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A tunable mechanism to control photo-dissociation with invariant tori with variable energies

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HIGHLIGHTS

- The particle moves out of the potential well.
- The particle moves into the potential well.
- The tori in phase space are bent.
- The particle does not dissociate.
- Photo-dissociation is tunable.

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ABSTRACT

In this work, we investigate the classical dynamics of a polar diatomic molecule under the action of a space and time-dependent laser field. In the absence of laser fields, the phase space consists of a bound and an unbound region divided by a separatrix. When an interacting laser field is present, some surviving invariant tori are deformed. Therefore, the initial conditions in the bound region which are over the surviving tori may visit the unbound region but still undergoing a bounded motion. Based on this analysis, we propose a mechanism to control the photo-dissociation process using the driven Morse oscillator as a model.

1. Introduction

In a photo-dissociation process, a molecule absorbs photons from an applied laser field leading to the breaking of a chemical bond. Although this process is precisely described by only quantum mechanics, the classical mechanics has been often invoked to tackle this problem [1–12]. Among the reasons that justify the classical approach is the existing correspondence between quantum and classical results. From the classical point of view, it is recognized that multiphoton dissociation occurs through chaotic orbits [7,13–16]. In the absence of interactions with the external field, the corresponding phase space presents two distinct regions, one associated with libration tori, i.e., bounded motion, and another with unbounded motion. These two regions are divided by a separatrix. The introduction of a laser field can lead to the destruction of some invariant curves and to the formation of a chaotic sea, which allows the transition from bound to unbound motion.

In a recent paper [17], we have presented a mechanism to control photo-dissociation through the creation of a resonance island in the region of excited states. The island corresponds to a local stable structure that can trap trajectories which have started with appropriate initial conditions. This result raised the question of how we could improve the idea of controlling the

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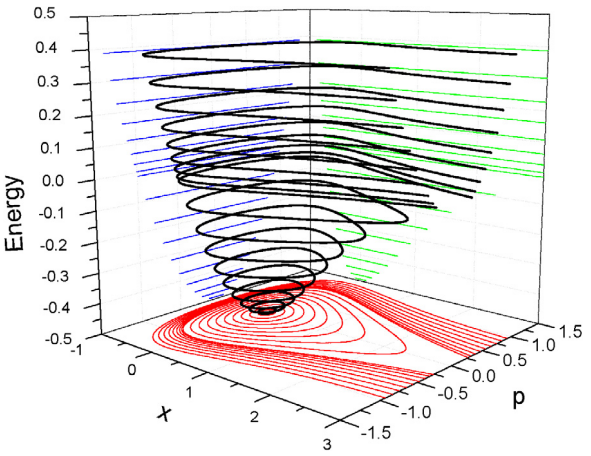

Fig. 1. The energy cube: curves of constant energy of the unperturbed Morse oscillator.

photo-dissociation process and obtain a wider stable structure, which may permeate the regions with bound and unbound energies. Here, we propose to substitute the only island structure by a family of bent invariant tori in such way that they could pass through the energy of the separatrix.

In the present work, we consider the Morse oscillator as our non-perturbed system and a time-periodic perturbation is applied in order to globally break the constant of motion, associated with the total energy of system. The energy of a polar diatomic molecule under the action of an external laser field depends on the interaction of the position-dependent permanent dipole of the molecule with the laser electric field. Thus, the shape of the dipole and the time-dependence of the field play essential roles. Results considering the role of the dipole functional forms in controlling the dynamics of some molecular systems have been reported in various works [18–21]. The intensity of the perturbation, the set of parameters, as well as the spatial shape of the dipole, are appropriately chosen in order to keep some invariant tori in the phase space. The process of classical photo-dissociation is discussed in different scenarios. The paper is organized as follows, in Section 2 we describe the main properties of the Morse oscillator, with linear and non-linear coupling with the external field, and we construct the corresponding *energy cubes*. We close the paper with concluding remarks in Section 3.

2. The energy cube and the linear and non-linear dipoles

The dimensionless unperturbed Hamiltonian $H_0\,(x, p)$ describing the relative motion of the nuclei of a diatomic molecule is given by,

$$H_0\,(x, p) = \frac{p^2}{2} + V_{Morse}\,(x) \tag{1}$$

with $V_{Morse}\,(\mathrm{x}) = \frac{1}{2}\left\{e^{-2x} - 2e^{-x}\right\}$, in which x is the distance between the nuclei and p is the conjugate momentum of the molecular particle. For the above choice of Morse parameters, the well depth is 0.5 and the separatrix is located at energy $E = 0$.

We take the level curves of the system governed by the Hamiltonian (1) and we plot in Fig. 1 the energies of some libration tori and of a few open curves. The projections on the planes (Energy, x) and (Energy, p) evidence that the total energy of the system is a global constant of motion. We call this 3-dimensional plot as *energy cube*.

2.1. Linear dipole

In order to observe the mechanism of bending the tori in the phase space, we consider a time-dependent perturbation, representing the coupling of the electric field with the molecular dipole, which is assumed initially linear. The corresponding Hamiltonian is given as, $H_{laser}(x, t) = -\mu(x).\mathcal{E}(t)$, where $\mu\,(x) = qx$ is the moment of the dipole with q being the effective dipole charge and $\varepsilon\,(t) = \varepsilon_0 \sin(\omega t)$ is the laser electric field. Thus, the complete Hamiltonian of the system now is given as,

$$H\,(x, p, t) = H_0\,(x, p) + H_{laser}\,(x, t) = \frac{p^2}{2} + \frac{1}{2}\left\{e^{-2x} - 2e^{-x}\right\} - \varepsilon_0 qx \sin(\omega t) \tag{2}$$

where ε_0 is the amplitude and ω the frequency of the laser and it is assumed that the total particle charge is $q = 1$. We emphasize that the unperturbed part of the Hamiltonian $\mathrm{H}_0(x, p)$ does not remains constant under the action of the external field $H_{laser}\,(x, t)$. Thus, when the perturbation is turned on, we will call by E_0 the value of the unperturbed Hamiltonian,

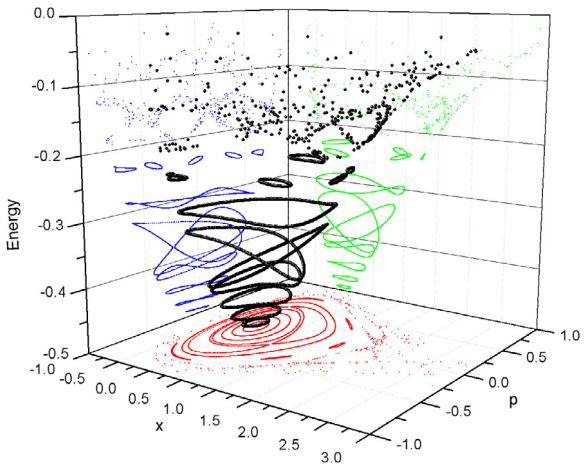

Fig. 2. Stroboscopic map (x, p, Energy) taken at each period of the external perturbation.

$H_0(x, p)$, at the values of t for which the perturbation vanishes, that is, for $t = (2n\pi/\omega)$, $n = 0, 1, 2, \ldots$. The value of E_0 for $t = k\pi/\omega$ is not necessarily the same value of E_0 for $t' = k'\pi/\omega$, when $k \neq k'$. In other words, E_0 is the energy stored in the system when the perturbation vanishes algebraically at these instants of time.

We investigate the effects of the perturbation through the analysis of the energy cube, which are constructed from the stroboscopic maps of the system recording (x, p) along with H_0 at each period of the external field. Fig. 2 shows the energy cube for $\omega = \sqrt{3}$ and $\mathcal{E}_0 = 0.02$. In the plane (x, P) we see the usual Poincaré section with libration tori and structures of resonances, while in the other two planes (p, Energy) and (x, Energy) we observe how bent the tori are. Even though it is well known that the energies are not more constant when a time-dependent term is included in the Hamiltonian (1), this plot clearly shows how this effect occurs. We call the deformation of the tori as *inclination*. The values of the parameters have been chosen after some numerical essays. It is worth noting that the remaining island chains also do not have constant energy.

The analysis of Fig. 2 raises the question of what is the role of each parameter for the inclinations of the structures in the phase space. In order to address this point, we consider individually the effect of the frequency ω and the amplitude $\mathcal{E}_0$ of the laser field on the structures of the phase space. Firstly, we consider the *low frequency regime* by fixing $\omega = \sqrt{3}$ and varying $\mathcal{E}_0$. The results are shown in the panels of Fig. 3. In panel (a) $\mathcal{E}_0 = 0.04$, in (b) $\mathcal{E}_0 = 0.06$, in (c) $\mathcal{E}_0 = 0.08$ and in (d) $\mathcal{E}_0 = 0.1$. We observe that as $\mathcal{E}_0$ increases, a growing number of tori are deformed, some of them are destroyed and give place to chaotic orbits, which dissociate when attain positive energies.

In order to quantify the effect of the amplitude of the electric field, for a fixed energy E_0 of the unperturbed Hamiltonian corresponding to a surviving torus, we compute the highest and the lowest energy of the deformed torus of the perturbed system. We call the difference between these energies as *inclination*, denoted by Δ_E. We plot in Fig. 4 the values of Δ_E as function of the unperturbed energies E_0 for some values of $\mathcal{E}_0$. We can observe that for $\mathcal{E}_0 = 0$, $\Delta_E = 0$, as expected and we count nine invariant tori (the black squares). For $\mathcal{E}_0 = 0.02$, $\Delta_E \neq 0$ and two tori have been destroyed. This destruction increases with $\mathcal{E}_0$; for $\mathcal{E}_0 = 0.08$ and $\mathcal{E}_0 = 0.10$ only three and two tori have respectively survived. It is worth commenting that the highest difference Δ_E occurs for $\mathcal{E}_0 = 0.06$ with five intact tori. Therefore, the role of the parameter $\mathcal{E}_0$ stays well established; it bends the structures in the phase space in such way that the surviving tori can present expressive inclinations.

The same analysis has been performed by fixing $\mathcal{E}_0 = 0.08$ and varying the laser-field frequency ω. In Fig. 5 we plot the inclination Δ_E in terms of the unperturbed energies E_0 varying ω from 1.0 to 8.0. We observe that for $\omega = 1.0$ there is only one invariant torus whereas for $\omega = 8.0$ there are nine tori. Comparing Fig. 4 with Fig. 5, we note that there were three tori for $\omega = \sqrt{3}$ and $\mathcal{E}_0 = 0.08$ and as ω is augmented, an increasing number of invariant tori are observed and the phase space tends to be regularized. This result shows that role of the laser-field frequency is different of the one of the amplitude, while varying $\mathcal{E}_0$ bends the tori, the variation of ω decreases the size of the chaotic sea.

Our proposal for controlling the dissociation dynamics is based on the existence of surviving tori that cross the separatrix. The above analysis indicates that this condition can be met if we chose high values of both frequency and amplitude of the external field. In Fig. 6 we consider the *high frequency regime* fixing $\omega = 15$, whose panels have been obtained for different values of the amplitude $\mathcal{E}_0$. We chose nine unperturbed energies corresponding to librations. In panel 6a, $\mathcal{E}_0 = 5.0$ and we observe that the tori are deformed and bent, some of them with positive and negative energy. In panel 6b, $\mathcal{E}_0 = 6.0$ and the six remaining tori present expressive inclination, the highest one changed its energy from ~ -0.3 until ~ 0.4. In panel 6c, $\mathcal{E}_0 = 6.5$, and only five initial tori have survived while four others have been destroyed giving rise to chaotic orbits. In panel 6d, $\mathcal{E}_0 = 7.0$, and the effect is more pronounced, the highest torus attains energy greater than 0.4.

Thus, the combination of high amplitude and high frequency allowed us to prepare the system with robust invariant structures in such a way that a polar molecule can visit regions of low and high energies crossing the separatrix, but remaining

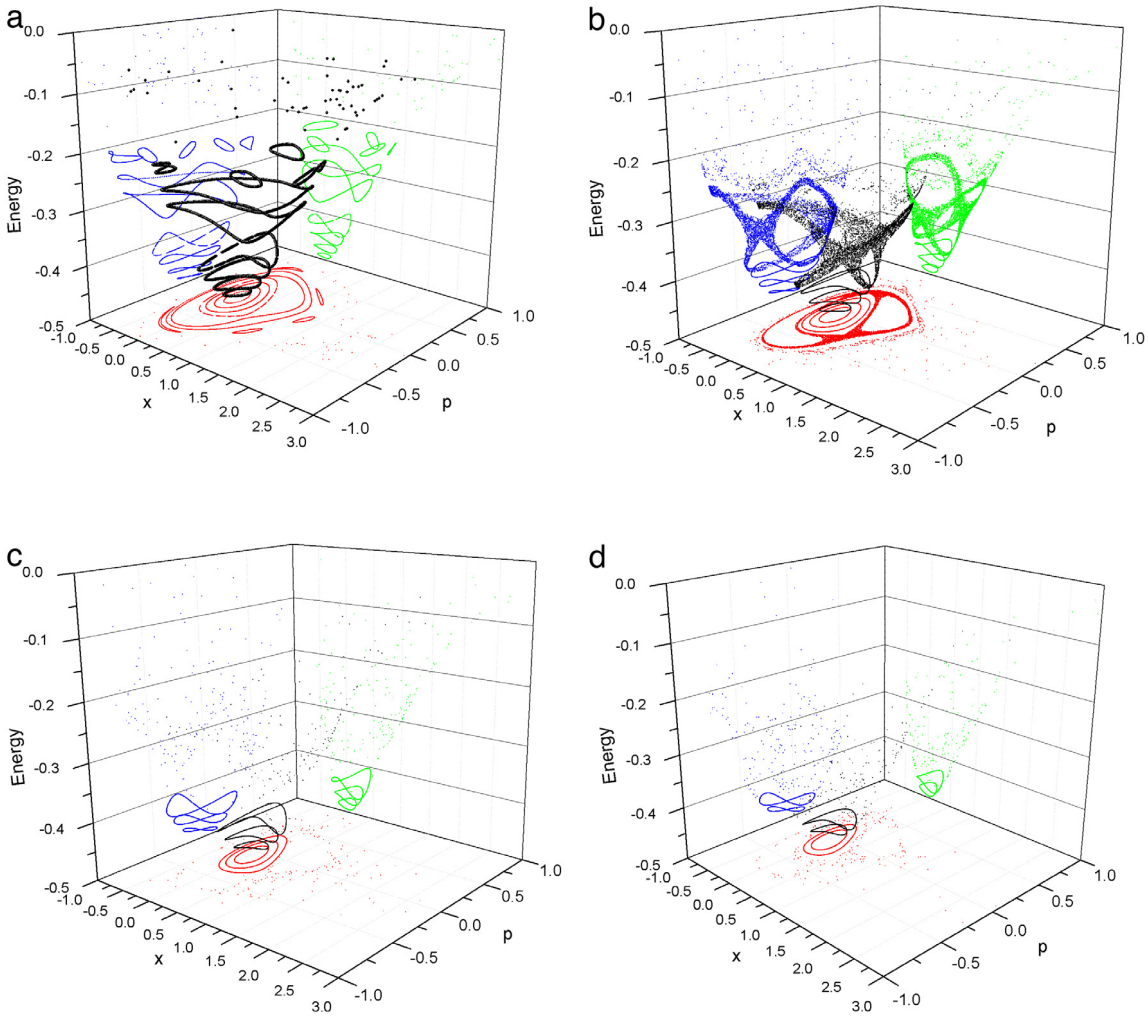

Fig. 3. Low frequency regime. $\omega = \sqrt{3}$ for the following values of ε_0: (a) $\varepsilon_0 = 0.04$, (b) $\varepsilon_0 = 0.06$, (c) $\varepsilon_0 = 0.08$, (d) $\varepsilon_0 = 0.1$. The increasing of ε_0 bends the tori.

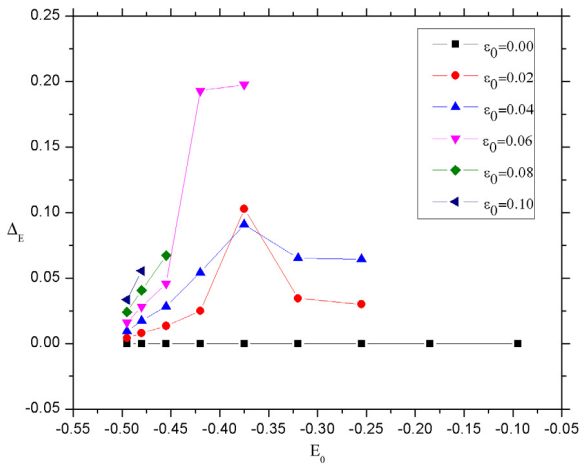

Fig. 4. Energy inclination versus unperturbed energy for several values of the amplitude of the external field.

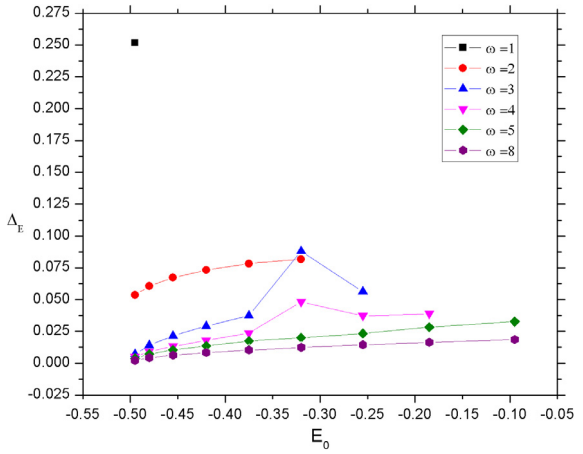

Fig. 5. Energy inclination versus unperturbed energy for several values of the frequency of the external field.

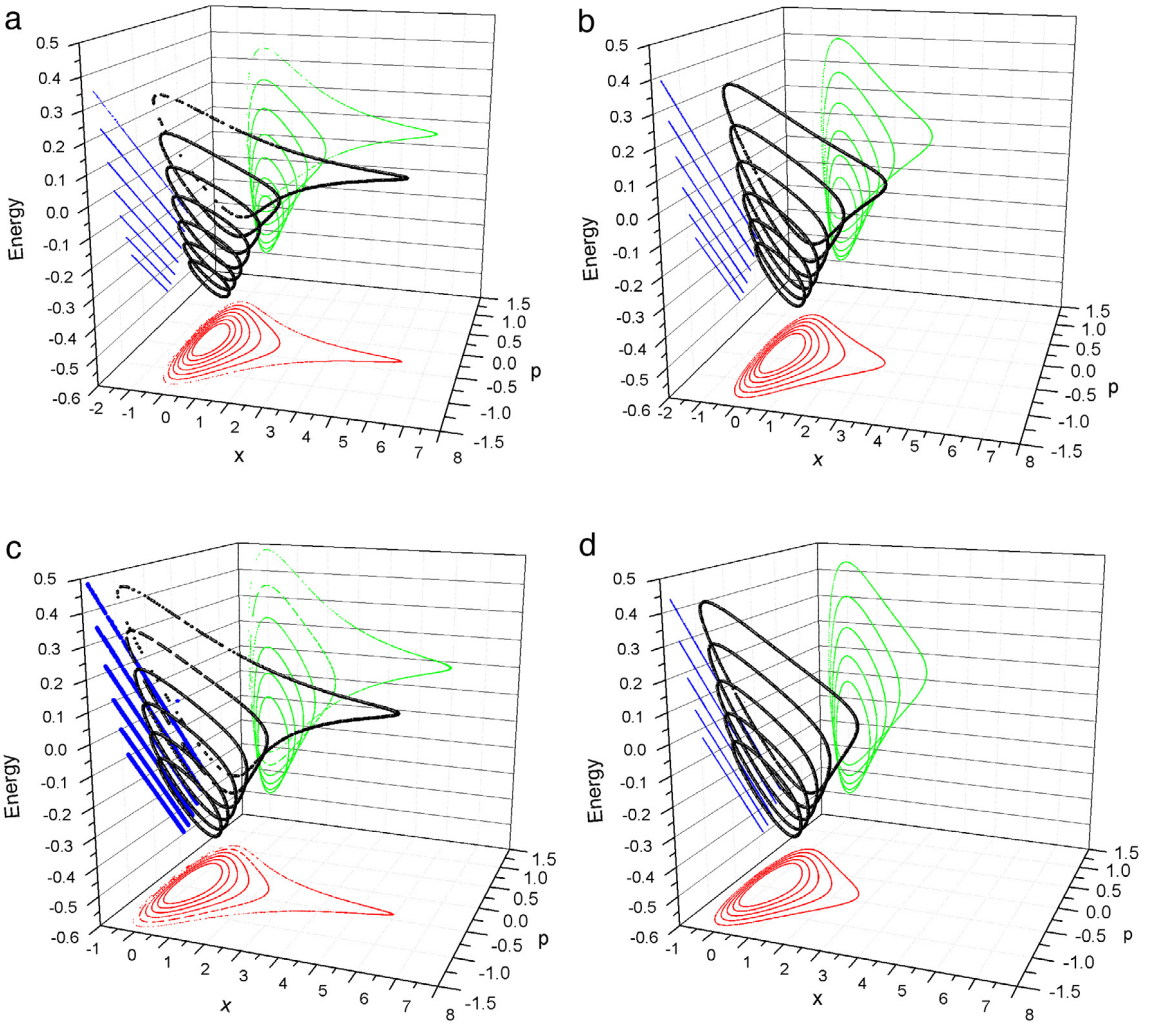

Fig. 6. High frequency regime. $\omega = 15$ for the following values of ε_0: (a) $\varepsilon_0 = 5.0$, (b) $\varepsilon_0 = 6.0$, (c) $\varepsilon_0 = 6.5$, (d) $\varepsilon_0 = 7.0$. The increasing of ε_0 bends the tori however they are more robust.

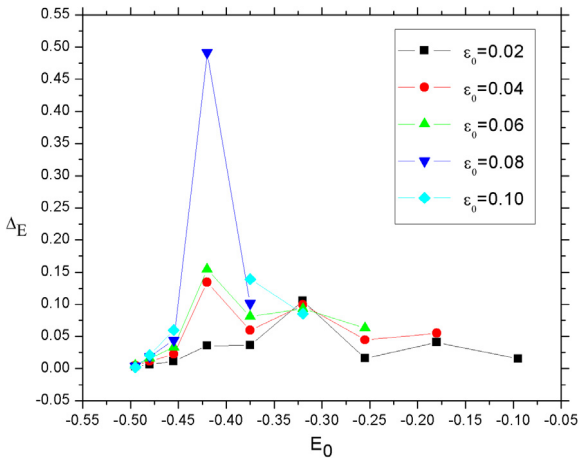

Fig. 7. Plot similar to Fig. 3. Energy inclination versus unperturbed energy for several values of the amplitude of the external field.

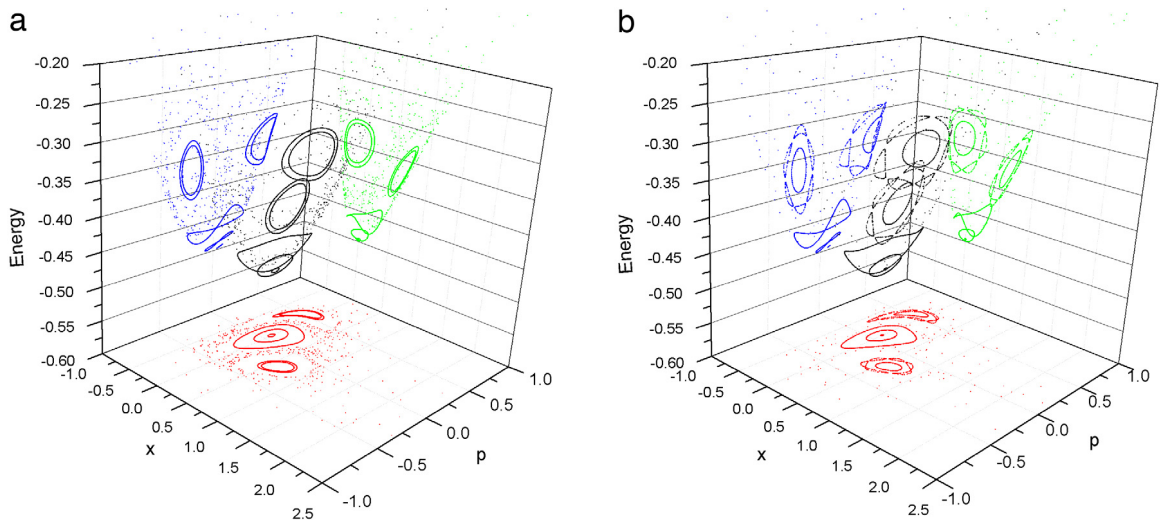

Fig. 8. Low frequency regime in analogy to Fig. 3 with $\omega = \sqrt{3}$. The bent tori are also observed. In (a) $\mathcal{E}_0 = 0.08$ and in (b) $\mathcal{E}_0 = 1.0$.

in the short range of the potential. Therefore, the dissociation can be controlled for instance by adjusting the timing of the interaction: the molecule will be dissociated if the external field is turned off when its energy is above the separatrix.

2.2. Non-linear dipole

In order to verify if there was some particularity concerning the linear dipole in the inclination mechanism, we consider the spatial shape of the dipole according to,

$$\mu\left(x,\eta\right) = \frac{e^{\xi\left(x+x_e\right)^4}\sin\left[\eta\left(x+x_e\right)\right]}{\eta} \tag{3}$$

where η, x_e and ξ are dimensionless adjustable parameters. x_e is related with the minimum of the Morse potential, while η introduces oscillations in the dipole function as it increases [18] and in the opposite direction, as η decreases $\mu\left(x,\eta\right)$does not oscillate in space and it is possible to model the HF molecule dipole with Eq. (3). This dipole shape is the same studied in the previous works [17,22] which with appropriate adjustment of the parameter can represent realistic dipole functions. Hence the perturbed Hamiltonian reads as,

$$H\left(x,p,t\right) = \frac{p^2}{2} + \frac{1}{2}\left\{e^{-2x} - 2e^{-x}\right\} - \varepsilon_0\sin\left(\omega t\right)\frac{\sin\left[\eta\left(x+x_e\right)\right]e^{-\xi\left(x+x_e\right)4}}{\eta} \tag{4}$$

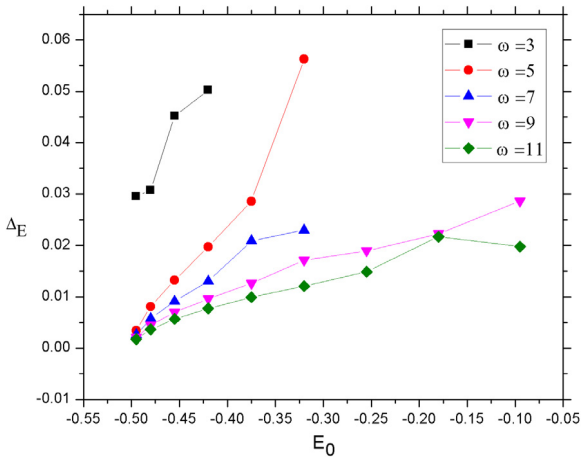

Fig. 9. Plot similar to Fig. 5. Energy inclination versus unperturbed energy for several values of the frequency of the external field.

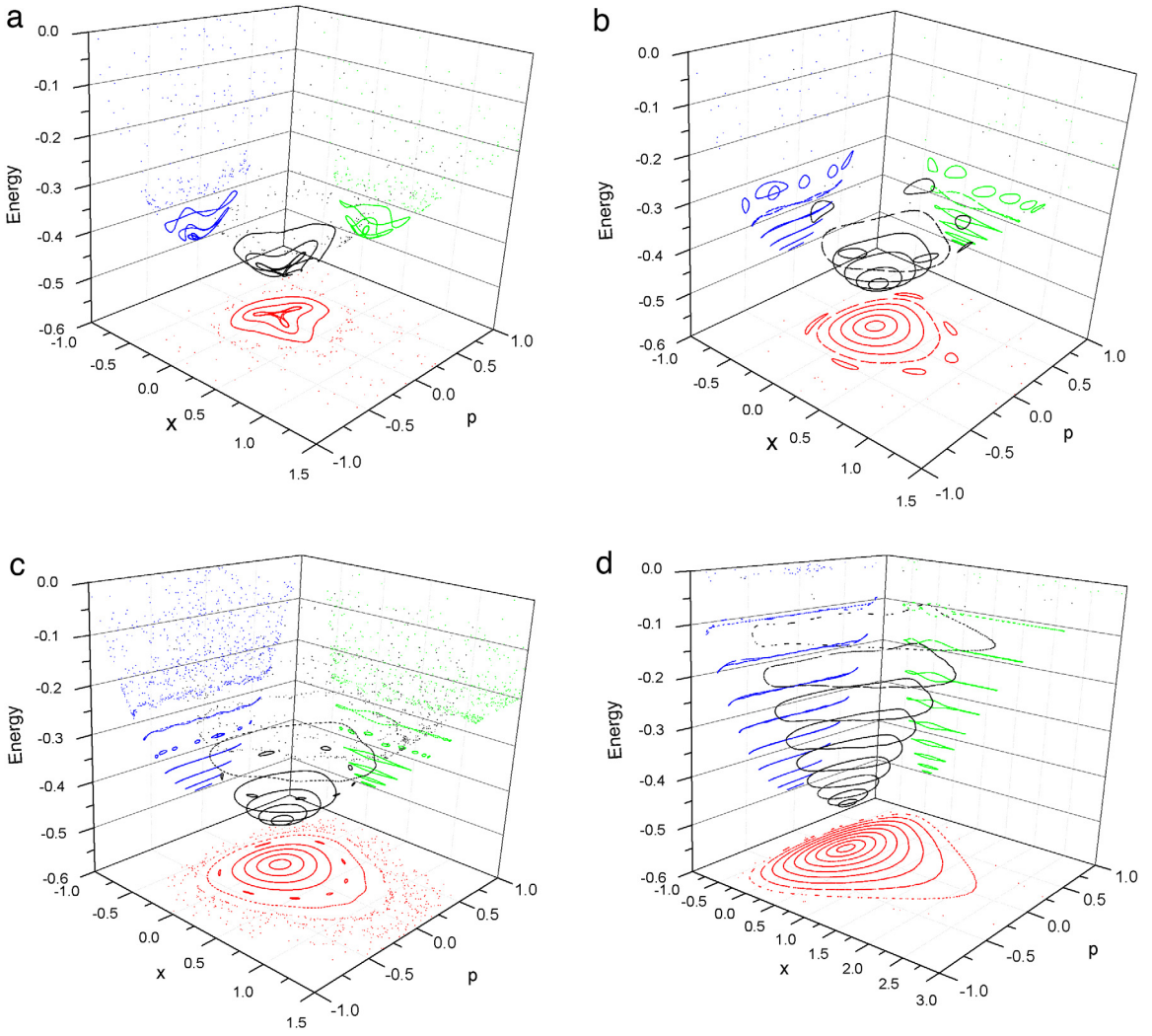

Fig. 10. Increasing frequency regime. $\mathcal{E}_0 = 0.01$ for the values of ω: (a) $\omega = 3$, (b) $\omega = 5$, (c) $\omega = 7$, (d) $\omega = 9$. The increasing of ω becomes the tori more robust.

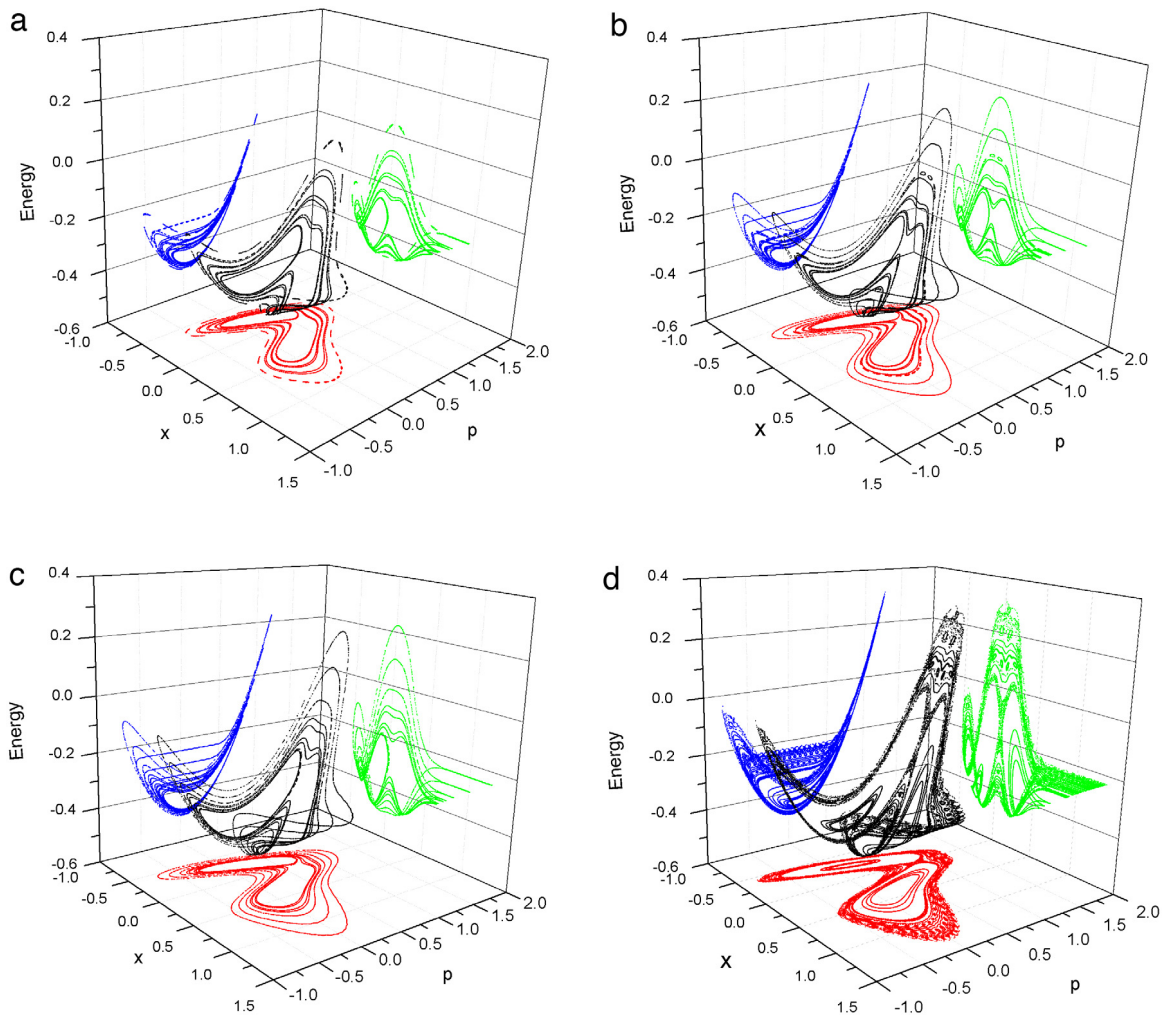

Fig. 11. High frequency regime in analogy to Fig. 6. $\omega = 15$ for the values of $\mathcal{E}_0$: (a) $\mathcal{E}_0 = 11.0$, (b) $\mathcal{E}_0 = 12.0$, (c) $\mathcal{E}_0 = 12.5$, (d) $\mathcal{E}_0 = 16.0$ The increasing of $\mathcal{E}_0$ bends the tori however they are more robust.

The Poincaré section is obtained again when $\sin(\omega t) = 0$. We start our analysis looking at the inclinations of the tori for the low frequency regime with five values of the parameter $\mathcal{E}_0$. In Fig. 7, we keep $\omega = \sqrt{3}$ and we observe a similar behavior to the linear dipole, as $\mathcal{E}_0$ increases the inclination also increases in such way that the more energetic tori are destroyed.

In the panels a and b of Fig. 8 we present two cubes of energy for $\mathcal{E}_0 = 0.08$ and $\mathcal{E}_0 = 1.0$ respectively, and $\omega = \sqrt{3}$, to illustrate the mechanism of the inclination.

In Fig. 9 we present the variation of the frequency ω keeping $\mathcal{E}_0 = 0.1$. The inclinations also follow the previous behavior of the linear dipole; as ω increases less tori are destroyed and the phase space tends to be regularized. We have chosen nine initial conditions with negative unperturbed energies; for $\omega = 3$ there are only four tori, while for $\omega = 11$ we find all the nine. As ω increases the tori become more robust.

Fig. 10 presents the associate cubes of energies for $\mathcal{E}_0 = 0.1$ and the values $\omega = 3$; 5; 7 and 9 in plots (a–d) respectively evidencing the regularization of the phase space as commented in Fig. 9.

Following the procedure developed previously, now we fix a high value for the laser-field frequency, $\omega = 20$ and we also choose some high values for $\mathcal{E}_0$. In Fig. 11 (a–d) we used $\mathcal{E}_0 = 11.0$, 12.0, 12.5 and 16.0 respectively.

The chaotic orbits that attain positive energies will lead to dissociation. We observe that there are invariant and bent tori visiting both regions, the one with positive energies and the other with negative energies. Hence, the change of the spatial dipole shape did not alter qualitatively the results obtained for the linear dipole function, i.e. the system can present invariant structures which allow the molecule to vibrate with high energies as well as with low energies without dissociating.

3. Concluding remarks

We have considered the classical dynamics of a polar diatomic molecule under the action of an external laser-field. We have described the atomic interaction through the Morse potential and the system was represented with dimensionless variables. A space and time-dependent laser-field was continuously applied with two tunable parameters, its amplitude and its frequency. The time-dependence is always sinusoidal while the term depending on the position assumes two different shapes. We considered linear and non-linear dipole functions. In both scenarios we analyzed the effects of the amplitude and the frequency of the time-dependent term and we have observed that the amplitude bends the structures of the phase space and the frequency makes the tori more robust. Hence, we combined both parameters to bend tori in such tori has positive and negative energies. This is a remarkable approach for the photo-dissociation process since it shows a proposal for a route to allow a particle experience positive energies without dissociating, i.e. the particle can attain highly excited energies, turn back to negative energies and keep this vibrational motion staying bounded. It is to be noted that our approach is general in the sense that can be applied to other potentials function beyond the Morse potential. Our results are robust and we believe that they can be performed experimentally. A final comment we would like to make is that in the case of the nonlinear dipole, some ponderomotive contribution could occur, but if it exists its effect is practically negligible because the same effects of the linear case were observed as qualitatively as at similar scales. In this sense, we evaluate that the effects we report here are not of ponderomotive origin. The specific cause of the tori stiffening mechanism is still not entirely clear to us. This will be subject of further investigations.

Acknowledgments

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