Unraveling the highly non-linear dynamics of the KCN molecular system by using Lagrangian descriptors

F. Revuelta[1], F. J. Arranz[1], R. M. Benito[1], and F. Borondo[2,3]

[1]Grupo de Sistemas Complejos, Universidad Politécnica de Madrid, av. Puerta de Hierro 2-4, 28040 Madrid, Spain

[2]Departamento de Química, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

[3]Instituto de Ciencias Matemáticas (ICMAT), Cantoblanco, 28049 Madrid, Spain

The mathematical objects currently known as Lagrangian descriptors [1, 2] have shown their usefulness in different applications to the dynamics of non-linear systems. Particularly, their usefulness has also been shown in the study of non-linear molecular systems, as in the case of the LiCN molecule [3, 4].

For a mechanical system with $N/2$ degrees of freedom, the Lagrangian descriptors are defined as follows,

$$M_{\pm}(\mathbf{z}_0; p, \tau) = \pm \sum_{k=1}^{N} \int_0^{\pm\tau} |\dot{z}_k(t)|^p \, \mathrm{d}t, \tag{1}$$

where $\mathbf{z} = (z_1, \ldots, z_N)$ is the vector formed by the $N/2$ position variables and their corresponding conjugate momenta, such that, Lagrangian descriptors are a function which depends on the initial condition $\mathbf{z}_0$ and two fixed parameters, the exponent p $(0 < p < 1)$ and the integration time τ $(\tau > 0)$. For the exponent, we have taken the value $p = 0.4$, which has been shown as adequate for other molecular systems [3, 4], whilst for the integration time, the value $\tau = 437.5$ fs has been used, which corresponds to the inverse of the stability exponent of the periodic orbit of interest. Notice that the overall Lagrangian descriptors M, as are defined in the literature [1, 2], are given by the sum of backward M_- and forward M_+ expressions in Eq. (1), namely, $M = M_- + M_+$.

In this contribution, we present the results obtained in the application of the Lagrangian descriptors to the dynamics of a remarkable system: the highly non-linear KCN molecular system. By using a suitable two-dimensional model (considering the motion of the K atom around the CN group), based on *ab initio* calculations for the potential energy function [5], it has been shown the emerging of above saddle-point regions of order in the sea of chaos [6]. Therefore, we have calculated the Lagrangian descriptors, and also the invariant manifolds, corresponding to the hyperbolic fixed point that appears on this interesting saddle-point.

First, in order to verify the optimum value of the integration time, given by the inverse of the stability exponent of the periodic orbit, we will show the Lagrangian descriptors calculated with different values of the integration time, above and below the optimum value.

Next, we will present the (optimal time) Lagrangian descriptors, as well as the invariant manifolds, both represented in a suitable Poincaré surface of section, corresponding to the hyperbolic fixed point of interest, showing a clear correspondence between both representations (see Fig. 1). In both cases, Lagrangian descriptors and invariant manifolds, we can observe the appearance of intriguing loops. We will study in detail the first discontinuity that leads to a one of these closed curves.

Last, in order to understand this interesting behavior, we will present calculations in the three-dimensional phase-space, beyond the dimension of the Poincaré surface of section, showing that the appearance of the closed curves is due to the highly non-linear dynamics of the system. This highly non-linear dynamics causes the twisting and wrinkling of the two-dimensional invariant manifolds, such that, in the crossing with the Poincaré surface, discontinuities and loops appear.

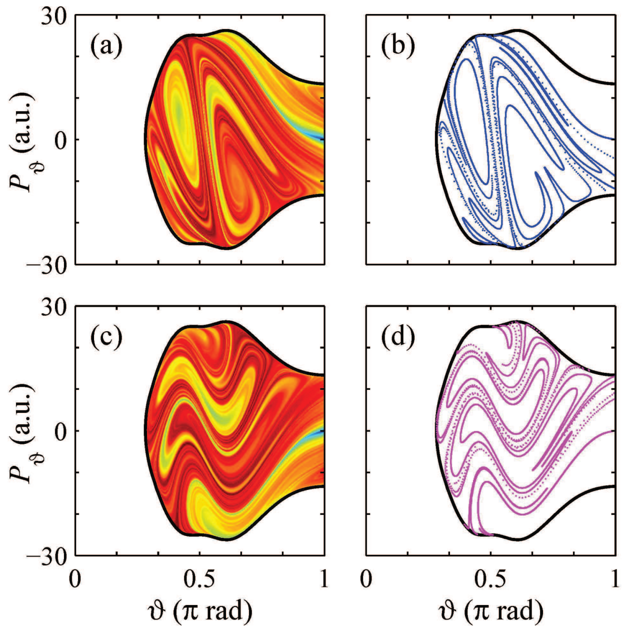

Fig. 1. Lagrangian descriptors computed forward (a) and backward (c) in time, and stable (b) and unstable (d) invariant manifolds, all of them represented in a suitable Poincaré surface of section (ϑ, P_ϑ), corresponding to a hyperbolic fixed point located at $(\vartheta, P_\vartheta) = (\pi, 0)$, with total energy $E = 1300$ cm^{-1}. Note the loops appearing in this Poincaré representation of the invariant manifolds.

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