Superscars in the LiNC $\rightleftharpoons$ LiCN isomerization reaction

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received 4 September 2009; accepted in final form 27 October 2009
published online 26 November 2009

PACS 05.45.Mt – Quantum chaos; semiclassical methods
PACS 03.65.Sq – Semiclassical theories and applications
PACS 82.30.Qt – Isomerization and rearrangement

Abstract – We demonstrate the existence of superscarring in the LiNC $\rightleftharpoons$ LiCN isomerization reaction described by a realistic potential interaction in the range of readily attainable experimental energies. This phenomenon arises as the effect of two periodic orbits appearing “out of the blue” in a saddle-node bifurcation taking place in the dynamics of the system. Potential practical consequences of this superlocalization in the corresponding wave functions are also considered.

Introduction. – The localization of certain quantum eigenstates along unstable periodic orbits (PO) in classically chaotic systems —i.e., quantum scarring [1]— has profound consequences for the dynamics of quantum systems. It was first observed in numerical calculations on the Bunimovitch stadium billiard [2]. At the most basic level, scarring [3,4] is a spectacular example of the influence of classical structures, i.e. PO [5] and their associated manifolds [6–8] on quantum behavior [9]. Scarring is responsible, for example, for significant deviations from the predictions of random matrix theory [10]. It has also been conjectured recently that they are important in open systems to understand the semiclassical structure of resonances [11,12], the number of which has been seen to scale with $h$ according to a fractal Weyl law [13,14]. At the same time, scarring has important practical consequences in various fields, including tunnel currents in mesoscopic devices [15], quantum dots [16], optical cavities [17], optical fibers [18], and very recently the existence of relativistic quantum scars has been demonstrated [19] in the emerging field of graphene applications [20].

The vast majority of the work published on scars has concentrated on fully chaotic systems, where the POs are isolated and unstable. However, Keating and Prado (KP) [21] recently considered the specific peculiarities of generic systems (with mixed dynamics), where bifurcations of the scarring PO occur. By extending Bogomolny theory [3], they found that the density localization around bifurcated POs are wider and with amplitudes at least as large as those far from bifurcations. This led KP to introduce the term superscars to name this new localization phenomenon which they illustrated with numerical examples in perturbed cat maps. The influence of bifurcating orbits on the density of states was studied by Schomerus and Sieber [22], who also found different scaling exponents on the dependence of such magnitude with $h$. Due to the nature of the arguments used by KP, which only apply to high excitation energies ($h \rightarrow 0$ limit), an open question has remained and concerns the transferability of KP's conclusions beyond maps to actual physical systems over experimentally realizable energy ranges.

In this letter, we address this crucial point, namely the existence of a universal behavior in the exponents of the moment distribution characterizing superscars [21]. This is done in the context of a realistic model for the LiNC $\rightleftharpoons$ LiCN isomerization reaction [23]. More specifically, for this system we investigate the superscarring associated with POs which originate in a saddle-node (SN) bifurcation of the isomerization dynamics [24].

Isomerization plays a fundamental role in many biochemical processes and it is an ideal benchmark for dynamical systems theory [23,24]. Also, the example that we have chosen can be considered as a prototype for this kind of processes (see description of the model...
below), which has the added bonus of exhibiting a rich and complex vibrational dynamics. Moreover, the superscarring phenomenon discussed here is closely related to some particular aspects of the transition state (TS) theory (TST) [25] at quantum level. This theory, that was developed in the 1930s after the seminal work of Eyring [26] and Wigner [27], envisions the physical processes associated to chemical reactions as “skinning the reaction slopes” [28] or landscapes [29], so that the barriers existing between reactants and products are surpassed. Quantum mechanically, these barriers accommodate the corresponding Gamow-Siegert resonant states [30,31], and the topology of the associated wave functions configures the doorways controlling the quantum reactivity [32].

In the title reaction there exists, apart from the reaction barrier corresponding to the saddle point in the potential energy surface that was previously studied in ref. [33], another interesting barrier of dynamical origin [34,35], associated to the POs arising from a SN bifurcation in the corresponding dynamics [24]. According to KP’s results the characteristics of this barrier changes dramatically with the excitation energy. At high energy, where the two POs are isolated, the quantum density localization effect due to scarring is less pronounced. On the contrary, when lower values of the energy, close to the bifurcation point, are considered a strong superlocalization takes place. The fundamental difference in the widths taking place in this two different situations is expected to have some relevant influence in the corresponding flux [36], leading to a different behavior in the respective reactive dynamics.

Finally, it should be pointed out that other interesting, although completely different, effects of SN bifurcations in the vibrational dynamics of molecular systems (HCP molecule) have been described in the literature [37].

Model and calculations. – As a working model, we choose the LiNC/LiCN isomerizing molecular system, which has been extensively studied in connection with quantum chaos [23]. This system is representative of a large class of small polyatomic molecules, which exhibit similar behavior, mainly due to the presence of a large amplitude (floppy) motion in one of the vibrational modes. This class includes other cyanides, such as HCN/HNC [38], alkaline cyanides [39], and other similar species, such as, HCP [37], the HO$_2$ radical, or the van der Waals complexes.

Our system can be modelled by a realistic two degrees of freedom vibrational ($J=0$) Hamiltonian, which is given by

$$H = \frac{P_R^2}{2\mu_1} + \frac{1}{2} \left( \frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 \vartheta^2} \right) P_\vartheta^2 + V(R, \vartheta).$$

Here we use Jacobi coordinates, which are common for example in scattering theory [40] and celestical mechanics [41]. In our case these coordinates, ($r, R, \vartheta$), are defined as the C–N distance, the distance between the Li atom and the center of mass of the CN fragment, and the angle formed by these two vectors, respectively (see fig. 1). The corresponding reduced masses are defined as $\mu_1 = m_{Li} m_{CN}/m_{LiCN}$ and $\mu_2 = m_{CN}/m_{CN}$. The C–N motion is kept frozen at its equilibrium value, $r_e$, since the associated frequency is high, thus decoupling very effectively from the rest of coordinates in the molecule. The interaction potential is expressed as a series of Legendre polynomials,

$$V(R, \vartheta) = \sum_{\lambda=0}^9 P_\lambda (\cos \vartheta) v_\lambda (R),$$

whose coefficients consist of a sum of short-range and long-range contributions whose explicit forms have been taken from the literature [42]. It is shown in the top panel of fig. 2 as a contours plot. As can be seen, it presents two wells at $\vartheta = 0$ and 180°, corresponding to the linear isomers LiCN and LiNC, which are separated by a modest energy barrier. The motion in $\vartheta$ is very floppy and chaos sets in at moderate values of the excitation energy. Superimposed to the potential surface, we also present in the plot the POs which are relevant for our discussion on superscars, at two different values of the interaction energy. They all run almost vertically, and correspond to a 1 : 1 resonance which appear “out of the blue” due to a SN or tangent bifurcation at $E_{bif} = 3440.64$ cm$^{-1}$, as discussed in ref. [24]. At this energy, the two orbits are indistinguishable, since they both coalesce in the central (shorter) trajectory shown in the figure. As energy increases the two POs separate, the unstable one moving to the right and the stable towards the left. This stability is later lost for $E > 4960.1$ cm$^{-1}$. These two POs have also been plotted in the top panel of fig. 2 for an energy far away from the bifurcation point, namely $E_1 = 9196.0$ cm$^{-1} \simeq 3 E_{bif}$.

The corresponding classical dynamics can be adequately followed by computing Poincaré surfaces of section (SOS) using the minimum energy path, $R_e(\vartheta)$, connecting the two isomers, as the sectioning plane. This choice requires an extra canonical transformation,

$$\psi = \vartheta, \quad P_\psi = P_\vartheta - \left( \frac{d R_e(\vartheta)}{d \vartheta} \right)_{\vartheta = \psi} P_R,$$

Fig. 1: Definition of the Jacobi coordinates used in our calculations.

to make the SOS an area preserving map [43]. Composite SOSs for $E_{bif}$ and $E_1$ are shown in the middle and bottom panels of fig. 2, respectively. Two comments are in order.

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Fig. 2: Top: potential energy surface for LiNC/LiCN. The
minimum energy path (dotted line), and three saddle-node
periodic orbits (full line) at $E_{\text{bif}} = 3440.64 \text{ cm}^{-1}$ (central orbit)
and $E_1 = 9196.0 \text{ cm}^{-1}$ (lateral trajectories) relevant to our
work have been plotted superimposed. Middle and bottom:
composite Poincaré surface of sections for the same energies.
The position of the fixed points corresponding to the periodic
orbits are represented with full squares.

First, the dynamics is mixed, being chaotic in the region
of interest — i.e. where the two bifurcated POs sit—and regular around the isomer configurations. Second, the
obvious signature of a cantori [44], seen as an accumulation
of points next to the region of stability around $\vartheta = 180^\circ$,
is apparent for $E_{\text{bif}}$, and this bottleneck disappears at $E_1$.

As mentioned before, one critical element in our work
is the computation of the scarred wave functions. The
reason for this should be clear. Since we want to perform
our study far from the high-$E$ (low-$\hbar$) semiclassical limit,
where the quantum oscillations in the local configurations
and energy averages implied in scarring [3] easily cancel
out, an algorithm able to introduce the subtle dynamical
effects associated to the scarring PO in the scar functions
is forcefully needed. In our case, this is achieved by using
the method described in [45] consisting in time evolving a
wave packet, $|\phi(t)\rangle$, initially launched at one of the turning
points of the PO under study, obtaining afterwards all the
relevant information by Fourier transform.

We start with the (infinite resolution) stick spectrum:

$$I_{\infty}(E) = \int_{-\infty}^{+\infty} dt \, e^{iEt/\hbar} \langle \phi(0)|\phi(t)\rangle$$

$$= \sum |\langle \phi(0)|n\rangle|^2 \delta(E - E_n), \quad (4)$$

where kets $|n\rangle$ represent the eigenfunctions of the system.

An example of the results obtained from such calculations
is shown in fig. 3. As can be observed, the distribution
of sticks, both in separation and length, is rather irregu-
lar, but when examined closely they are seen to be nicely
shaped into clumps. This is due to the recurrences in the autocorrelation function induced by the PO
motion [5], and it shows up as well-defined bands in the
low-resolution version of the spectrum,

$$I_T(E) = \int_{-\infty}^{\infty} dt \, e^{-t^2/T^2} \, e^{iEt/\hbar} \langle \phi(0)|\phi(t)\rangle,$$  \quad (5)

where the cutoff parameter $T$ has been introduced in
order to eliminate the long term dynamics not directly
associated to the scarring process. The result for $T$ equal
to the period of the scarring PO is displayed in fig. 3.

Here, a series of bands are seen to appear centered at
the discrete values of the energy, $E_{\text{BS}}$, that are obtained
semiclassically using the suitable Bohr-Sommerfeld (BS)
quantization condition of the action along the PO (see eq.
(8) below). In a second step, we focus our attention
in one single of these bands, and calculate the scar wave
function, $|\psi_n\rangle$, associated to it by Fourier transform-
ing the original packet, $|\phi(t)\rangle$, at the corresponding BS
energy, $E_{\text{BS}}$,

$$|\psi_n\rangle = \int_{-\infty}^{\infty} dt \, e^{-t^2/T^2} \, e^{i(E_{\text{BS}}-H)t/\hbar} |\phi(0)\rangle.$$  \quad (6)
Here we choose the Ehrenfest time\(^1\) as the value for the cutoff parameter \(T\), since it is known [7] that this procedure guarantees that the dynamical information concerning the hyperbolic structure associated to the scarring PO is embedded in the topology of \(|\psi_n\rangle\). By expanding \(|\phi(0)\rangle\) in the basis set of the system eigenstates, the integral in eq. (6) can be solved explicitly, and one obtains

\[
|\psi_n\rangle = \sqrt{T_E} \sum_n e^{-(E_n - E_{BS})^2 / 4\hbar^2} |n\rangle |\phi(0)\rangle |n\rangle. \tag{7}
\]

This equation clearly shows how the scar states defined by us fulfill the two most important criteria accepted in scar theory. On the one hand, they are built by averaging over the eigenstates within an energy window of width \(\hbar / T_E\) around \(E_{BS}^{\text{cl}}\), in the spirit of Bogomolny’s interpretation of scarring [3]. On the other hand, the particular average that we use incorporates the dynamical correlations existing in \(\langle \phi(0)|\phi(t)\rangle\), in agreement with the view introduced by Heller [5]. It should be stressed that these correlations are so strong that the scar functions acquire a very pronounced semiclassical character, independently of particular details of the individual eigenfunctions used in the construction, and in this sense our method is very robust. In the inset to fig. 3 we show as an example \(|\psi_3\rangle\), whose (mean) energy roughly corresponds to \(E_{\text{bif}}\) and it is constructed with the eigenstates in the fourth clump. Let us imagine now that \(\hbar\) were reduced to one half of its value. The energy density would increase, and the clumps of fig. 3 would shift to the left, i.e. to the region of smaller energies. The eigenfunctions contributing to each clump would then be different, but our computed scar wave functions would be the same.

In conclusion, a scar function is defined by the number of excitations along the PO, and this number depends both on the values of \(E\) and \(\hbar\), which are given by the Bohr-Sommerfeld quantization condition. Another relevant characteristic of the scar functions is related to the direction transverse to the PO. In the case of an unstable PO, a hyperbolic Hamiltonian dominates the flux in its neighborhood and the wave packet, \(|\phi(0)\rangle\), moves quickly along the associated manifolds. On the other hand, at bifurcations the dynamics acquire some stability, and the original wave packet move away from the central PO, but in a more slowly way. These two different behaviors have an influence in the width of the related scar functions, as will be demonstrated in the present article.

**Results and discussions.** – Let us next quantify the scarring effect on \(\psi_n\) due to the 1:1 SN POs that we are considering. As described by KP [21], this can be achieved with the aid of the second moment of the wave function amplitude distribution averaged over regions shrinking as \(\hbar \to 0\) but containing an increasing number of de Broglie wavelengths. In the case of an isolated unstable PO this magnitude follows, in the limit, a universal power law \(\hbar^{1/2}\).

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\(^1\)The Ehrenfest time is defined as \(T_E = (2\lambda)^{-1} \ln(S/\hbar)\), \(\lambda\) being the stability index of the PO and \(S\) a typical action transverse to it (here taken as the area of the surface of section).
However, for just bifurcated POs of the type that we are considering here, i.e., tangent bifurcation, this expression goes as $\hbar^{1/3}$ due to the superscarrning effect of the bifurcated orbits [21]. In order to carry out this calculation, we first select two values of the vibrational energy, one corresponding to the bifurcation energy, $E_{bif}$, and the other one, $E_1$, sufficiently far away from it to ensure that the PO is isolated. Second, we compute a series of scar functions, $|\psi_n\rangle$, with different values of the excitation quantum number $n$ at the same energy, $E$. In order to do this, we vary $\hbar$ according to the BS quantization condition for the PO

$$h(n) = S_E \left( n + \frac{\nu_E}{4} \right)^{-1},$$

where $S_{E_{bif}} = 3.5$, $\nu_{E_{bif}} = 2$, $S_{E_1} = 13.75$, $\nu_{E_1} = 3$ in our case. Notice that for the second energy the Maslov index has increased by one due to the appearance of a self-focal point in the PO. The net effect of the $h$ scaling represented by (8) is to shift the center of the $n$-th band to the value of the working energy, $E_{bif}$ or $E_1$. Some scar wave functions computed in this way are shown in fig. 4.

As can be seen, they all correspond to different excitations in the $R$ motion with no nodes in the $\vartheta$ coordinate. Moreover, their widths (transverse to the PO) change very slowly at $E_{bif}$, which is a distinctive property of the phenomenon of superscarrning. In order to make this assertion quantitative, we evaluate the variance of the probability density at a fixed value of $R$,

$$\sigma_R^2(n) = \int d\vartheta \left| \psi_n(R, \vartheta) \right|^2 W(R) - \left[ \int d\vartheta \left| \psi_n(R, \vartheta) \right|^2 W(R) \right]^2,$$

with $W(R) = \int d\vartheta \left| \psi_n(R, \vartheta) \right|^2$. To illustrate this procedure, the profile of each function in fig. 4 is shown for $R = 4.2$ a.u. in the insets. Then, we calculate the mean width weighted by $W(R)$ as

$$\sigma(n) = \left[ \int dR W(R) \sigma_R^2(n) \right]^{1/2}.$$

The corresponding results for $E_{bif}$ and $E_1$ are shown in fig. 5. Several comments are in order. First, as can be seen in the log-log plot both sets of data follows remarkably well a scaling power law, $\left( n + \nu_E/4 \right)^{-\alpha}$, with the excitation quantum number, $n$ (equivalent to $\hbar$). Second, from the slopes of least-squares fittings we have that $\alpha_{E_{bif}} = 0.32 \pm 0.01$ and $\alpha_{E_1} = 0.53 \pm 0.02$. Third, these values agree extremely well, within the numerical error, with the universal behavior predicted in the theory of KP, according to which the exponent is $1/3$ at the bifurcation point, and $1/2$ far from the bifurcation, respectively.

This last result confirm beyond any doubt that the SN POs studied in this letter, which corresponds to an excited molecular motion for the LiNC/LiCN isomerizing molecular systems taking place mainly along the stretching coordinate, $R$, is able to produce superscarrning on the corresponding quantum wave functions for energies near the bifurcation point, and this effect disappears as we move away from this point.

**Conclusions.** – Summarizing, in this letter we have reported for the first time conclusive evidence for the existence of superscarrning associated to bifurcated POs [21] in a realistic molecular system. More interestingly, this happens in the regime of very low excitations along the PO, which opens the possibility for considering the influence of scarring in quantum processes where the probability flux is strongly affected by the existence of dynamical barriers. In particular, the effect of scarring on LiNC $\rightleftharpoons$ LiCN isomerization rates and specially its dependence on the value of the vibrational excitation energy is a topic that is currently under investigation.

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This work has been supported by the Ministerio de Ciencia e Innovación (Spain) under projects MTM2006-15533, MTM2009-14621 and CONSOLIDER 2006-32 (i-Math), Comunidad de Madrid under the project S-0505/ESP-0158 (SIMUMAT), and a grant (to SDP) from Fundación Carolina (AECl-Spain).

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