{H}_0(R, P)$ and the other for the molecule–field interaction $\mathcal{H}_1(R, P)$,

$$\mathcal{H}(R, P, t) = \mathcal{H}_0(R, P) + \mathcal{H}_1(R, P, t), \quad (1)$$

where R is the internuclear distance and P is the conjugate momentum. The Hamiltonian $\mathcal{H}_0(R, P)$ is given by the free Morse oscillator,

$$\mathcal{H}_0(R, P) = \frac{P^2}{2M} + D \left[e^{-2\alpha(R-R_e)} - 2e^{-\alpha(R-R_e)} \right], \quad (2)$$

where M is the reduced mass of the diatomic molecule, D is the dissociation energy, R_e is the equilibrium position and α^{-1} is the range of the potential.

The interaction Hamiltonian $\mathcal{H}_1(R, t)$ representing the coupling between the laser field and the diatomic molecule is given by

$$\mathcal{H}_1(r, t) = -d(R) \cdot \mathcal{E}(t), \quad (3)$$

where $d(R)$ is the permanent dipole function and $\mathcal{E}(t)$ is the electric field component along the molecular dipole orientation. For instance, the dipole function for hydrogen fluoride can be expressed by

$$d_{\text{HF}}(R) = AR e^{-BR^4}, \quad (4)$$

where A and B are fixed constants. The value of these constants and of the Morse parameters for the HF molecule in atomic units are $D_{\text{HF}} = 0.2101$, $\alpha_{\text{HF}} = 1.22$, $R_e^{\text{HF}} = 1.75$, $M_{\text{HF}} = 1732$, $A = 0.4541$ and $B = 0.0064$ [19].

The external field acts from $t = 0$ to $t = t_f$ and it is given by a single color

$$\mathcal{E}(t) = \mathcal{E}_0 \sin(\Omega t) \quad (5)$$

with \mathcal{E}_0 and Ω being the field amplitude and frequency, respectively.

In the absence of external interactions, a particle in the Morse potential with energy E such that $-D < E < 0$ oscillates in the bound part of the well, which represents the molecular vibration; whereas the motion of a particle with $E > 0$ is not confined to a finite region in space and the particle escape to infinity. Therefore, these two kinds of motion are divided by a separatrix at $E = 0$. All initial conditions with energy starting inside the libration region ($E < 0$) will never escape until the external field is turned on. Depending on the field strength and also on the shape of the dipole, the initial conditions can be carried to infinity, which corresponds to the molecular dissociation, or still be trapped into regular regions of the phase space.

In analogy with quantum predictions, a classical dissociation probability may be defined. This is done by propagating a large number of trajectories N_{traj} according to Hamilton's equations of motion. The ensemble of initial conditions are chosen with energy E_ν corresponding to a given quantum vibrational level ν . The classical dissociation probability P_D is calculated by counting the number n of escaping trajectories for which the energy is greater than the separatrix energy by the end of the external excitation at $t = t_f$ and calculating the fraction

$$P_D = \frac{n}{N_{\text{traj}}}. \quad (6)$$

2.2. Parametrization of the dipole function

The Hamiltonian function and the equations of motion for the driven Morse oscillator can be conveniently written in terms of

dimensionless variables defined by

$$x = \alpha(R - R_e), \quad (7)$$

$$p = \frac{P}{\sqrt{2MD}}, \quad (8)$$

$$x_e = \alpha R_e, \quad (9)$$

$$\tau = \Omega_0 t, \quad (10)$$

where $\Omega_0 = \alpha\sqrt{2D/M}$ is the frequency for small harmonic oscillations around R_e . The free-molecule Hamiltonian is then rewritten as

$$H_0 = \frac{p^2}{2} + \frac{1}{2}(e^{-2x} - 2e^{-x}), \quad (11)$$

where the Hamiltonian has been rescaled as $H_0 = \mathcal{H}_0/(2D)$, with the well depth being $1/2$. Therefore, for the rescaled Hamiltonian in the absence of external fields, trajectories with energies in the interval $[-1/2, 0]$ will remain trapped inside the well, whereas trajectories with energies greater than zero will escape to infinity.

From the following definitions

$$\mu(x) = \frac{\alpha}{q} d(R), \quad (12)$$

$$\epsilon_0 = \frac{q\mathcal{E}_0}{2\alpha D}, \quad (13)$$

where q is some unit of charge, the rescaled field-molecule Hamiltonian $H_1 = \mathcal{H}_1/(2D)$ is written as

$$H_1 = \mu(x) \cdot \epsilon(\tau), \quad (14)$$

where the time-dependent external field is

$$\epsilon(\tau) = \epsilon_0 \sin(\omega\tau), \quad (15)$$

acting from $\tau = 0$ to $\tau_f = \Omega_0 t_f$ and with $\omega = \Omega/\Omega_0$ being the external frequency measured in units of Ω_0 .

For the purpose of this work, we introduce the dimensionless dipole function $\mu(x, \eta)$ given by

$$\mu(x, \eta) = \frac{\sin[\eta(x + x_e)]}{\eta} e^{-\xi(x+x_e)^4}, \quad (16)$$

where η , ξ and x_e are dimensionless adjustable parameters. Here, we are most interested in the role of the parameter η and we will fix ξ and x_e through the parameters of the HF molecule $\xi = B\alpha_{\text{HF}}^{-4}$ and $x_e = \alpha_{\text{HF}} R_e^{\text{HF}}$. Thus, in the limit $\eta \rightarrow 0$, we recover the HF dipole function

$$\lim_{\eta \rightarrow 0} \mu(x, \eta) = \frac{\alpha_{\text{HF}}}{A} d_{\text{HF}}(R). \quad (17)$$

Therefore, η plays the role of a deformation parameter introducing oscillations on the dipole function as it increases and recovering the HF dipole function as it decreases. In Fig. 1, the dipole function for different values of η are shown in order to observe the effects of η on $\mu(x, \eta)$. We see that for $\eta \gtrsim 0.5$, the oscillatory behavior of the dipole becomes apparent. As we show in the following, this oscillatory behavior has remarkable effects on the dissociation probability. Our aim here is to determine the effects of increasing η on the dissociation of the driven Morse oscillator by solving the Hamilton equations of motion for an ensemble of initial conditions,

$$\begin{aligned} \frac{dx}{d\tau} &= p, \\ \frac{dp}{d\tau} &= e^{-2x} - e^{-x} + \frac{\partial \mu(x, \eta)}{\partial x} \epsilon_0 \sin(\omega\tau). \end{aligned} \quad (18)$$

3. Results and discussions

In the subsequent calculations, ensembles of $N_{\text{traj}} = 10^3$ initial conditions distributed on a fixed energy shell have been propagated according to Eq. (18). This number proved to be satisfactory

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