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Signatures of discrete breathers in coherent state quantum dynamics

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In classical mechanics, discrete breathers (DBs) – a spatial time-periodic localization of energy – are predicted in a large variety of nonlinear systems. Motivated by a conceptual bridging of the DB phenomena in classical and quantum mechanical representations, we study their signatures in the dynamics of a quantum equivalent of a classical mechanical point in phase space – a coherent state. In contrast to the classical point that exhibits either delocalized or localized motion, the coherent state shows signatures of both localized and delocalized behavior. The transition from normal to local modes have different characteristics in quantum and classical perspectives. Here, we get an insight into the connection between classical and quantum perspectives by analyzing the decomposition of the coherent state into system’s eigenstates, and analyzing the spacial distribution of the wave-function density within these eigenstates. We find that the delocalized and localized eigenvalue components of the coherent state are separated by a mixed region, where both kinds of behavior can be observed. Further analysis leads to the following observations. Considered as a function of coupling, energy eigenstates go through avoided crossings between tunneling and non-tunneling modes. The dominance of tunneling modes in the high nonlinearity region is compromised by the appearance of new types of modes – high order tunneling modes – that are similar to the tunneling modes but have attributes of non-tunneling modes. Certain types of excitations preferentially excite higher order tunneling modes, allowing one to study their properties. Since auto-correlation functions decrease quickly in highly nonlinear systems, short-time dynamics are sufficient for modeling quantum DBs. This work provides a foundation for implementing modern semi-classical methods to model quantum DBs, bridging classical and quantum mechanical signatures of DBs, and understanding spectroscopic experiments that involve a coherent state. © 2013 American Institute of Physics.

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I. INTRODUCTION

Understanding the properties of quantum discrete breathers (QDBs) is important for applications in many areas, including chemistry,1–5 medicine,6–10 nano-materials,11–15 and quantum computers.16 From the classical mechanics perspective, discrete breathers (DBs) are fairly well understood phenomena. They occur as spatial energy localization in a system for an infinite amount of time. The effect is due to an interplay of the nonlinearity of the site potentials and the coupling between the sites. The DB phenomenon is different in quantum mechanics; the infinite-time localization is not possible due to tunneling. Experimentally, one can observe traces of QDBs in the form of anomalously long relaxation times and structural stabilities.17 QDBs and their equivalents have been observed in proteins,7,9,10 π-conjugated polymers,18 crystals,14,15,17,19 micro-mechanical systems,11 anti-ferromagnets,20 Bose-Einstein condensates,21 interacting Josephson junctions,16 and intramolecular vibrational energy redistribution.3,5 Advances in experimental techniques and theoretical modeling promise occurrence of QDB in upcoming fields. Theoretical descriptions of QDBs stem from quantizing classical solutions for both integrable and non-integrable systems.22 Theoretically, DBs and their equivalents have been studied in a number of systems of practical importance, including biomolecules,6,8 polymers12,13 nanotubes,2 graphene,4 and water.1,5 Higher order femtosecond spectroscopy allows to observe dynamics of coherent states in anharmonic potential,24–27 where QDB may occur when effects of anharmonicity dominate normal-mode motion.

Investigating the quantum dynamics of a coherent state in the context of DBs targets two areas of research: bridging classical and quantum descriptions of DBs and building a foundation for numerical methods that use coherent states. A coherent state is a quantum equivalent of a point in the classical phase space. Comparing the signatures of DBs in the dynamics of a classical point and a coherent state highlights the conceptual differences and similarities between the classical and quantum descriptions of DBs. Numerically, large, experimentally interesting systems are difficult to model using exact quantum dynamical methods. One needs approximations that represent the quantum effects and scale well with system size. Methods that rely on time-evolution of coherent states are effective for large systems. They include frozen,28 thawed,29 and thermal30,31 Gaussians, the Herman-Kluk (HK) propagator.32

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and its higher order extensions,\textsuperscript{33,34} coupled coherent states (CCS),\textsuperscript{35} matching-pursuit/split-operator Fourier transform (MP-SOFT),\textsuperscript{36,37} coherent-state path-integrals (CSP),\textsuperscript{38} multiple-spawning,\textsuperscript{39} multi-configuration Hartree,\textsuperscript{40,41} quantized Hamilton dynamics (QHD),\textsuperscript{42} etc. Exact for harmonic systems, these and related methods have been used successfully for moderately nonlinear and anharmonic systems. For instance, the anharmonicity of the coupled quartic dimer studied with the semi-classical methods\textsuperscript{43,44} is too small to produce DBs. Even if signatures of QDBs would appear in a semi-classical simulation, they might not be recognized as such. The analysis presented here clearly identifies the QDB signatures in the dynamics of a coherent state. Modeling highly nonlinear phenomena, such as DBs, can be a challenge. Few semi-classical techniques have been used for this purpose. QHD\textsuperscript{45} and HK\textsuperscript{46} provide rare exceptions. Studying the quantum dynamics of a coherent state illustrates the advantages and limitations of these techniques when applied to QDBs.

This study connects to the previous work in related fields in three distinct directions: modeling of DBs in systems that may have non-negligible quantum effects, fundamental theory on QDBs, and applicability of semi-classical methods to highly nonlinear systems. Due to the high computational cost of quantum simulation, in many nano-scale and atomic-scale systems with DB solutions, quantum effects are neglected.\textsuperscript{2,4,6,8,13} Contributing to the previous work in this field,\textsuperscript{47–49} our work highlights the limitations of a classical models of DBs by outlining the quantum effects seen in the dynamics of a coherent state that provides the simplest extension of classical mechanics. Conventionally, QDBs are studied by finding eigenstates of the system Hamiltonian.\textsuperscript{50}

Previous theoretical work focused on the quantization of integrable\textsuperscript{22} and non-integrable\textsuperscript{23} dimers, the analysis of QDB mode splitting,\textsuperscript{51} and the existence of avoided crossings between the energy levels.\textsuperscript{52} We extend the previous work by providing an analysis of distribution of probability density between sites within eigenstates and its targeted contribution to coherent states. Previously, theory of quantum ergodicity helped to understand the relation between delocalized (non-tunneling) and localized (tunneling) eigenstates in anharmonic systems and their relation to the classical limit.\textsuperscript{47,48}

An influence of this phenomena on the dynamics of a coherent state is useful for both, theory and experiment. Some dynamical properties of coherent state has been studied by means of quantum phase space entropy.\textsuperscript{49} We offer an alternative perspective by decomposing a coherent state into eigenstates. Spectra of this dynamics is useful for the comparison of quantum theory to experiment and more efficient semi-classical methods. Understanding the nature of the spectra lines is unclear from previous work. To gain this understanding, we plot the distribution of the eigenstate wavefunction among the sites. Seeing this distribution allows us to have qualitative understanding of the dynamics of a composition of eigenstates that overlap with coherent state. This procedure allows us to understand the tunneling versus non-tunneling nature of the lines in the spectrum and the full versus partial transfer of the coherent state from one site to another. Since the energy of the eigenstates are not multiples of each other, the period of the phase corresponding to each eigenstate will be also different. The coherent state will evolve with time and the part that overlaps with the tunneling modes will require up to an infinite time to transfer from one site to another. By having a qualitative understanding of the anatomy of the dynamics of the coherent state, one can have an insight into the phenomena just by analyzing a spectrum plot. Coherent state based path-integral semi-classical methods are more effective at generating spectrum and can simulate systems with many-degrees of freedom and energies closer to the quasi-continuum. Our previous studies showed that these semi-classical methods are effective in representing a quantum effects in DB;\textsuperscript{45,46} however, a deeper analysis of the spectra was needed resulting in this study.

The paper is organized as follows. The system Hamiltonian, theoretical methods and numerical procedures are described in Sec. II. Section III starts with an analysis of the spectrum of the coherent state and relates the energy eigenstates to the localized and delocalized dynamics. Section III B focuses in detail on the mixed region, in which the dynamics switches from the delocalized to the localized regime, with increasing energy. Section III C discusses additional effects, including avoided crossings between tunneling (localized) and non-tunneling (delocalized) modes, the existence and properties of higher order tunneling modes (HOTM), control over HOTM by choice of initial conditions, and behavior of the auto-correlation function (ACF) corresponding to the energy spectrum. The paper concludes with a summary of the key results.

II. SYSTEM AND METHODS

Breathers appear in a wide range of systems.\textsuperscript{1–5} In order to focus on the fundamental concepts of QDBs and to guarantee an accurate quantum mechanical description, we consider a simple model that is computationally accessible and conceptually simple. The model consists of two anharmonic sites, represented by quartic oscillators, and bi-linear coupling. It is congruent with realistic systems. Interactions between atoms or molecules are governed by anharmonic potential, for example, Lennard-Jones potential. Generalizing to other anharmonic potentials (ion traps, mechanical cantilever arrays, and others), a system with strong anharmonicities and loss of resonance between the sites would have conceptually the same dynamics as our model. The Hamiltonian of our model system is

\[ H = c_h \left( P_1^2 + P_2^2 + X_1^2 + X_2^2 \right) + c_a \left( X_1^4 + X_2^4 \right) + c_c X_1 X_2, \]  

(1)

where \( P_1, P_2, X_1, \) and \( X_2 \) are either classical coordinates or quantum mechanical operators, \( c_h \) is the harmonic constant equal to 1/2, \( c_a \) is the anharmonicity parameter, and \( c_c \) is the linear coupling coefficient.

The anharmonicity and coupling terms of the Hamiltonian govern the DB phenomenon, since energy localization arises due to anharmonicity, while energy exchange and delocalization occur due to coupling. For fixed values of the \( c_a \) and \( c_c \) constants, the ratio of the anharmonic and
coupling terms is determined by the $X_1$ and $X_2$ coordinate values, which, in turn, depend on the energy. When the energy is low, the quadratic term dominates over the quartic term, the motion is harmonic, the energy is exchanged between the oscillators, and the eigenstates are delocalized between the sites. When the energy is high, the quartic term dominates over the quadratic term, the energy is not exchanged. If one of the oscillators is excited, it never shares the excitation energy with the second oscillator in classical mechanics, while in quantum mechanics the energy transfer is very slow and occurs by tunneling.

For our purposes, it is convenient to represent the Hamiltonian in the occupation number basis set of harmonic oscillators, also known as Fock states. The occupation basis set of the system is a direct product of the occupation states of all oscillators: $|N_1 N_2 \ldots N_N\rangle$, where $N_i$ is the occupational state on the $i$th oscillator. For our calculations, $i = 2$. The occupation number operator $\hat{N}$ is closely related to the creation $a\dagger$ and annihilation $a$ operators, $\hat{N} = a\dagger a$. Using the creation and annihilation operators, the system Hamiltonian is expressed as

$$H = c_b H_b + c_a H_a + c_c H_c,$$  \hspace{1cm} (2a)

$$H_b = \sum_i a_i^\dagger a_i + a_i a_i^\dagger,$$  \hspace{1cm} (2b)

$$H_a = \sum_i a_i a_i^\dagger + a_i^\dagger a_i + a_i a_i a_i a_i^\dagger + \cdots + a_i a_i a_i a_i^\dagger a_i a_i^\dagger + \cdots,$$  \hspace{1cm} (2c)

$$H_c = \sum_i (a_i a_{i+1}^\dagger + a_{i+1}^\dagger a_i + a_{i+1}^\dagger a_{i+1}^\dagger + \cdots + a_{i+1}^\dagger a_{i+1}^\dagger a_{i+1}^\dagger + \cdots).$$  \hspace{1cm} (2d)

The number of levels in the basis set and the size of the matrix required for the calculation depend on the initial conditions, such as the displacement of the coherent state from the ground state, and anharmonicity of the system. The basis set can be truncated at high energies, where the overlap between the initial state and the energy eigenstates is small. For example, if $c_a \leq 0.05$ and a coherent state is initially displaced by 1.0 a.u., the basis set can be truncated after as few as 10 occupation states. The size of the total basis set is given by the number of states for a single oscillator to the power of the number of the oscillators.

A coherent state is a state of the minimum uncertainty.$^{53}$ A coherent state of a single site is expressed in the occupation number basis $|i\rangle$ as

$$|\alpha(x_0)\rangle = \sum_i c_i(x_0) |i\rangle,$$  \hspace{1cm} (3a)

$$c_i(x_0) = e^{-|x_0|^2 |i\rangle \over \sqrt{i!}},$$  \hspace{1cm} (3b)

where $c_i(x_0)$ represents the contribution from the $i$th energy level and $x_0$ is the displacement of the coherent state from the ground energy eigenstate. The basis set for the current model is a direct product of the occupation states of two harmonic oscillators

$$|\psi(x_0)\rangle = \sum_{i,j} c_{ij}(x_0) c_j(x_0) |ij\rangle,$$  \hspace{1cm} (4a)

$$c_{ij}(x_0) = e^{-|x_0|^2 |ij\rangle \over \sqrt{j!}},$$  \hspace{1cm} (4b)

$$c_j(x_0) = e^{-|x_0|^2 |j\rangle \over \sqrt{j!}}.$$  \hspace{1cm} (4c)

The dynamics of classical and quantum DBs can be compared by displacing one of the two oscillators away from the lowest energy state.

The energy spectrum represents the dynamics of the system in the frequency domain. The spectrum of a bound quantum system consists of discrete energy values. The energy eigenstates and eigenvalues are found by diagonalization of the Hamiltonian expressed in the occupation number basis, Eq. (2). The diagonalization is performed using the symmetric QR routine from GMM++ library providing an interface to LAPACK. The projection of the initial state onto the energy eigenstate

$$c_k = \langle \psi_{\text{initial}} | e_k \rangle \langle e_k | \psi_{\text{initial}} \rangle$$  \hspace{1cm} (5)

determines the intensity of the corresponding spectral line. Here, $|e_k\rangle$ is the $k$th energy eigenstate.

The ACF represents the system dynamics in the time-domain. It is defined as the projection of the initial state onto the state at time $t > 0$. By expressing the initial state and the time-propagation operator $e^{-iHt}$ in the energy eigenstate basis, one obtains the following expression for the ACF:

$$\langle \psi_t \psi_0 \rangle = \sum_k |c_k|^2 e^{-iE_k t}.$$  \hspace{1cm} (6)

Fourier transformation of the ACF provides an alternative route for computing the spectral line intensities, Eq. (5).

III. RESULTS AND DISCUSSION

A. Tunneling and non-tunneling modes

Signatures of breathers are observed in the system spectrum, where one can identify two types of eigenstates, corresponding to non-tunneling and tunneling modes. Tunneling modes arise when the coupling between the oscillators is not sufficiently strong to create eigenstates that are shared between the sites. The particle has to tunnel from one site to the other. In the classical limit, the tunneling time approaches infinity, and the tunneling modes become DB modes. Eigenstates shared between the sites correspond to an alternative type of motion – non-tunneling modes. These modes occur in the low energy region, where coupling dominates. Besides the limiting cases, where there is either a small or a large amount of density shared between the sites, it is sometimes hard to distinguish between tunneling and non-tunneling modes. In Secs. III B and III C, we show that the transition between
In the middle panel are tunneling modes – the anharmonic limit (\(c_a = 0\)) with no anharmonicity (Figure 1 (top)) and anharmonic standing of how the two coexist in the same energy region, let us first focus on the limiting cases: coupled harmonic oscillators with no anharmonicity (Figure 1 (top)) and anharmonic oscillators with no coupling (Figure 1 (middle)). We then analyze the case where the potential combines both anharmonicity and coupling (Figure 1 (bottom)). The system is governed by Hamiltonian in Eq. (2) with initial state described by Eq. (4), where \(x_0 = 3.5\) and \(x_0 = 0\).

In the coupled case (Figure 1 (top)), we see a splitting of the energy levels. All of the eigenstates in this case are non-tunneling. For example, at 2 a.u., a system of uncoupled harmonic oscillators would have the second lowest eigenstate \(|00\rangle\) of a system of uncoupled harmonic oscillators. For example, \(|00\rangle\) and \(|09\rangle\) are involved in splitting; for example, \(|09\rangle\) and \(|09\rangle\) are involved in splitting, \(|01\rangle\) and \(|01\rangle\) are not involved in the same splitting. In the harmonic coupled case, all of the levels with the same number of quanta split together.

The system that includes both coupling and anharmonicity (Figure 1 (bottom)) resembles both limiting cases: \(c_d = 0\) (Figure 1 (top)) and \(c = 0\) (Figure 1 (middle)). The non-tunneling modes dominate at lower energy, and tunneling modes dominate at higher energy. A classical mechanical description of DBs separates the localized and delocalized modes by a separatrix in the energy domain. Non-tunneling modes are the quantum equivalent of delocalized modes. This is because there exists no clear separation between the regions with non-tunneling and tunneling modes in quantum mechanics. As energy increases, tunneling modes slowly emerge out of non-tunneling modes. We call the region in energy, where both tunneling and non-tunneling modes co-exist, a mixed region (Figure 1 (bottom), a region of 10–15 a.u.). The tunneling modes appear as isolated peaks that resemble the modes in an uncoupled quartic potential. The tunneling modes can be seen clearly at energies higher than the mixed region. The analysis presented below shows that the wave function of the tunneling modes is localized on the sites. These modes are equivalent to localized modes in a classical mechanical description of DBs. The non-tunneling modes resemble the modes in a coupled harmonic potential. They have a significant wave-function density between the sites and appear lower in energy where nonlinear contributions are not significant. The non-tunneling modes are an equivalent of delocalized modes in the classical mechanics description of DBs.

We choose the values for the \(c_d\) and \(c_a\) coefficients, and the position of the coherent state on site 1 \((q_1)\) with the intention to show clearly the mixed region and the interplay between the non-tunneling and tunneling modes. In some cases, DBs are seen with low energy eigenstates. For example, the anharmonicity dominates the coupling already in the second excited state of the C–H stretch.\(^{34}\) Our choice of the system parameters and initial conditions gives a general understanding of the dynamics. Similar to our model, the displaced state spans a large number of eigenstates in heavy oscillators, such as nano-mechanical cantilever arrays or large molecules with hydrogen bonding.

The spectrum shows the overlap of the initial state with the eigenstates; the intensity of each line is determined by a projection of an initial state on the corresponding eigenstate. A displaced initial state shows little intensity in the low and high energy regions of the spectrum. The majority
of the intense states are at the energy \( H(q_1 = 3.5, q_2 = 0.0) \) (Figure 1 (bottom)). At lower energy, non-tunneling eigenstates have a considerable amount of overlap with the coherent state. Anharmonicity prevails at higher energies, and the initial state overlaps strongly with tunneling eigenstates. The wave-functions of tunneling eigenstates localize on individual oscillators and is not shared between them. These tunneling eigenstates correspond to the highest energy states in the group arising from a single, degenerate level of uncoupled oscillators.

Contour plots illustrate the energy distribution within an eigenstate among the oscillators (Figure 2). Quantum dynamics of the coherent state result from the projection of the initial state onto the eigenstates. By visualizing and comparing the density distribution of the initial wave function and eigenstates, one can understand how the spectrum forms. For example, the wave-function of tunneling eigenstates has higher density concentrating on the sites; it can be seen as higher overlap with the \( |i, j⟩ \) states, where \(|i - j| \approx i + j\). Therefore, the initial state, which is localized on the sites rather than delocalized between the sites, will have a higher intensity.

The contour plots are obtained using the following procedure. The Hamiltonian matrix is written in the Fock basis, which is a direct product of the occupation states of each oscillator. The matrix is diagonalized. The eigenstates expressed in the Fock basis are represented as a 2D matrix. The columns of the matrix are enumerated according to the Fock states of the first oscillators: \( |0, i⟩, |1, i⟩, \ldots, |n, i⟩ \); where \( i = 0 \ldots n \). The rows are enumerated according to the Fock states of the second oscillator: \( |i, 0⟩, |i, 1⟩, \ldots, |i, n⟩ \). The matrix elements represent the projections of the eigenstate onto the Fock state basis. The contour plot value at a coordinate \((x, y)\) corresponds to the component of the \(|x, y⟩\) basis vector. Figure 2 gives an example of such a contour plot. In the plot, one can see 237th eigenstate of the Hamiltonian in Eq. (2) in the earlier mentioned Fock basis set of two harmonic oscillators \((H_{ab} = a_1^† a_1 + a_i a_i^†)\). The figure also explains how to interpret the plot in terms of the occupation levels of the harmonic oscillators.

The contour plots (Figure 2) help to visualize and distinguish localized states from delocalized states. In addition, the contour plots of the eigenstates are well suited to illustrate the transition between localized and delocalized modes, and to identify modes that have signatures of both regimes. Finally, the contour plots help to describe the origin of the higher order breathers, the small satellite peaks that are slightly lower in energy than the localized modes in Figure 1 (bottom).

Figure 3 provides examples of tunneling ((d) and (e)) and non-tunneling modes (a), (b), and (c). Tunneling mode contour plots show a non-zero density next to the axis, where the value on one axis is high and on the other axis is low. This density distribution indicates that one of the oscillators is in lower energy states, and the other oscillator is in higher energy states. Another way to identify the tunneling modes is to observe that the value of the plotted eigenstate along the increasing, \( y = x \) diagonal is close to zero. Non-tunneling modes, on the other hand, have higher values of the wave-function on the increasing diagonal, meaning that the eigenstate wave-function is shared between both oscillators.

The value of the wave-function for non-tunneling and tunneling eigenstates oscillates differently along the decreasing diagonal – the line connecting \( |0, n⟩ \) and \( |n, 0⟩ \). The wave-function of tunneling modes varies slightly. It either does not change sign at all along the decreasing diagonal for the symmetric modes, or changes the sign only once for the anti-symmetric modes. For the non-tunneling modes on the other
hand, the wave function varies quickly. This variation is seen as blue and red peaks alternating along the diagonal.

The contour plot of the tunneling modes (Figures 3(d) and 3(e)) correspond to the pair of peaks at 16.33 a.u. found in the spectrum (Figure 1 (bottom)). The pair appears as a single peak; the two states are only 0.003 a.u. apart. The eigenstate that is higher in energy is symmetric, and the lower energy eigenstate is anti-symmetric. The small splitting between the symmetric and anti-symmetric states of the tunneling modes pair is consistent with the classical formulation of DBs. If both symmetric and anti-symmetric states are occupied, then the density on one of the oscillators cancels out, and the energy is localized to the other oscillator. A superposition of symmetric and anti-symmetric states will evolve in time, and at some point the energy will transfer between the oscillators. Since the splitting is very small, the energy transfer time is very long.

Investigating the intensity and distribution of energy between the sites allows us to study in detail the mixed region, the evolution of non-tunneling modes into tunneling modes, the influence of the variation of coupling and initial conditions on the spectrum, and the properties of HOTM. Contour plots provide an important tool to distinguish between localized and delocalized modes. They are particularly important for cases when the density of states increases and the spectrum becomes complex; for example, in soft potentials or for high energy initial conditions.

**B. The mixed region**

Most of the systems in nature, such as molecules, crystals, and nano-materials, consist of a network of coupled sites. At higher energies, the coupling between sites of the system becomes negligible when compared to the nonlinearity of on-site potential. At lower energies, the on-site potential can be modeled with a linear approximation. The approximation is similar to the sine approximation for the motion of a pendulum and may be familiar to the readers from their introductory physics class. With an increase in energy, the nonlinearity becomes more important and the system dynamics change from delocalized modes to localized modes. This transition is important because the behavior of the system changes significantly. In the delocalized regime, the system transfers the energy from one site to the next site. In the localized regime, quantum, and classical mechanics differ in how they model the distribution of energy between the sites. In classical mechanics, the energy does not transfer between the sites. Quantum mechanics allows the energy to transfer from one site to another through tunneling. Without the loss of generality, we model this transition in the simplest potential – two coupled quartic oscillators.

In addition to the difference in describing localized modes, the transition from the non-tunneling region to the tunneling region also differs between classical and quantum mechanics. In classical mechanics, the two regions are divided by a point called the separatrix. Such a sharp division does not exist in quantum mechanics. As mentioned earlier, the energy does not localize but takes an almost infinite amount of time to transfer by tunneling. Therefore, in contrast to the localization seen with classical mechanics, quantum tunneling modes slowly evolve from the non-tunneling modes as energy increases. Understanding the quantum equivalent of the transition between delocalized and localized modes will help in understanding the limitations of a classical model, while providing insight into semi-classical dynamics and complementing experiments on QDBs.

Depending on the system’s Hamiltonian and the initial conditions, the mixed region can contain part or all of the coherent state. In the mixed region, non-tunneling and tunneling modes co-exist. Figure 1 (bottom) shows that as the energy increases, these modes alternate. Non-tunneling modes can have higher energy than tunneling modes and vice versa. Tunneling modes are the highest energy modes found in same-quanta groups. The mixed region may contain a number of same-quanta groups. It can also contain non-tunneling states followed by the tunneling states of the same-quanta group. They are then followed by non-tunneling states and tunneling states of the next same-quanta group. Figure 4 gives an example of alternating tunneling and non-tunneling modes.

In classical mechanics, the transition from localized to delocalized modes happens instantly. Quantum mechanics shows this transition to happen smoothly. Figure 5 shows the highest energy eigenstates from the same-quanta groups within the mixed region. In this figure, one can observe an iterative transformation from non-tunneling to tunneling modes. This phenomenon is quantum in nature and strongly contrasts with the step-like transition from delocalized to localized modes observed in classical mechanics.

Unlike in a classical mechanical perspective, the transition from tunneling modes to non-tunneling modes is smooth. Figure 5 shows this transition. The last two plots on the right ($d_-$ and $d_+$) are tunneling modes; there is no shared density.

**FIG. 4.** Contour plots (see Figure 2) of delocalized (b) and (d)) and tunneling ((a), (c), and (e)) modes within the mixed region (12–23 a.u.). The plots are in the order of increasing energy; plot (a) is the 55th state with the energy 12.1386 a.u., (b) – 75th – 14.454 a.u., (c) – 110th – 17.7796 a.u., (d) – 145th – 20.82 a.u., and (e) – 163rd – 22.2542 a.u. The figure shows that in the mixed region, the tunneling and the non-tunneling modes alternate.
between the sites and the wave-function has to tunnel through. The major contribution to the tunneling eigenstates comes from basis states that have only one of the sites excited; for example, \( |14, 0\rangle \) and \( |0, 14\rangle \). The two plots on the left of Figure 5 (\(a_-\) and \(a_+\)) are a pair of eigenstates that resemble the tunneling mode. The pair of states \(b_-\) and \(b_+\) (Figure 5) have features similar to the tunneling modes, but they are more delocalized than the tunneling mode. There is significant density on the increasing diagonal, meaning that there is an overlap with basis set states that have the density delocalized between the sites. The pair of states in the middle is between the two cases.

C. Additional observations

1. Effects of coupling variation on discrete breather signatures

Slight changes in the setup of an experiment can vary the shape of the potential. For example, one can change parts of the molecules to be heavier or lighter, or use a different solvent. These perturbations can control the interplay between the nonlinearity and coupling in the potential.

Figure 1 illustrates the signatures of breathers in a spectrum. We extend those results by investigating how these signatures depend on the parameters of the potential. First, we analyze the evolution of the eigenvalues with respect to the coupling coefficient in the Hamiltonian (Eq. (2)). Starting from zero coupling \(c_c = 0\), we increase it to the point, where the coupling is much larger than the anharmonicity, so that the system approaches the limit of coupled harmonic oscillators. We focus on eigenvalues of the same-quanta group of states between 9.1 and 11.4. The coefficient of anharmonicity is constant: \(c_a = 0.02\).

Figure 6 shows the dependence of anharmonic oscillator (Eq. (2)) eigenvalues on coupling \(c_c\). The plot shows the variation of eigenvalues from one extreme of two uncoupled anharmonic oscillators \(c_c = 0.0\) to another extreme that has coupling \(c_c = 0.3\) much larger than anharmonicity \(c_a = 0.02\). With this plot, we would like to focus on a group of same-quanta states. At \(c_c = 0\), the eigenstates of that group have energy in the interval \(\approx (10, 10.6)\) a.u. The figure clearly shows how an increase in coupling causes degenerate states to split. The tunneling states, which are the top states of the same-quanta group, are the last ones to split. Keeping in mind that the size of splitting is inversely proportional to the transfer time between the sites and noting that the size of the splitting between tunneling states approaches the size of the splitting between lower lying non-tunneling modes, one can conclude that the transition from tunneling to non-tunneling states is smooth from a quantum mechanical perspective. This observation complements our result in Sec. III B on the smooth transition between tunneling and non-tunneling modes.

We observe avoided crossings for states from the same-quanta group. At \(c_c \approx 0.8\), the top (symmetric) state that starts at \(\approx 10.34\) avoids crossing with the low state that starts at \(\approx 10.14\). Another avoided crossing happens at \(c_c \approx 0.04\) for the next lowest pair of states. In the harmonic case, there is no crossing since the degenerate states split linearly and do not cross. Previously, avoided crossing was observed in an anharmonic trimer.\(^{32}\) The avoided crossing is expected since the eigenstates belong to the same symmetry group of irreducible representations. The practical importance of this result shows up in systems with many degrees of freedom. In multidimensional systems, the avoided crossings become conical intersections that allow for radiationless transitions between the energy surfaces.\(^{35}\)

2. Higher order tunneling modes

In the spectrum plots (Figure 1), one can notice that beside tunneling modes, there are eigenstates of smaller
intensity in the anharmonic regime, where there are not any non-tunneling modes – the energy region beyond 16 a.u. (Figure 1 (bottom)). These eigenstates do not classify as non-tunneling modes. In this higher energy regime the influence of coupling is small, and contrary to the case with non-tunneling modes, they increase in intensity as they increase in energy. The eigenstates also do not fit our previous definition of tunneling modes. They do not have the highest intensity in their same-quanta groups, and they are not a linear combination of modes that have one of the sites in the ground state and the other site occupying a high state.

The anomaly becomes clear when we analyze the contour plots of these eigenstates (Figure 7). In these eigenstates, the energy has to tunnel from one site to the other in a similar manner to the tunneling eigenstates. The contour plots evidence a distinction of these eigenstates from tunneling modes – the majority of the wave function density is not on the axis. These two observations motivate us to define them as HOTM. To be more precise, we define HOTM as a group of eigenstates that satisfy the following conditions: (1) the energy from the displaced oscillator can transfer to the other oscillator(s) only through tunneling, and (2) the undisplaced oscillator has the highest wave-function density on non-ground state(s). Figure 7, specifically, is an example of second order tunneling modes (SOTM). In the basis set of a direct product of anharmonic oscillators, they are a linear combination of \(|n-1, 1\rangle\) and \(|1, n-1\rangle\) states. Figure 1 shows other HOTM that are even smaller in intensity than SOTM and manifest at an even higher energy limit. Next, we compare HOTM and first order tunneling modes and outline a couple of other interesting points.

To identify the relation of HOTM to tunneling modes, we would like to point out a few similarities. As seen from Figure 7, HOTM are a pair of symmetric and anti-symmetric states with a higher probability of being on the oscillators than states shared between them. In the figures, one can see the lack of density on the increasing diagonal; the density closer to the axis. As seen in Figure 6 at the energy 10.33 a.u., HOTM start as degenerate states but further along, they split into a pair, similar to the first order tunneling states. Since we are interested at a lower value of coupling, we can see HOTM at 10.33, rather than at 16 a.u.

To emphasize that HOTM should be treated differently from the first order tunneling modes, we would like to point out some key differences. The probability density in HOTM shifts towards the other oscillator by one occupational level. Figure 7 shows this shift in density for the second order tunneling modes; they correspond to \(|n-1, 1\rangle\) and \(|1, n-1\rangle\) occupational states. The maxima of the wave-functions are not on the axes anymore but are closer to the increasing diagonal. Compared to the energy region 10.3–10.6 a.u. of the tunneling modes in Figure 6, the SOTM have larger splitting between symmetric and anti-symmetric modes than the first order modes. The distance between the top left and bottom right density concentrations in the contour plot is related to the tunneling probability; therefore, it is rational to assume that with a decrease in this distance the splitting and the tunneling probability increases.
3. Influence of the initial conditions

The initial state determines the intensities in the spectrum. We show that when both of the sites are displaced initially, HOTM have higher intensity than tunneling or non-tunneling modes. The impact of this observation is twofold: we gain insight into experiments with displaced coherent states on all sites and we understand the influence of HOTM on the dynamics. Depending on the experimental system setup, the initial conditions can be different. When an experimental setup cannot target a specific site, multiple sites will be displaced. An example of this would be exciting a number of sites in a system from a ground state to an excited state, where the excited state is displaced. One application may be an understanding of DNA breaking under THz radiation.56

Emphasizing the presence of the HOTM in the dynamics, on the other hand, results in a new type of dynamics – the energy is neither localized on sites nor distributed between the sites. Figure 8 illustrates the effects of displacing the coherent states symmetrically on both sites (the bottom panel), in contrast to displacing just one of the sites (the top panel). The figure shows the spectrum of a coherent state \( x_0 = q_1 \) and \( x_0 = q_2 \) in Eq. (4)) in Eq. (2). In the lower energy region (<6 a.u.), the effect of displacing both sites is clear. At 2 a.u., for example, the case with both sites displaced (BSD) has only one line corresponding to a symmetric eigenstate; the case with one site displaced (OSD) has both symmetric and anti-symmetric modes. In the case of BSD, the pattern continues at higher energies – only the symmetric eigenstates have intensity. Furthermore, in the same-quanta group the highest energy eigenstate has the highest intensity. In the mixed region (10–15 a.u.), SOTM start to have the highest intensity. The OSD case shows the opposite trend. At lower energies, the highest intensity is in the middle of the same-quanta group. In the mixed region, tunneling modes start to dominate. However, the most interesting contrast is in the anharmonic region, where in the OSD case, tunneling modes dominate. In BSD, SOTM, and other HOTM dominate.

In classical mechanics if both sites have the same amount of the initial energy, there is no transfer of energy. In quantum mechanics, a coherent state is a superposition of eigenstates so the dynamics are more complex. To get a brief understanding, let us analyze the dynamics around 20 a.u. In the case of OSD, the tunneling mode pair has the most intensity. As we mentioned earlier, the energy is transferred from one site to the other. In the case of BSD, the intensity is distributed only among the symmetric modes – there is no transfer of energy between the sites. However, the energy is distributed almost evenly among HOTM. HOTM have some density shared between the sites. With time, the density oscillates from being localized on the sites to being partially shared between the sites.

4. Auto-correlation of the displaced coherent state

A number of time-domain methods are based on propagation of coherent states. Examples include HK,32 QHD,42 CSPI,38 CCS,35 and MP-SOFT.36,37 Earlier we calculated eigenstates to analyze dynamic properties of the system. Eigenstates represent stationary properties of dynamics. To compare our results to time-domain methods, we calculate the ACF. Besides showing evolution of the initial state in time, the ACF is used to calculate spectroscopic properties, diffusion rate, and reaction rate constants. Figure 9 shows the ACF (Eq. (6)) for different values of anharmonicity in the potential Eq. (2). The system is the same as in Figure 1 with \( c_s = 0.2 \).

The top panel shows the dynamics of coupled harmonic oscillators. The wave-function returns to the previous state with a period of 65 a.u. Once there is anharmonicity \( c_s = 0.01 \), middle panel), the eigenstates have frequencies that are not multiples of each other anymore. The condition for
resonance is lost, and the tails of the coherent state move at different frequencies. The coherent state spreads with time. The wave function does not come back to the same state. The case with \( c_a = 0.05 \) (bottom panel) is an even more extreme example. The coherent state spreads even faster. Calculating rapidly spreading coherent states is difficult. This result shows the challenge faced by coherent state based path-integral methods – they have to track quickly spreading tails of the coherent state. Nevertheless, the time-window that we used proves to be sufficiently large to get satisfying results. In addition, a quick decrease of the ACF in time justifies using shorter propagation times. Time-domain methods that are based on propagation of a coherent state will prove to be an effective and accurate tool to model signatures of QDBs in multidimensional systems.

IV. CONCLUSION

Understanding signatures of QDBs in the quantum dynamics of coherent states is a step towards elucidating the localization phenomenon in large scale systems and bridging the gap between the concepts of quantum and classical DBs. We have analyzed tunneling modes, a quantum counterpart of classical DBs, in the spectrum of a quartic dimer, and characterized in detail the properties of the eigenstates within the mixed region where the dynamics switch from the delocalized to localized regime. Additional important observations include the following: tunneling modes avoid crossing with non-tunneling modes arising from the same states of the uncoupled oscillators; new types of modes, HOTM appear at higher energies; controlling initial conditions allows us to enhance the contribution of HOTM to the spectrum and faster ACF decay with increasing nonlinearity shortens the time required for modeling DBs.

Tying our results to the classical mechanical interpretation of DBs, we show that tunneling and non-tunneling modes are the quantum mechanical counterpart of the localized and delocalized modes that appear in classical mechanics. Since coherent states span a large number of eigenstates, they simultaneously contain both tunneling and non-tunneling modes. In the classical mechanical analogue, the initial energy localized on one of the sites cannot completely transfer to the other site. In quantum mechanics, the energy tunnels to the other site; however, as the size of the system approaches a classical limit, the tunneling time approaches infinity.

From the analysis of the mixed region, we concluded that tunneling and non-tunneling modes alternate with increasing energy, and that the transition from non-tunneling to tunneling modes is gradual. Both of these conclusions are in contrast with the classical mechanical model of breathers, where localized and non-localized modes are separated sharply at a certain energy. The convergence of the mixed region in quantum mechanics to the separatrix point in classical mechanics can be reached by scaling the quantum result to the classical limit.

Many semi-classical methods that are capable of describing large systems rely on the propagation of coherent states. We show that both tunneling and non-tunneling modes are present in the coherent state. Therefore, a coherent state representation is capable of reflecting both types of dynamics simultaneously: part of the coherent state would stay localized and part would be delocalized. It is likely that coherent state based methods would have difficulty tracing the width or other metrics of the coherent state, especially in the mixed region, where both types of states have a nearly equal contribution. Nevertheless, coherent state based methods should be able to identify the location of the mixed region, and represent non-tunneling, tunneling, and HOTM.

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