TOPICAL REVIEW

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Topical Review

Continuous vibronic symmetries in Jahn–Teller models

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Abstract

Explorations of the consequences of the Jahn–Teller (JT) effect remain active in solid-state and chemical physics. In this topical review we revisit the class of JT models which exhibit continuous *vibronic* symmetries. A treatment of these systems is given in terms of their algebraic properties. In particular, the compact symmetric spaces corresponding to JT models carrying a vibronic Lie group action are identified, and their invariants used to reduce their adiabatic potential energy surfaces into orbit spaces of the corresponding Lie groups. Additionally, a general decomposition of the molecular motion into pseudorotational and radial components is given based on the behavior of the electronic adiabatic states under the corresponding motions. We also provide a simple proof that the electronic spectrum for the space of JT minimum-energy structures (trough) displays a universality predicted by the epikernel principle. This result is in turn used to prove the topological equivalence between bosonic (fermionic) JT troughs and real (quaternionic) projective spaces. The relevance of the class of systems studied here for the more common case of JT systems with only discrete point group symmetry, and for generic asymmetric molecular systems with conical intersections involving more than two states is likewise explored. Finally, we show that JT models with continuous symmetries present the simplest models of conical intersections among an arbitrary number of electronic state crossings, and outline how this information may be utilized to obtain additional insight into generic dynamics near conical intersections.

Keywords: Jahn–Teller, vibronic, symmetry

(Some figures may appear in colour only in the online journal)

1. Introduction

Jahn–Teller (JT) models [1, 2] explain a rich variety of phenomena in condensed matter and chemical physics [3–6]. Modern studies have explored the role of JT distortions in e.g. possible mechanisms for unconventional superconductivity [6], colossal magnetoresistance [7], multiferroics [8], and single-molecule transport [9]. The unifying feature of these phenomena is that they involve significant coupling of orbital and vibrational degrees of freedom.

One of the simplest JT models is that consisting of a degenerate pair of electronic states coupled to a similarly degenerate vibrational mode [10], the so-called $E \otimes e$ system [11] (we employ the standard convention that the irreducible representation (irrep) corresponding to the electronic multiplet is labeled by an upper case letter, while that of the vibrations is given by a lower case). This model has been employed, for example, to describe the distortion of Cu^{II} and Mn^{III} in an octahedral environment [12] (figure 1), and properties of triatomic systems near the equilateral configuration [13]. A well-known characteristic of this system is that when only linear vibronic couplings are included, it displays circular symmetry [11] (figure 2). The reason is the linear $E \otimes e$ Hamiltonian is invariant under simultaneous rotations of the electronic states

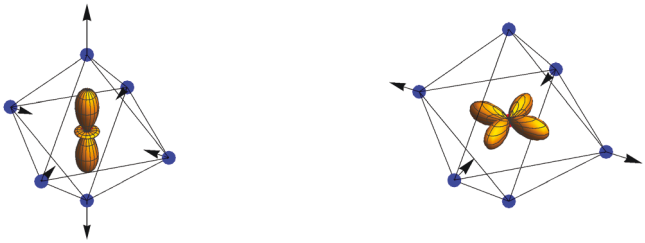

Figure 1. E_g vibrational modes and electronic orbitals for a system with O_h symmetry.

and vibrational coordinates (see equation (7)). The space of rotations of the plane [SO(2)] is topologically equivalent to the one-dimensional circle S^1. Therefore, the symmetry group of linear $E \otimes e$ is *continuous* (as opposed to the discrete point groups). This has extreme implications, e.g. there exists a continuous family of minima (trough) in the ground-state adiabatic potential energy surface (APES) (figure 2), the vibronic ground-state is doubly degenerate, and the vibronic (pseudo) angular momentum is quantized in odd half-integral units, thus indicating a vibronic motion with spinorial character [3, 11]. All of these are surprising, as none are generic properties of finite molecular systems irrespective of the existence of point group symmetry. They are also intrinsically quantum-mechanical (even though a semiclassical treatment leads to an effective classical Hamiltonian which describes the properties of the system when $\hbar \to 0$ [14]).

Continuous symmetries in JT systems have sometimes been described as accidental or emergent, since the molecular Hamiltonian is only constrained to be a molecular point (double) group scalar. Deeper mathematical analysis has revealed the continuous invariance properties of JT models follows from the interplay between the representations of molecular point (double) groups adopted by the electronic and nuclear degrees of freedom [15–17]. In particular, Pooler laid out the representation theory underlying linear JT problems with continuous symmetries [15, 16]. Roughly speaking, for the latter to occur, the JT distortions need to be isotropic, and the space of electronic Hamiltonians must be equivalent to the vibrational configuration space as irreducible representations (irreps) of a Lie group G. In this way, the molecular Hilbert space $\mathcal{H} \equiv \mathcal{H}_{\text{vib}} \otimes \mathcal{H}_{\text{el}}$ carries a G-action.

Due to the constraints on the fundamental parameters of continuously-symmetric JT models, these have been only rarely employed to extract quantitative information about physical systems (though some examples are given below). Quadratic or non-degenerate linear vibronic couplings are known to break continuous symmetries [3, 18]. For instance, in the presence of quadratic couplings, the continuous set of $E \otimes e$ minima imposed by SO(2) symmetry becomes a discrete set separated by saddle points [3, 18, 19]. The APES associated to this model is said to be *warped* (figure 3). However, if the distorted JT surfaces can be obtained by a gap-preserving continuous deformation (homotopy) of the electronic ground-state APES, then basic features of the continuously-symmetric JT system will remain relevant (figure 3) [19]. These include the vibronic ground-state degeneracy and symmetry, as well as any other non-trivial effects originating from the existence

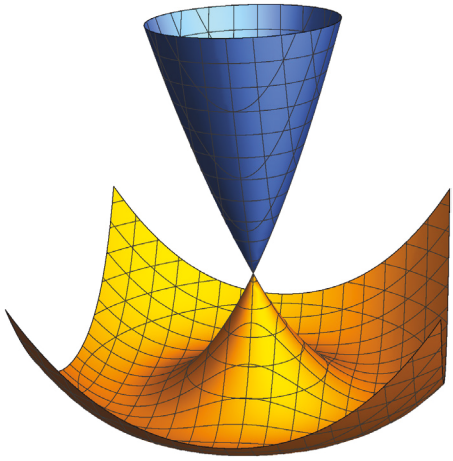

Figure 2. Ground and excited-state branches of the $E \otimes e$ APES.

of a Berry phase [19–21]. On the other hand, if the warping generates new electronic-state intersections (esis, which include the ubiquitous conical intersections (cis) [22–24]) on the electronic ground-state APES in regions accessible at low-energies, then the warped JT system becomes topologically different [19, 25]. In other words, the symmetry and degeneracy of the vibronic ground-state changes. While it is well-known that warping necessarily generates additional esis on the JT APES [19, 26, 27], these are brought from the vibrational configuration space infinity (where they coalesce when nonlinear vibronic couplings vanish) (see figure 3). Thus, if the warping is weak enough, and the new esis are as a result far away, then at low-energies the molecular system will be confined to a region that excludes esis other than that which defines the JT model; in this case, homotopic invariants of the continuously-symmetric electronic ground-state APES will be preserved [19, 20].

A less known example of the robustness of the properties of JT models with continuous symmetries was given by Markiewicz [28]. To understand, recall that continuous-symmetry breaking in the dynamical JT problem *without* quadratic or higher-order vibronic couplings will happen under one of the following three conditions: (a) different vibrational frequencies for the JT active modes irreps, but equal JT stabilization energies, (b) equal vibrational frequencies, but different JT stabilization energies, and (c) different vibrational frequencies and JT stabilization energies. In [28], the linear $E \otimes (b_1 \oplus b_2)$ model (which can be understood as arising from symmetry breaking of the vibrational modes of $E \otimes e$) was employed to study case (a). This has a continuous set of ground-state minima, but pseudoangular momentum is not conserved (the b_1 and b_2 vibrations have different frequencies). However, the average wavepacket pseudoangular momentum was numerically verified to be quantized for different values of vibrational frequency anisotropy. While the dynamical continuous symmetry was broken, it left clear signatures.

There have been also some experimental studies of JT centers which benefited from an analysis based on an ideal model admitting continuous symmetries. For example, O'Brien [29] employed the SO(3)-invariant version of $T \otimes (e \oplus t_2)$ to investigate the spectra of F^+ centers (crystal

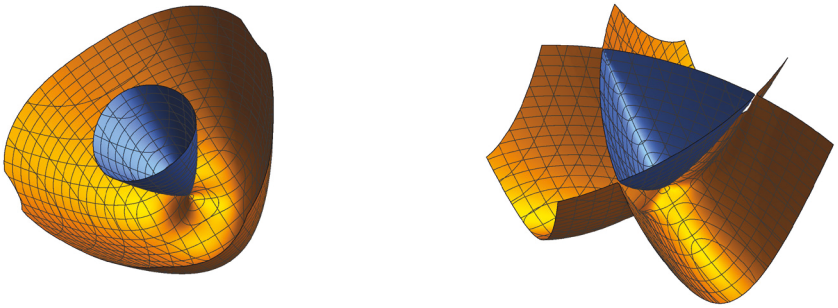

Figure 3. Left: weakly warped APES for $E \otimes e$; right: strongly-warped APES for the same model.

vacancies occupied by holes) in CaO, and obtained quantitatively accurate absorption bandshapes. The same model also provided accurate fits to the absorption spectrum of F-centers (electron-occupied vacancies) in CsF. Another example is Pooler's and O'Brien's [30] study of the $P^2_{1/2} \to P^2_{3/2}$ lineshapes of Tl atoms in halides. Tl is a heavy-atom and its energy levels are strongly influenced by spin–orbit coupling. The JT problem for this model is $\Gamma_8 \otimes (e \oplus t_2)$, where Γ_8 (also denoted by $G_{3/2}$) refers to the quartet double group representation of cubic systems [31]. With the assumption of degenerate vibronic couplings and harmonic frequencies, qualitative agreement with experimental data was also obtained.

In summary, while strong constraints need to be satisfied for a JT system to feature continuous symmetries, i.e. to carry a Lie group action, their study adds valuable insight to the generic problem of cis, as they are minimal models featuring universal properties of systems that contains them. Moreover, the high symmetry of such systems imply that they form convenient starting points for the investigation of the complex interplay between orbital, structural, and charge order in extended systems with JT active sites.

The connection between JT models and Lie groups has been explored before [15, 16, 18, 32–38]. In this work we review and present some novel perspectives on this relationship based on the theory of *symmetric spaces* [39–41]. The general relevance of symmetric spaces to quantum mechanics can be illustrated with the Threefold way classification of non-relativistic Hamiltonian ensembles [42]. Dyson proved that, in the absence of anticommuting symmetries, any quantum-mechanical system belongs to either one of three symmetry classes: real orthogonal, real symplectic and complex unitary. The real orthogonal class contains all time-reversal invariant (TRI) bosonic systems, while the TRI fermionic Hamiltonians correspond to the real symplectic, and the complex unitary ensemble contains models with broken time-reversal symmetry. Dyson's classification (and its generalization [43, 44]) is the basis for the application of random matrix models in condensed matter, nuclear [45], and chemical physics [46, 47]. In fact, as we will see later, there exist several connections between topological phenomena arising in JT models and condensed matter physics (section 3.3).

Let us illustrate some of the previous remarks with the simplest JT model with continuous symmetry, the linear $E \otimes e$ system. The molecular Hamiltonian can be written as a sum of a purely vibrational part and a vibronic component,

$$H(\mathbf{Q},\mathbf{P}) = H_{\text{vib}}(\mathbf{Q},\mathbf{P}) + H_{\text{JT}}(\mathbf{Q}), \mathbf{Q} \in \mathbb{R}^2, \tag{1}$$

where $\mathbf{Q} = (Q_1, Q_2)$, and $\mathbf{P} = (P_1, P_2)$ are the displacements from the JT center (the molecular shape with $\mathbf{Q} = 0$, hosting the electronically degenerate multiplet) and their canonically conjugate momenta, respectively (figure 1). The vibrational contribution is given by the 2D isotropic harmonic oscillator Hamiltonian,

$$H_{\text{vib}}(\mathbf{Q},\mathbf{P}) = \frac{P_1^2}{2} + \frac{P_2^2}{2} + \frac{1}{2}\omega^2(Q_1^2 + Q_2^2), \tag{2}$$

where ω is the vibrational frequency for the e modes. The JT Hamiltonian $H_{\text{JT}}(\mathbf{Q})$ contains the interaction between nuclear and electronic degrees of freedom. Given that $E \otimes e$ is a TRI spinless model, the time-reversal symmetry operator T satisfies $T^2 = 1$, and we can take the electronic Hilbert space $\mathcal{H}_{\text{el}}$ to be a real vector space with basis functions invariant under T. Thus, the vibronic $E \otimes e$ Hamiltonian can be written as:

$$H_{\text{JT}}(\mathbf{Q}) = FQe^{-i\frac{\sigma_2}{2}\phi}\sigma_3 e^{i\frac{\sigma_2}{2}\phi}, \tag{3}$$

where $F \in \mathbb{R} - \{0\}$ is the reduced vibronic coupling constant (from the Wigner–Eckart theorem), $Q = \sqrt{Q_1^2 + Q_2^2} \in \mathbb{R}^+$, $\tan\phi = Q_2/Q_1, \phi \in S^1$, and $\sigma_j, j = 1, 2, 3$, are the Pauli matrices acting on $\mathcal{H}_{\text{el}}$. A change of electronic frame (basis) that preserves the reality of the electronic eigenvectors for all $\mathbf{Q}$ can be parametrized by

$$M(\theta) = e^{-i\frac{\sigma_2}{2}\theta} \in \text{SO}(2), \theta \in \mathbb{S}^1. \tag{4}$$

Let $R(\theta)$ be the rotation of *vibrational configuration space* defined by

$$R(\theta) : \ (Q,\phi) \mapsto (Q,\phi+\theta). \tag{5}$$

It is equivalent to mapping $\phi \mapsto \phi + \theta$ in equation (3). Hence, a change of electronic frame is equivalent to a rotation of the vibrational configuration space,

$$M(\theta)H_{\text{JT}}(\mathbf{Q})M^{-1}(\theta) = H_{\text{JT}}\left[R^{-1}(\theta)\mathbf{Q}\right]. \tag{6}$$

As we now see, the JT Hamiltonian (and therefore, also the molecular) is invariant under the simultaneous action of SO(2) on the electronic and vibrational Hilbert spaces defined by

$$M(\theta)H_{\text{JT}}\left[R(\theta)\mathbf{Q}\right]M^{-1}(\theta) = H_{\text{JT}}(\mathbf{Q}). \tag{7}$$

The equation above explains the circular symmetry of figure 2: the SO(2) action on the space of molecular (nuclear)

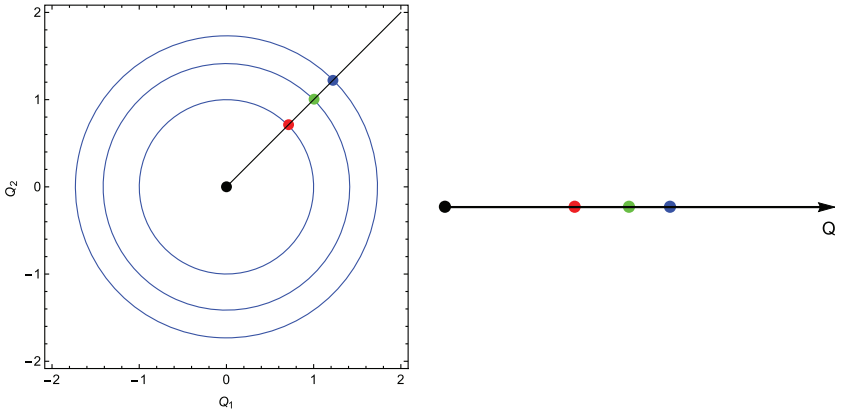

Figure 4. Lhs: $E \otimes e$ contours with equal adiabatic electronic spectrum; Rhs: reduced orbit space.

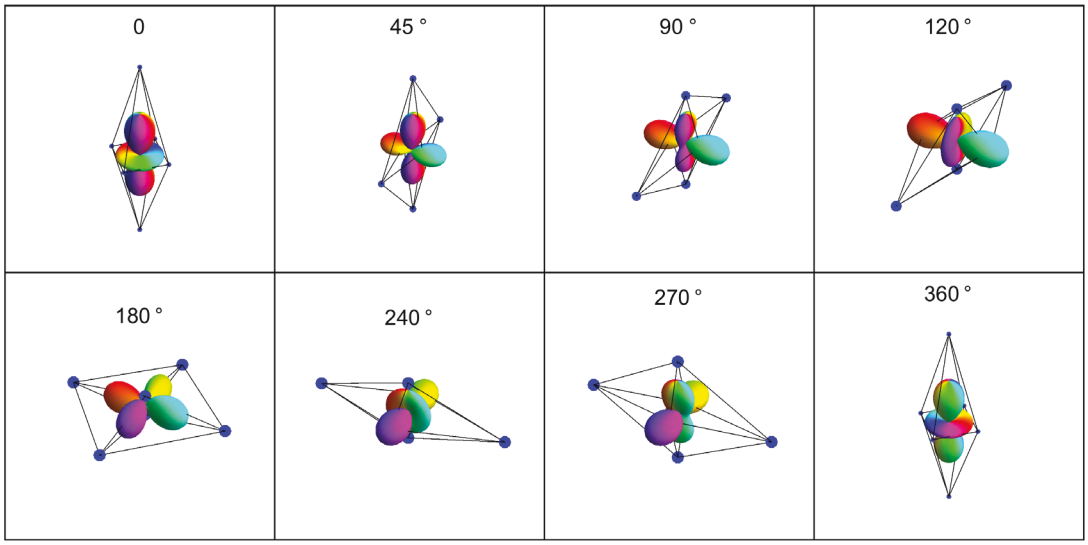

Figure 5. Pseudorotational motion in vibrational and electronic configuration space (the orbital at the center is the adiabatic electronic ground-state).

geometries maps a nuclear configuration into another with the same Q, but that is equivalent to a change of (electronic) basis of $\mathcal{H}_{\rm el}$. Therefore, all invariant properties of the electronic Hamiltonian are preserved (e.g. its eigenvalues) under a vibrational space rotation (pseudorotation). This explains the choice of displacement coordinates for JT distortions ($\mathbf{Q} \neq 0$): ϕ is changed under SO(2) action on the vibrational configuration space (pseudorotation), while variation of Q corresponds to (radial) motion that modifies the adiabatic electronic spectrum.

Equation (7) demonstrates the invariance of the linear $E \otimes e$ Hamiltonian with respect to the continuous SO(2) action on electronic and nuclear degrees of freedom. It also implies a conserved quantity by Noether's theorem [48], the vibronic pseudoangular momentum J (setting $\hbar = 1$ hereafter),

$$J = -\mathrm{i}\frac{\partial}{\partial\phi} + \frac{\sigma_3}{2}, \tag{8}$$

where the first term is a linear operator on the vibrational Hilbert space $\mathcal{H}_{\rm vib}$, while the second acts on the electronic $\mathcal{H}_{\rm el}$ [11, 12] (see equation (3)). Equation (8) is a simple, but exotic result: it implies fractionalization of the vibronic pseudoangular momentum.

We also find that every molecular geometry of $E \otimes e$ lives in an SO(2) orbit labeled by the radial coordinate (figure 4). Formally, to each $Q \neq 0$ we assign the space of molecular structures

$$O(Q) = \{\phi \in [0, 2\pi) | R(\phi)(Q, 0)^T = (Q_1, Q_2)^T\}, \tag{9}$$

containing all $\mathbf{Q} = Q(\cos\phi, \sin\phi)$ with equal electronic energy spectrum. Therefore, the APES can be decomposed into a one-dimensional space of SO(2) orbits, i.e.

$$\mathbf{Q} \in \bigcup_{Q' \geqslant 0} O(Q'). \tag{10}$$

Each point $O(Q)$ of the orbit space, with the exception of $O(0)$, has an internal space corresponding to a circle S^1 of molecular geometries which can be mapped into each other by free pseudorotational motion (figure 5).

These simple considerations on the SO(2) invariance of $E \otimes e$ have allowed us to quickly understand a variety of its non-trivial features. In particular, (i) the APES was simplified by decomposing it into a space of orbits of the 2D proper rotation group SO(2), (ii) the existence and meaning of radial and pseudoangular coordinates were explained, and (iii) the

anomalous vibronic angular momentum conservation law of $E \otimes e$ was quickly obtained. In more complex JT systems carrying a Lie group action, the above points are going to be generalized. For instance, there will be more than one angular and one radial coordinate, so that orbits will require more than a single number to be specified uniquely. There will also be orbits of different types with qualitatively distinct internal (pseudorotational) motion.

In the remainder of this topical review we will employ the invariance properties of symmetric spaces to investigate several aspects of the higher-dimensional generalizations of the SO(2)-invariant $E \otimes e$ model discussed above. In the process we will present simple proofs of established facts about JT systems, as well as obtain some new fundamental results on the topological properties of JT APESs. The content is organized as follows: in section 2 we discuss the general relationship between linear JT problems with continuous symmetries and symmetric spaces. Section 3 applies the framework presented in the previous to characterize local and global properties of the JT APES. In section 4 we discuss the connection between the investigated models and molecular systems with accidental cis involving more than two APESs. A summary of the presented material and a discussion of future directions is given in section 5.

2. Symmetric spaces underlying JT models with continuous symmetries

We start this section by revisiting the conditions satisfied by JT systems admitting continuous symmetries. These are used to determine the symmetric spaces corresponding to each element of the set of JT models studied in this article. We also discuss some general properties of symmetric spaces which will be useful for establishing several universal properties of JT systems carrying a Lie group action.

Consider a JT problem defined by the coupling between electronic states belonging to the irrep Γ of a point group S (S is the symmetry group of the nuclear geometry at the JT center $\mathbf{Q} = 0$) spanned by the basis vectors $\{\gamma_i\}_{i=1,2,...,|\Gamma|}$, and JT active vibrations transforming like the vectors of the (generically) reducible representation $\Lambda = \oplus_i \Lambda_i$, where Λ_i is a non-totally symmetric irrep of S with basis $\{\lambda_{i_1}, \lambda_{i_2} ... \lambda_{i_{|\Lambda_i|}}\}$. The electronic multiplet is only defined to belong to a single irrep, for none of the studied models contain reducible electronic representations (Wiseman showed how to generalize the theory of [16] to the case of direct sum electronic Hilbert spaces [37]). Generalizing equations (1)–(3), the molecular Hamiltonian of the system including only linear vibronic couplings is given by [3]

$$H(\mathbf{Q},\mathbf{P}) = \sum_{\Lambda_i} \frac{\mathbf{P}^2_{\Lambda_i}}{2m_{\Lambda_i}} + \sum_{\Lambda_i} \frac{1}{2} m_{\Lambda_i} \omega^2_{\Lambda_i} \mathbf{Q}^2_{\Lambda_i} + H_{\mathrm{JT}}(\mathbf{Q}), \tag{11}$$

$$H_{\mathrm{JT}}(\mathbf{Q}) = \sum_{\Lambda_i} F_{\Lambda_i \Gamma} \mathbf{Q}_{\Lambda_i} \cdot \mathbf{V}_{\Lambda_i \Gamma}, \tag{12}$$

where $\mathbf{Q}_{\Lambda_i} = (Q_{\Lambda_i \lambda_{i_1}}, Q_{\Lambda_i \lambda_{i_2}} ..., Q_{\Lambda_i \lambda_{i_{|\Lambda_i|}}})$ (with similar notation for $\mathbf{P}_{\Lambda_i}$), m_{Λ_i} and ω_{Λ_i} are the mass and harmonic frequency of the nuclear displacements Λ_i, F_{Λ_i} is the reduced vibronic coupling constant associated with the same modes (from the Wigner–Eckart theorem), and $\mathbf{V}_{\Lambda_i \Gamma}$ is a vector of Clebsch–Gordan matrices, i.e. $\mathbf{V}_{\Lambda_i \Gamma} = (V_{\Lambda_i \lambda_{i_1} \Gamma}, V_{\Lambda_i \lambda_{i_2} \Gamma} ..., V_{\Lambda_i \lambda_{i_{|\Lambda_i|}} \Gamma})^T$, with e.g.

$$V_{\Lambda_i \lambda_{i_1} \Gamma} = \sum_{\gamma_k \in \Gamma} \sum_{\gamma_l \in \Gamma} \langle \Gamma \gamma_k | \Lambda_i \lambda_{i_1} \Gamma \gamma_l \rangle | \Gamma \gamma_k \rangle \langle \Gamma \gamma_l |. \tag{13}$$

Pooler has given the formal theory underlying the construction of molecular JT Hamiltonians with continuous symmetries, i.e. invariant under the action of a Lie group [15, 16]. First, it was shown that the space of electronic tensor operators living in $\Gamma \otimes \Gamma$ can be decomposed into even and odd subspaces, which we will denote by $\mathcal{M}$ and $\mathcal{P}$, respectively. The operators in $\mathcal{M}$ belong to the symmetric part of $\Gamma \otimes \Gamma - A_1$ (where A_1 is the totally symmetric irrep) if the system is spinless (we discuss the fermionic case later). The odd live in the antisymmetric. Therefore, $\mathcal{P}$ is a Lie subalgebra of $\Gamma \otimes \Gamma - A_1$ (since the commutator of antisymmetric matrices is antisymmetric). Conversely, the commutator of even operators is an odd element, so the latter do not span a Lie algebra. For example, in $E \otimes e\mathcal{M}$ is spanned by the Pauli matrices σ_1 and σ_3, while σ_2 is the generator of $\mathcal{P}$.

$\mathcal{P}$ generates the $|\Gamma|$-dimensional special orthogonal group, SO($|\Gamma|$). If $\mathcal{M}$ is isomorphic to an irrep $\overline{\Lambda}$ of SO($|\Gamma|$), then $H(\mathbf{Q},\mathbf{P})$ is invariant under the action of the same group on both electronic and nuclear degrees of freedom, if and only if the vibrational configuration space can also be embedded in (i.e. transforms like) the irrep $\overline{\Lambda}$ of SO($|\Gamma|$) [16]. In $E \otimes e$, σ_2 generates SO(2), as the elements of the latter can be written as $U(\phi) = \mathrm{e}^{-\mathrm{i}\phi\sigma_2/2}$. Conjugation of σ_1 and σ_3 with $U(\phi)$ shows that $\mathcal{M}$ transforms in the vector irrep of SO(2), and so do the JT coordinates Q_1 and Q_2 (see equations (2)–(6)). Hence, linear $E \otimes e$ shows vibronic SO(2) invariance.

In other words, sufficient conditions for invariance under continuous transformations of electronic and vibrational degrees of freedom in JT models are that: (a) only linear vibronic couplings are non-vanishing, and (b) the space of traceless electronic Hamiltonians and the vibrational configuration space are isomorphic as irreps of a Lie group G.

The above conditions require that the electronic multiplet Γ is equally coupled to every JT active mode, while $m_{\Lambda_i} = m$ and $\omega_{\Lambda_i} = \omega_\Lambda$ for all $\Lambda_i \subset \Lambda$. Physically, they imply equal JT stabilization energies for molecular distortions along each Λ_i, and (pseudo)rotational symmetry in the purely vibrational part of $H(\mathbf{Q},\mathbf{P})$, respectively.

The embeddings of the vibrational and electronic point group irreps $\Lambda = \oplus \lambda_i$ and Γ into Lie group irreps will not be subject of future discussion. The interested reader may consult [15, 16, 49] for details. Henceforth, we take the conditions for continuous invariance of JT Hamiltonians to be fulfilled and study its consequences. For the sake of simplicity, we will not make a distinction between the continuous and point group

irreps anymore, so that from now on Λ and Γ correspond to the appropriate continuous group irreps of SO(N) or USp($2N$) (in the fermionic case discussed below) depending on the total spin of the considered electronic JT multiplet.

The relations satisfied by the $\mathcal{H}_{\rm el}$ operators in $\mathcal{P}$ and $\mathcal{M}$ can be summarized by

$$[\mathcal{M},\mathcal{M}]=\mathcal{P},\ [\mathcal{P},\mathcal{M}]=\mathcal{M},\ [\mathcal{P},\mathcal{P}]=\mathcal{P}. \tag{14}$$

They imply that $\mathcal{L}=\mathcal{M}\oplus\mathcal{P}$ is a Lie algebra [41]. In other words, $\mathcal{L}$ corresponds to the tangent space of a Lie group L at the (group) identity. The odd operators define a subalgebra $\mathcal{P}$. They generate the Lie subgroup $P\subset L$. Importantly, the electronic matrices in $\mathcal{M}$ define tangent vectors for the *symmetric space L/P* [39–41]. In fact, the algebraic definition of symmetric spaces is encapsulated by the relations shown in equation (14). Some of their relevant properties will be discussed below.

Time-reversal symmetry implies the existence of a basis where the electronic Hamiltonian matrix elements are *real*. Thus, only the electronic tensor operators of $\mathcal{L}\subset sl(|\Gamma|,\mathbb{R})$ (the space of traceless real matrices) which are in the symmetric part of $\Gamma\otimes\Gamma-A_1$ lead to allowed quantum Hamiltonians. Hence, $H_{\rm JT}(\mathbf{Q})$ belongs to $\mathcal{M}=\mathcal{L}/\mathcal{P}$. Moreover, the *antisymmetric* electronic tensor operators generate the special orthogonal group SO($|\Gamma|$). Its generators define the Lie algebra $so(|\Gamma|)$: the space of infinitesimal rotations of $\mathcal{H}_{\rm el}$. Thus, $so(|\Gamma|)$ acts on the electronic Hilbert space operator $H_{\rm JT}(\mathbf{Q})$ by infinitesimal rotations. As we show below, while the defined $so(N)$ action occurs on $\mathcal{H}_{\rm el}$, it is equivalent to infinitesimal rotation of the internal displacements $\mathbf{Q}\rightarrow\mathbf{Q}+\delta\mathbf{Q}$ in JT models with continuous symmetries.

In the spinless case, $\mathcal{M}\oplus\mathcal{P}$ spans either (a) $sl(|\Gamma|,\mathbb{R})$ (see below for the $T^2=-1$ case), or (b) one of its proper subsets [15]. Examples of class (a) are the Lie group invariant formulations of $E\otimes e$ [11], $T\otimes(e\oplus t_2)$ [50], $T\otimes h$ [51], $G\otimes(g\oplus h)$ [35], $H\otimes(g\oplus 2h)$ [36, 49, 52]. These include JT active distortions representing *all* independent ways to split the electronic degeneracy at $\mathbf{Q}=0$. In these models, the continuous symmetry is *maximal*, since the symmetry of the molecular Hamiltonian cannot be increased without changing the number of dimensions of $\mathcal{H}_{\rm el}$. Conversely, class (b) contains $H\otimes h$ [36, 51], $H\otimes(g\oplus h)$ [36], etc [15]. Their vibronic coupling matrices only span a proper subset of $sl(N,\mathbb{R})/so(N,\mathbb{R})$, and the molecular Hamiltonian symmetry can be increased by including the remaining symmetry-allowed independent JT active couplings. Thus, the latter models do not include one or more of the possible JT active distortions. In this paper we focus on the JT models with maximal continuous symmetries (see table 1), for they share a variety of deeply related properties. Thus, from now on, anytime we mention JT models carrying a Lie group action, it should be understood that we are referring to models in class (a), unless otherwise noted.

The electronic Hamiltonian can only be constructed with the even tensor operators $V_\alpha\in\mathcal{M}$. Therefore, the constraints given above imply the most general JT Hamiltonian for a $\Gamma\otimes\Lambda$ system with a continuous symmetry can be written as:

$$H(\mathbf{Q},\mathbf{P})=\frac{\mathbf{P}_\Lambda^2}{2m}+\frac{1}{2}k_\Lambda\mathbf{Q}_\Lambda^2+F_\Lambda\sum_{\alpha\in\mathcal{M}}Q_\alpha V_\alpha, \tag{15}$$

Table 1. JT models with continuous symmetries investigated in this paper. The last column gives examples of discrete symmetry groups from which each model may be obtained by imposing the appropriate constraints [55]. S* refers to the double group obtained from a point group S.

JT model	T^2	Symmetric Space	Examples
$E\otimes e$ [11]	1	SU(2)/SO(2)	C_{3v}, O_h
$T\otimes(e\oplus t_2)$ [50]	1	SU(3)/SO(3)	Td, O_h, I, I_h
$G\otimes(g\oplus h)$ [35]	1	SU(4)/SO(4)	I,I_h
$H\otimes(g\oplus 2h)$ [36]	1	SU(5)/SO(5)	I,I_h
$\Gamma_8(G_{3/2})\otimes(e\oplus t_2)$ [30]	−1	SU(4)/USp(4)	Td^*, O_h^*, I_h^*
$\Gamma_9(I_{5/2})\otimes(g\oplus 2h)$ [38]	−1	SU(6)/USp(6)	I^*, I_h^*

where $k_\Lambda=m\omega_\Lambda^2$. Note the matrices $V_\alpha\subset\mathcal{M}$ and the $so(|\Gamma|)$ generators are both real and traceless, so their direct sum is the algebra $sl(|\Gamma|,\mathbb{R})$, i.e. $\mathcal{L}=sl(|\Gamma|,\mathbb{R})$. As a consequence, the underlying symmetric spaces for the spinless class of JT Hamiltonians with continuous symmetries is SL($|\Gamma|,\mathbb{R}$)/SO($|\Gamma|$) (or SU($|\Gamma|$)/SO($|\Gamma|$) if we take the skew-hermitian $\mathcal{H}_{\rm el}$ time-evolution generators iV_α as the generators of the symmetric space).

A fundamental property of symmetric spaces is their *rank* [39, 41]: the number of *anisotropic* spatial directions on these manifolds. Physically, the rank of a given JT model is equal to the number of linearly independent JT active nuclear distortions unrelated by SO($|\Gamma|$) (or USp($|\Gamma|$) in the fermionic case) transformations on electronic or vibrational degrees of freedom. In other words, motion along anisotropic directions induces changes in the eigenvalues of the electronic Hamiltonian. For instance, in $E\otimes e$ only geometries with the same radial coordinate Q are related by nuclear pseudorotation (figure 4). Therefore, in the space of time-evolution operators of $E\otimes e$, there exists a single direction which is anisotropic. This conforms with the fact that the rank of SU(2)/SO(2) is one [39, 41].

Another view on the rank of a symmetric space is that it specifies the dimensionality of its maximal abelian (commutative) subalgebra (also commonly denoted as *Cartan subalgebra*) $\mathcal{C}$ [39]. By a theorem of symmetric spaces theory, any $\mathfrak{m}\in\mathcal{L}/\mathcal{P}$ is related to an element $\mathfrak{m}_C$ of the Cartan subalgebra $\mathcal{C}$ by conjugation with an element of the Lie group P (with tangent space $\mathcal{P}$ at the identity of P) [39],

$$\mathfrak{m}=g\mathfrak{m}_C g^{-1}, g\in P, \mathfrak{m}_C\in\mathcal{C}. \tag{16}$$

The rank of the symmetric space SL($|\Gamma|,\mathbb{R}$)/SO($|\Gamma|$) (or SU($|\Gamma|$)/SO($|\Gamma|$)), is equal to $|\Gamma|-1$ [41].

We can always take the Cartan subalgebra of $sl(|\Gamma|,\mathbb{R}|)/so(|\Gamma|)$ to be given by $|\Gamma|-1$ linearly independent traceless diagonal matrices of $sl(|\Gamma|,\mathbb{R})$ [41]. In this case, equation (16) is the simple statement that any real traceless symmetric matrix $\mathfrak{m}$ can be diagonalized by an orthogonal transformation. We note that conjugation preserves commutation relations, so the choice of Cartan subalgebra is not unique. Thus, a set of diagonal matrices may be the simplest, but it is not the only.

It follows that the electronic part of the molecular Hamiltonian (equation (15)) can be rewritten as

$$H_{\mathrm{JT}}(\mathbf{Q}) = F_\Lambda \sum_{\alpha\in\mathcal{M}} Q_\alpha V_\alpha = U(\mathbf{Q}) \left(F_\Lambda \sum_{\alpha_C\in\mathcal{M}_C} Q_{\alpha_C} V_{\alpha_C} \right) U^{-1}(\mathbf{Q}),$$
$$U(\mathbf{Q}) \in \mathrm{SO}(|\Gamma|), \tag{17}$$

where $\mathcal{M}_C \subset \mathcal{M}$ is a choice of Cartan subalgebra for $\mathcal{M} \equiv sl(|\Gamma|,\mathbb{R})/so(|\Gamma|)$. By the invariance of $H(\mathbf{Q},\mathbf{P})$ under simultaneous SO($|\Gamma|$) action on electronic and vibrational degrees of freedom, there exists an embedding of SO($|\Gamma|$) in SO($|\Lambda|$) [since proper rotations (orthogonal transformations with determinant equal to one) of the vibrational configuration space are described by the latter group]. Hence, there is a continuous injective map, $R:\ \mathrm{SO}(|\Gamma|) \to \mathrm{SO}(|\Lambda|)$ satisfying

$$\sum_{\alpha_C\in\mathcal{M}_C} U(\mathbf{Q}) Q_{\alpha_C} V_{\alpha_C} U^{-1}(\mathbf{Q}) = \sum_\alpha [R^{-1}(\beta)\mathbf{Q}_C]_\alpha V_\alpha, \tag{18}$$

where β denotes an SO($|\Lambda|$) point, $R(\beta)$ specifies the SO($|\Lambda|$) rotation satisfying $R^{-1}(\beta)\mathbf{Q}_C = \mathbf{Q}$, and $\mathbf{Q}_C$ is the nuclear displacement with nonvanishing components only along the directions which are dual to the Cartan subalgebra matrices V_{α_C}. Equation (18) is the mathematical representation of the statement that in JT models with continuous symmetries, *a rotation of the electronic frame is equivalent to a rotation of the space of JT distorted structures*. It is the generalization of equation (6) for N-dimensional electronic Hilbert spaces.

In cases where spin–orbit coupling is strong and time-reversal symmetry is implemented by T satisfying $T^2 = -1$, the JT active modes live in the *antisymmetric* part of the $\Gamma \otimes \Gamma - A_1$ space, where Γ is now a spinorial double group irrep [2, 53]. The electronic Hilbert space for a fixed geometry can thus be given the structure of a quaternionic vector space [54]. The unitary transformations which preserve this structure form the unitary symplectic group $\mathrm{U}(|\Gamma|/2,\mathbb{H}) \cong \mathrm{USp}(|\Gamma|)$ [41]. In this case, the molecular Hamiltonian is invariant under the simultaneous action of the symplectic group on the electronic and nuclear degrees of freedom whenever the *symmetric* part of $\Gamma \otimes \Gamma$ generates the $usp(|\Gamma|)$ algebra, the traceless antisymmetric part lives in $su^*(|\Gamma|)/usp(|\Gamma|)$ ($su^*(|\Gamma|) \cong sl(|\Gamma|/2,\mathbb{H})$ is the space of traceless $|\Gamma| \times |\Gamma|$ complex matrices invariant under conjugation by an antiunitary operator T satisfying $T^2 = -1$, or simply the space of traceless $|\Gamma|/2 \times |\Gamma|/2$ matrices with quaternionic entries [41]), and the vibrational degrees of freedom transform in the same irrep of USp($|\Gamma|$) as the traceless antisymmetric electronic tensor operators [15, 16]. Therefore, in cases with strong spin–orbit coupling, the underlying symmetric spaces for JT models carrying a Lie group action consist of SU*($|\Gamma|$)/USp($|\Gamma|$) (or SU($|\Gamma|$)/USp($|\Gamma|$), if instead of taking the Hamiltonians as generators, we consider the corresponding time-evolution generators iH). A list of all JT models carrying a Lie group action encompassed by this study is given in table 1, along with their corresponding symmetric spaces, and examples of point groups giving rise to these models.

3. Local and global structure of JT orbits

We now take advantage of the framework introduced in the previous section to quickly obtain insight into the APESs of JT models carrying a Lie group action. As we show in section 4, the results which we present here also have some significance for the treatment of dynamics in the neighborhood of electronic degeneracies of generic molecular systems beyond JT models. Therefore, they display a degree of universality which is perhaps unanticipated in view of the non-generic constraints satisfied by the continuous symmetries of the investigated models.

3.1. Symmetry-adapted coordinates and orbit spaces

Consider first the problem of choosing coordinates for vibrational motion, which are adapted to the invariance properties of the underlying symmetric space. These have various advantages compared to cartesian coordinate systems, since they reduce the complexity of molecular potential energy surfaces (e.g. figure 4). For instance, in $E \otimes e$ [10, 11] and $T \otimes h$ [56, 57], the identification of radial and angular coordinates introduces significant simplification to treatments of the dynamical JT problem. They are also useful in describing the warped ground-state APES [18].

As we showed in section 1, coordinates adapted to the circular symmetry of the SO(2) $E \otimes e$ model can be trivially obtained. However, this is not the case for higher-dimensional models with $\mathrm{SO}(N), N > 2$ or USp($2N$) symmetries. The situation is ameliorated if only the space of minima of the JT APES is of interest, for the ground-state APES is homemorphic with the real (if $T^2 = 1$ [18]) or quaternionic (when $T^2 = -1$) projective space (see sections 3.2.2 and 3.2.3). The real projective space ($\mathbb{R}P^N$) can be obtained from the sphere S^N by identifying antipodal points of the latter [58]. Therefore, hyperspherical coordinates are a natural choice for the study of vibrational motion on the spinless ground-state trough [35, 36] of the continuously-symmetric JT models. While profitable in discerning properties of the space of minima of the electronic ground-state APES, this approach gives no insight into the motion which is normal to the extremal subspace of the APES, nor does it explain the spectral flow of the Born–Oppenheimer JT Hamiltonian in non-stationary regions of the molecular vibrational configuration space. Thus, hyperspherical coordinates do not take full advantage of the invariance properties of the systems studied here to maximally simplify the description of the molecular APES.

We will employ the isomorphism between traceless electronic Hamiltonian operators and vibrational displacements as irreps of a Lie group G, to choose vibrational coordinates adapted to the corresponding SO(N) (or USp($2N$)) action. Consider first the specific case of the cubic JT problem $T_1 \otimes (e \oplus t_2)$ [50], or equivalently the icosahedral $T \otimes h$ (the generalization to more complex models will be made later) [49]. The continuous symmetry of this system in the presence of degenerate couplings was originally investigated by O'Brien [50, 59]. The JT active displacements are characterized by

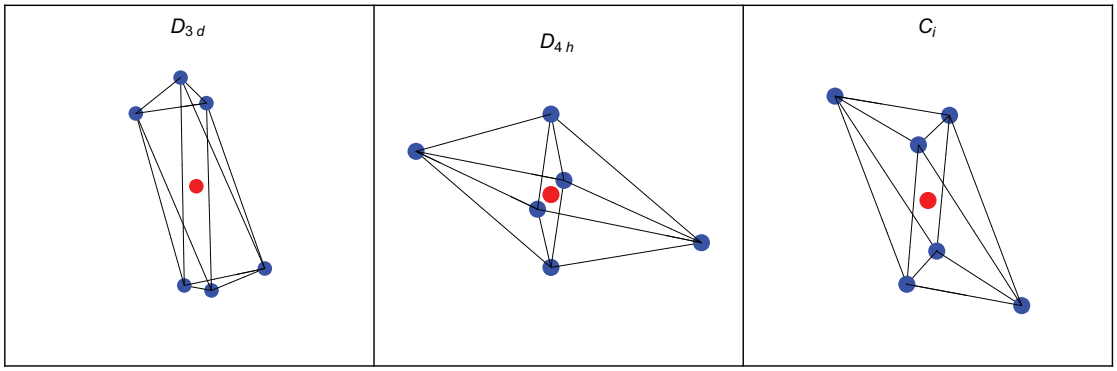

Figure 6. D_{3d}, D_{4h} epikernel and C_i kernel structures for the $T_1 \otimes (e_g \oplus t_{2g})$ JT model. The first two have the same spectrum (in the presence of SO(3) symmetry) including a non-degenerate electronic ground-state and a doubly-degenerate excited state, while the latter is a lower symmetry structure with the same $r_1(\mathbf{Q})$ as the first two, but different $r_2(\mathbf{Q})$, reflecting the presence of three non-degenerate electronic states in its spectrum.

the vector $\mathbf{Q} = (Q_\theta, Q_\epsilon, Q_{xy}, Q_{zx}, Q_{yz})$ [3]. A global diabatic basis for $\mathcal{H}_{\rm el}$ is defined by $\mathcal{H}_{\rm el} = {\rm span}\{|x\rangle, |y\rangle, |z\rangle\}$ (which may be thought of as p_x, p_y and p_z atomic orbitals). The traceless Hermitian electronic tensor operators are in the symmetric part of $T_1 \otimes T_1 - A_1$ and will be labeled by V_α, $\alpha \in \{\theta, \epsilon, xy, zx, yz\}$,

$$V_\theta = \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix}, V_\epsilon = \begin{pmatrix} -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$(V_{ij})_{ab} = -\frac{\sqrt{3}}{2}\left(\delta_{ia}\delta_{jb} + \delta_{ja}\delta_{ib}\right), \tag{19}$$

where $i,j \in \{x,y,z\}$, $i \neq j$, $\delta_{ab} = 1$ if $a = b$ and 0 otherwise.

The JT active distortions and the space of electronic Hamiltonians are isomorphic to the space of quadrupoles [54] (the **2** irrep of SO(3)), which is also isomorphic to the tangent space of $\mathrm{SL}(3,\mathbb{R})/\mathrm{SO}(3)$ at the identity, i.e. $sl(3,\mathbb{R})/so(3)$. Its Cartan subalgebra is two-dimensional. It may be taken to be for example, ${\rm span}\{V_\epsilon, V_\theta\}$ or alternatively ${\rm span}\{V_\theta, V_{xy}\}$. Importantly, this implies there exists two SO(3) invariants in the universal enveloping algebra of $sl(3,\mathbb{R})/so(3,\mathbb{R})$ [39]. From the SO(3)-equivalence between symmetric electronic tensor operators (minus the identity) and vibrational displacements, it follows that there exists also two functions $r_1(\mathbf{Q})$ and $r_2(\mathbf{Q})$ of the nuclear degrees of freedom which are invariant under the action of SO(3). They will be denoted *radial coordinates*. Let r_1 denote the quadratic SO(3) invariant of $sl(3,\mathbb{R})/so(3)$, $r_1(\mathbf{Q}) = |\mathbf{Q}|^2 = Q$, and $r_2(\mathbf{Q})$ be the cubic. The latter may be obtained from the secular determinant of $H_{\rm JT}(\mathbf{Q})$ [39], or as the totally symmetric SO(3) irrep **0** in the decomposition of the tensor product $\mathbf{2} \otimes \mathbf{2} \otimes \mathbf{2}$, since the cubic invariant is a homogeneous polynomial of third degree in the vibrational coordinates (which transform like the **2** irrep of SO(3)) [33]. We provide a simple derivation of $r_2(\mathbf{Q})$ below.

This simple analysis indicates that each molecular geometry of $T \otimes (e \oplus t_2)$ belongs to a single SO(3) orbit characterized by two radial coordinates, r_1 and r_2 (compare to the $E \otimes e$ case which has orbits described by a single real number (figure 4, equations (9) and (10))). We denote a specific orbit of this model by $O(r_1, r_2)$. It only includes molecular geometries with the same electronic spectrum, since r_1 and r_2 are SO(3) invariants (no electronic SO(3) rotation will correspond to nuclear motion normal to $O(r_1, r_2)$). It follows that given a representative $\mathbf{Q} \in O(r_1, r_2)$, any element $\mathbf{Q}' \in O(r_1, r_2)$ may be obtained by an SO(3) action on $\mathbf{Q}$, this rotation in turn corresponding to the electronic Hilbert space SO(3) transformation $U(\mathbf{Q}', \mathbf{Q})$ satisfying $U(\mathbf{Q}, \mathbf{Q}')H_{\rm JT}(\mathbf{Q})U^{-1}(\mathbf{Q}, \mathbf{Q}') = H_{\rm JT}(\mathbf{Q}')$. Thus, the 5-dimensional APES of $T \otimes (e \oplus t_2)$ may be reduced into a 2-dimensional orbit space.

The remaining three vibrational degrees of freedom are expected to parametrize the internal space of the orbits $O(r_1, r_2)$. Thus, SO(3)-adapted coordinates for the molecular displacements are given by $\mathbf{Q} = \mathbf{Q}(r_1, r_2, \beta, \alpha, \phi)$, $\forall\ r_1 \in \mathbb{R} - \{0\}, r_2 \in [-1, 1]$ (see below), where (β, α, ϕ) parametrize SO(3) rotations. They can be understood as Euler angles in the space of JT active distorted structures [33, 60]. We employ the *zyz* convention for the parametrization of SO(3) elements,

$$U(\beta, \alpha, \phi) = \mathrm{e}^{-\mathrm{i}\phi J_z}\mathrm{e}^{-\mathrm{i}\alpha J_y}\mathrm{e}^{-\mathrm{i}\beta J_z}, \tag{20}$$

where $U(\beta, \alpha, \phi)$ acts on the **1** (vector) irrep of SO(3), the J_i are its Hermitian generators, $(J_i)_{jk} = \mathrm{i}\epsilon_{ijk}$, $\phi, \beta \in [0, 2\pi)$, and $\alpha \in [0, \pi]$.

In order to understand the internal space of each orbit, note that the JT distortion-induced electronic multiplet splitting can only happen in two different ways: either $H_{\rm JT}(\mathbf{Q})$ (with $\mathbf{Q} \neq 0$) has three distinct eigenvalues or two degenerate and a single non-degenerate. The matrices representing the vibronic coupling due to t_2 or e displacements demonstrate this point (equation (19)). $H_{\rm JT}(\mathbf{Q})$ is related by an orthogonal transformation to an element of the Cartan subalgebra of $sl(3,\mathbb{R})/so(3)$ (section 2). In particular, if we choose V_θ and V_ϵ to be a basis for the Cartan subalgebra, we find from equation (17),

$$H_{\rm JT}(\mathbf{Q}) = F_v U(\beta, \alpha, \phi)\left(Q_c^\epsilon V_\epsilon + Q_c^\theta V_\theta\right)U^{-1}(\beta, \alpha, \phi), \tag{21}$$

$$H_{\rm JT}(\mathbf{Q}) = -F_v|\mathbf{Q}|U(\beta, \alpha, \phi) \times \begin{pmatrix} \cos[\gamma(\mathbf{Q}_c) - \frac{2\pi}{3}] & 0 & 0 \\ 0 & \cos[\gamma(\mathbf{Q}_c) + \frac{2\pi}{3}] & 0 \\ 0 & 0 & \cos[\gamma(\mathbf{Q}_c)] \end{pmatrix} U^{-1}(\beta, \alpha, \phi), \tag{22}$$

where F_v denotes the vibronic coupling constant, $\mathbf{Q}_c = (Q_c^\theta, Q_c^\epsilon, 0, 0, 0)$ defines an element of the Cartan subalgebra of $sl(3,\mathbb{R})/so(3)$ specifying the eigenvalues of the JT Hamiltonian for a given geometry $\mathbf{Q} = R^{-1}\mathbf{Q}_c, R \in \mathrm{SO}(3)$, and $\gamma(\mathbf{Q}) = \tan^{-1}(Q_c^\epsilon/Q_c^\theta)$. These considerations drastically simplify the task of finding the coordinate mapping $\mathbf{Q} \mapsto r_2(\mathbf{Q})$ (the cubic invariant of $sl(3,\mathbb{R})/so(3)$). It is proportional to the $O(\lambda^3)$ term of $\det[H_{\mathrm{JT}}(\mathbf{Q}) - I\lambda]$ [39], which may now be easily calculated from equation (22),

$$r_2(\mathbf{Q}) = \cos[3\gamma(\mathbf{Q}_c)]. \tag{23}$$

For any $\mathbf{Q}$, $H_{\mathrm{JT}}(\mathbf{Q})$ is related by an orthogonal transformation to a *unique* $H_{\mathrm{JT}}(\mathbf{Q}_c)$ with $\gamma \in [0, \pi/3]$ [54], so $r_2 \in [-1, 1]$.

According to the above, motion along the $\mathbf{Q}_\theta$ and $\mathbf{Q}_\epsilon$ directions provides all distinct possibilities for the splitting of the electronic multiplet when $Q \neq 0$. This may also be seen by checking that the eigenvalues of V_{ij} are equal to those of V_ϵ, which in turn are different from those of V_θ. The orbit obtained by SO(3) action on V_θ defines a 2D subspace of the vibrational configuration space, since $[J_z, V_\theta] = 0$. In more detail, suppose $\mathbf{Q} = Q\mathbf{e}_\theta = (Q, 0, 0, 0, 0)$. Then, $\mathbf{Q}_c = \mathbf{Q}$, and

$$U(0,0,\phi)QV_\theta U^{-1}(0,0,\phi) = QV_\theta. \tag{24}$$

electronically degenerate doublet iff $\gamma = 0$ or $\gamma = \pi/3$, i.e. for $r_2 = \pm 1$. For any other values of $\gamma \in [0, \pi/3]$, the corresponding electronic JT Hamiltonian belongs to a 3D orbit of SO(3).

Our analysis also reveals the topology of each type of orbit. The 2D orbits are parametrized by a 3D rotation axis. Thus, each 2D orbit is isomorphic to $\mathbb{R}P^2$. The 3D orbits are copies of SO(3)/V $\cong \mathbb{R}P^3/V$ [58], where $V = \{U(0,0,0), U(0,0,\pi), U(0,\pi,0)\, U(\pi/2,\pi,\pi/2)\}$. The latter follows from the fact that all elements of V are diagonal matrices, and both V_ε and V_θ are left invariant under conjugation by an element of the subgroup V. Therefore, electronic Hilbert space transformations by elements of V correspond to trivial action on the vibrational configuration space.

The qualitative analysis carried to this point indicates the APES of the SO(3)-invariant $T \otimes (e \oplus t_2)$ can be decomposed into a 2D orbit space. Only two topologically non-equivalent types of orbits exist in agreement with the two linearly independent ways of lifting the degeneracy of triply-degenerate electronic states.

By applying equations (19)–(21) to (22), we obtain the SO(3)-adapted parametrization of JT distortions [50], $\mathbf{Q} = \mathbf{Q}(Q, \gamma, \beta, \alpha, \phi)$,

$$\begin{aligned}
Q_\epsilon &= Q\left[\frac{\sqrt{3}}{2}\cos(\gamma)\cos(2\phi)\sin^2(\alpha) + \frac{1}{2}\sin(\gamma)[[1+\cos^2(\alpha)]\cos(2\phi)\cos(2\beta) - \cos(\alpha)\sin(2\beta)\sin(2\phi)]\right]\\
Q_\theta &= Q\left[\frac{1}{2}\cos(\gamma)(\cos^2(\theta)-1) + \frac{\sqrt{3}}{2}\sin(\gamma)\sin^2(\alpha)\cos(2\beta)\right]\\
Q_{xy} &= Q\left[\frac{\sqrt{3}}{2}\cos(\gamma)\sin^2(\alpha)\sin(2\phi) + \frac{1}{2}\sin(\gamma)[(1+\cos^2\alpha)\sin(2\phi)\cos(2\beta) + 2\cos(\alpha)\cos(2\phi)\sin(2\beta)]\right]\\
Q_{zx} &= Q\left[\frac{\sqrt{3}}{2}\cos(\gamma)\sin(2\alpha)\cos(\phi) + \frac{1}{2}\sin(\gamma)[-\sin(2\alpha)\cos(2\beta)\cos(\phi) + \sin(\alpha)\sin(2\beta)\sin(\phi)]\right]\\
Q_{yz} &= Q\left[\frac{\sqrt{3}}{2}\cos(\gamma)\sin(2\alpha)\sin(\phi) + \frac{1}{2}\sin(\gamma)[-\sin(\alpha)\sin(2\phi)\sin(2\beta) - \sin(2\alpha)\sin(\phi)\cos(2\beta)]\right].
\end{aligned} \tag{25}$$

This equation implies the space of molecular geometries obtained by pseudorotation of the structure defined by $\mathbf{Q} = Q\mathbf{e}_\theta$ is specified by only two of the three SO(3) parameters. In fact, the elements of the orbits containing $Q\mathbf{e}_\theta$ or $-Q\mathbf{e}_\theta$, can be parametrized uniquely by a 3D rotation axis $\mathbf{n} = \mathbf{n}(\phi, \alpha) = \mathbf{n}(\pi + \phi, \pi - \alpha)$ (see equation (20)). Conversely, rotations of the non-degenerate Cartan subalgebra basis vector V_ϵ give a 3D subspace. If we take $r_1(\mathbf{Q}) = |\mathbf{Q}|^2 = 1$, the corresponding SO(3) orbit will be either two or three-dimensional depending on the value of $r_2(\mathbf{Q})$. For instance, while $\mathbf{Q} = \mathbf{e}_\theta$ lives in a 2D orbit, $\mathbf{e}_\epsilon = (0, 1, 0, 0, 0)$ belongs to a 3D. Note $r_2(\pm\mathbf{e}_\theta) = \pm 1$, while $r_2(\mathbf{e}_\epsilon) = 0$. In fact, the $T \otimes (e \oplus t_2)$ JT Hamiltonian contains an adiabatic

This parametrization was first given (in the context of JT models) by O'Brien [59]. It is also of paramount importance for studies of the fullerene $T \otimes h$ JT model [49, 56, 57]. The derivation above gives a simple systematic method for its construction, which can be applied to the other, more complex JT systems with continuous symmetries (see below).

The coordinate transformations described by equation (25) allow a quick visualization of some of the features of the two types of orbits we discussed: when $\gamma = 0$, it follows that for a given $|\mathbf{Q}|$, the geometry described by the displacement vector $\mathbf{Q}$ depends only on the pseudoangular variables α and ϕ, which thus characterize each 2D orbit. Pseudorotational motion in the 3D orbits (where $\gamma \neq 0$ or $\pi/3$) is specified by

the Euler angles β, α, ϕ. The classification of the vibrational configuration space given above is particularly useful when investigating the possible Berry phases of fullerene derivatives and other molecules which undergo JT distortion described by the SO(3) multiplet. [56, 57].

The considerations in this subsection can be generalized to the other JT models carrying a Lie group action (see table 1), including the fermionic cases with strong spin–orbit coupling (in the following, simply make the replacements $sl(n,\mathbb{R}) \to sl(n,\mathbb{H}) \cong su^*(2n,\mathbb{C})$, and $so(n) \to usp(2n)$ and all results will remain valid for the fermionic models). Given that the maximal commuting subalgebra of $sl(n,\mathbb{R})/so(n)$ is $n-1$-dimensional [41] (section 2), there exists a set of $n-1$ anisotropic directions (motion along which does not preserve the energy of the electronic states) in the corresponding JT APES. Thus, these displacements fully determine the electronic spectrum. In, particular, we can define $n-1$ radial coordinates $\{r_i(\mathbf{Q})\}$ which change the electronic energies in an independent way. In the $T \otimes (e \oplus t_2)$ the adiabatic electronic energies are only function of the two radial coordinates $r_1(\mathbf{Q}) = Q$ and $r_2(\mathbf{Q})$ (equation (23)). Motion along the former direction simply introduces a multiplicative factor to the spectrum (similarly to the radial coordinate of $E \otimes e$), while a change in $r_2(\mathbf{Q})$ may take the system from a geometry where the excited electronic states are doubly-degenerate to a JT distortion which does not have electronic degeneracies The values taken by the radial displacements $r_1, r_2, ..., r_{n-1}$ specify SO(N) orbits labeled by $O(r_1, ..., r_{n-1})$. Thus, the orbit space of an SO(N)-invariant model contains $n-1$ dimensions. Each orbit in this space corresponds to one of a finite number of types. The possibilities are determined by the degeneracies of the electronic Hamiltonian. As shown explicitly for the $T \otimes (e \oplus t_2)$ case, different orbits may have internal spaces with varying number of degrees of freedom. While the adiabatic electronic spectrum is completely specified by the radial displacements, a complete description of the molecular geometry requires specification of angular coordinates corresponding to the pseudorotational motion on each orbit. These can be parametrized by SO(n) variables (e.g. we used Euler angles in the SO(3) case). In the case of the icosahedral $G \otimes (g \oplus h)$ case (relevant to the investigation of fullerene excited-states as well as silicon and boron ion clusters [35, 49, 61, 62]), the symmetric space is SU(4)/SO(4). It has 3 radial and 6 angular coordinates which can be constructed from the set of JT active vibrations $g \oplus h$. SU(5)/SO(5) arises in the $H \otimes (g \oplus 2h)$ model, which includes four radial and ten angular coordinates. In all cases, the radial degrees of freedom can be directly obtained by looking at the coefficients of the invariant polynomials produced by the JT Hamiltonian secular determinant, $\det[H_{\mathrm{JT}}(\mathbf{Q}) - \mathrm{I}\lambda]$. Angular displacements adapted to a simple description of pseudorotation can be retrieved by a generalization of the procedure carried for $T_1 \otimes (e \oplus t_2)$. For example, in the case of $G \otimes (g \oplus h)$, a molecular geometry with non-degenerate electronic spectrum will be characterized by *at most* two sets of Euler angles, as $so(4) \cong so(3) \oplus so(3)$ [41].

In summary, we explored the invariant properties of JT models carrying a continuous group action to obtain symmetry-adapted coordinates, which fully take advantage of the high-symmetry of these systems. As we have shown, these coordinates are directly related to the decomposition of the JT active vibrational motion into pseudorotational and radial. Pseudorotation preserves the adiabatic electronic spectrum, while radial motion nontrivially modifies the latter. Therefore, the APES can be reduced into an orbit space, where each point (orbit) corresponds to a set of JT distortions with equal electronic spectrum. Motion on the internal space of an orbit is generated by pseudoangular momentum which is conserved for the models discussed here. Nonetheless, weak symmetry-breaking effects (see section 3.4) can be treated readily with perturbation theory. Thus, this analysis provides significant simplification of the dynamical JT problem, as the orbit space has a much smaller number of degrees of freedom than the vibrational configuration space.

3.2. APES troughs and higher-energy orbits

In this subsection, we explore further properties of JT models to classify their troughs and higher-energy orbits according to the qualitatively distinct splittings of the corresponding adiabatic electronic multiplets. In section 3.2.1, we show that the orbit corresponding to the space of electronic ground-state minima of all JT models with maximal continuous symmetries satisfy a simple condition, where the electronic ground-state is non-degenerate, but all other excited-states have equal energy. This result is utilized in section 3.2.2, where we prove that the ground-state trough of each spinless (fermionic) JT model with continuous symmetries is topologically equivalent to a real (quaternionic) projective space. Such equivalence is fundamental for the discussion of the Berry phase in section 3.3. We also provide comments on the properties of higher-energy orbits in section 3.2.3.

3.2.1. Ground-state trough for JT models with maximal continuous symmetries. Here we generalize an argument of O'Brien [50] to show that for spinless JT models with maximal continuous symmetries, the equilibrium molecular geometries live in the SO(N) orbit $\mathcal{O}$ with adiabatic electronic spectrum given by

$$\mathrm{spec}\left[\hat{H}_{\mathrm{JT}}(\mathbf{Q})\right] = \{x(Q), x(Q), ..., -(N-1)x(Q)\}, \quad \mathbf{Q} \in \mathcal{O}, x(Q) > 0. \tag{26}$$

where N is the dimensionality of the system's electronic Hilbert space.

Suppose the vibrational states live in the Λ irrep of a point group S, and let the adiabatic electronic ground-state and its corresponding JT APES be denoted by $|\psi_0(\mathbf{Q})\rangle$ and $V^{(0)}(\mathbf{Q})$, respectively. The latter has contributions from the JT stabilization energy $E_{\mathrm{JT}}^{(0)}(\mathbf{Q})$ and the harmonic potential energy $k_\Lambda \mathbf{Q}^2/2$, i.e.

$$V^{(0)}(\mathbf{Q}) = E_{\mathrm{JT}}^{(0)}(\mathbf{Q}) + \frac{1}{2}k_\Lambda \mathbf{Q}^2, \tag{27}$$

where $E_{\rm JT}^{(0)}(\mathbf{Q}) = \inf \hat{H}_{\rm JT}(\mathbf{Q})$. Equilibrium molecular geometries $\mathbf{Q}_0$ satisfy

$$\left(\nabla_{\mathbf{Q}} V^{(0)}\right)(\mathbf{Q}_0) = 0,$$
$$\sum_{i,j} \delta Q_{\Lambda i}\delta Q_{\Lambda j}\left(\nabla_{Q_{\Lambda i}}\nabla_{Q_{\Lambda j}} V^{(0)}\right)(\mathbf{Q}_0) > 0, \quad (28)$$

where $\delta Q_{\Lambda i} = (\mathbf{Q} - \mathbf{Q}_0)_{\Lambda i}$. Using equation (27), the first condition can be restated as

$$\frac{\partial E_{\rm JT}^{(0)}}{\partial Q_{\Lambda\lambda}}(\mathbf{Q})\bigg|_{\mathbf{Q}=\mathbf{Q}_0} = -k_\Lambda (Q_0)_{\Lambda\lambda},\ \forall\ \lambda \in \{1,2,...,|\Lambda|\}. \quad (29)$$

By the continuous symmetry assumption there is a continuous set of solutions to the above when $\mathbf{Q} \neq 0$, all of which are related by rotation of the vibrational displacements via an SO(N) action on $\mathbb{R}^{|\Lambda|}$.

Let a basis for linearly independent traceless symmetric electronic tensor operators be denoted by $M_{\Lambda\lambda}$. Then, $\hat{H}_{\rm JT}(\mathbf{Q})$ can be expressed by

$$\hat{H}_{\rm JT}(\mathbf{Q}) = F_\Lambda \sum_{\lambda=1}^{|\Lambda|} M_{\Lambda\lambda} Q_{\Lambda\lambda}. \quad (30)$$

The presence of SO(N) symmetry implies the existence of a choice of electronic states and vibrational coordinates such that, $N-1$ of the matrices $M_{\Lambda\lambda}$ are diagonal (which may be taken as the Cartan subalgebra discussed in sections 2 and 3), while the rest are symmetric with only two non-vanishing (off-diagonal) elements [63]. A general element of the former and latter sets will be called D_λ and O_λ, respectively. The diagonal matrices can be parametrized in the following manner [63]:

$$D_1 = \{1,-1,0,...,0\}, D_2 = \frac{1}{\sqrt{3}}\{1,1,-2,0,...0\},...,$$
$$D_{N-1} = \sqrt{\frac{2}{N(N-1)}}\{1,1,...,-N+1\}, \quad (31)$$

where each set contains the entries of the corresponding diagonal matrix. We take the entries of the O_Λ to be equal to -1. For instance, the matrices of equation (19) can be put in exactly this form by the mapping $V_\Lambda \mapsto (2/\sqrt{3})V_\Lambda$. We expect D_{N-1} to dictate the splitting of the JT degeneracy at the electronic ground-state minima, since a molecular distortion along the direction corresponding to D_{N-1} maximally stabilizes the electronic ground-state at the expense of destabilization of all higher-energy states. In fact, this insight agrees with Liehr's *minimax* conjecture [64, 65], which was later generalized and denoted *epikernel principle* by Ceulemans [18, 66, 67]. This states that the extrema of the JT ground-state APES are likely to be encountered in regions of the vibrational configuration space which preserve a large subgroup of the symmetry group at $\mathbf{Q} = 0$. The maximal subgroup of SO(N) is SO($N-1$). The latter is indeed preserved under a molecular distortion along the displacement $\mathbf{Q}_{N-1}$ corresponding to the JT splitting defined by D_{N-1}. To see this, note that D_{N-1} has $N-1$ degenerate eigenvalues. Hence, it is invariant with respect to SO$(N-1)\otimes 1$ transformations acting non-trivially only on the degenerate electronic subspace.

Let $M_{\Lambda N-1} = D_{N-1}$, and consider the ground-state JT APES at $\mathbf{Q} = \mathbf{Q}_{N-1} \equiv Q(0,0,...,1)$,

$$V^{(0)}(\mathbf{Q}_{N-1}) = -F_\Lambda\sqrt{\frac{2(N-1)}{N}}Q + \frac{1}{2}k_\Lambda Q^2. \quad (32)$$

The condition for $\mathbf{Q}_{N-1}$ to be an extremum of $V^{(0)}$ is satisfied by

$$Q = \frac{F_\Lambda}{k_\Lambda}\sqrt{\frac{2(N-1)}{N}},$$
$$V^{(0)}(\mathbf{Q}_{N-1}) = -\frac{F_\Lambda^2}{k_\Lambda}\frac{N-1}{N},$$
$$V^{(i)}(\mathbf{Q}_{N-1}) = \frac{F_\Lambda^2}{k_\Lambda}\frac{N+1}{N}, i \in \{1,2,...,N-1\}, \quad (33)$$

where $V^{(i)}(\mathbf{Q}_{N-1})$ is the generalization of equation (27) to the degenerate set of excited-states at $\mathbf{Q}_{N-1}$. We will use second-order perturbation theory to study the behavior of the JT ground-state APES in a neighborhood of $\mathbf{Q}_{N-1}$ with radius $|\delta\mathbf{Q}| = \epsilon \to 0^+$ [50]. The 0th-order distorted APES is defined by

$$H_0(\mathbf{Q}_{N-1} + \delta\mathbf{Q}) = H_{\rm JT}(\mathbf{Q}_{N-1}) + \frac{1}{2}k_\Lambda\left(\mathbf{Q}_{N-1} + \delta\mathbf{Q}\right)^2, \quad (34)$$

while the vibronic perturbation due to infinitesimal motion $\delta\mathbf{Q}$ can be written as:

$$H'(\delta\mathbf{Q}) = F_\Lambda \sum_\lambda \delta Q_{\Lambda\lambda} M_{\Lambda\lambda}. \quad (35)$$

Thus, to second-order in perturbation theory the electronic ground-state APES is given by:

$$V^{(0)}(\mathbf{Q}_{N-1} + \delta\mathbf{Q}) = V^{(0)}(\mathbf{Q}_{N-1}) + k_\Lambda \mathbf{Q}_{N-1}\cdot\delta\mathbf{Q} + \frac{1}{2}k_\Lambda(\delta\mathbf{Q})^2 + F_\Lambda\sum_{\lambda=1}^{|\Lambda|}[M_{\Lambda\lambda}]_{NN}\delta Q_{\Lambda\lambda} + \sum_{\lambda=1}^{|\Lambda|}\sum_{i=1}^{N-1}\frac{F_\Lambda^2\,[M_{\Lambda\lambda}]_{iN}^2}{V^{(0)}(\mathbf{Q}_{N-1}) - V^{(i)}(\mathbf{Q}_{N-1})}\delta Q_{\Lambda\lambda}^2. \quad (36)$$

The above can be simplified by using equation (33) to obtain the relation $V^{(0)}(\mathbf{Q}_{N-1}) - V^{(i)}(\mathbf{Q}_{N-1}) = -2F_\Lambda^2/k_\Lambda$, and equation (31) for $[M_{\Lambda\lambda}]_{NN}$, whence

$$\delta V^{(0)}(\mathbf{Q}_{N-1}) = k_\Lambda Q\delta Q_{\Lambda|\Lambda|} + \frac{1}{2}k_\Lambda(\delta\mathbf{Q})^2 - F_\Lambda\sqrt{\frac{2(N-1)}{N}}\delta Q_{\Lambda|\Lambda|} - k_\Lambda\sum_{\lambda=1}^{|\Lambda|}\sum_{i=1}^{N-1}\frac{[M_{\Lambda\lambda}]_{iN}^2}{2}\delta Q_{\Lambda\lambda}^2, \quad (37)$$

where $\delta V^{(0)}(\mathbf{Q}_{N-1}) = V^{(0)}(\mathbf{Q}_{N-1} + \delta\mathbf{Q}) - V^{(0)}(\mathbf{Q}_{N-1})$. As expected, the first and third terms cancel so that the ground-state JT APES is given by

$$\delta V^{(0)}(\mathbf{Q}_{N-1}) = \frac{k_\Lambda}{2}\sum_{\lambda=1}^{|\Lambda|}\left[1 - \sum_{i=1}^{N-1}[M_{\Lambda\lambda}]_{iN}^2\right]\delta Q_{\Lambda\lambda}^2. \quad (38)$$

Among the $|\Lambda|$ independent JT distortions, only those with electronic coupling matrix $M_{\Lambda\lambda}$ containing off-diagonal elements $[M]_{iN} = -1$ contribute to the second sum of the above equation. There exists $N-1$ such symmetric matrices. Their contributions to $\delta V^{(0)}(\mathbf{Q}_{N-1})$ will be cancelled by the first term of equation (38). Let $M_{\Lambda a}$ denote a matrix in the subset of the symmetric electronic tensor operators $M_{\Lambda\lambda}$ which includes all diagonal matrices D_a (equation (31)) *and* the symmetric matrices O_Λ with vanishing iN entry. Then, it follows that

$$\delta V^{(0)}(\mathbf{Q}_{N-1}) = \sum_a \frac{1}{2} k_\Lambda \delta Q_{\Lambda a}^2. \tag{39}$$

Hence, we find that the SO(N) orbit $\mathcal{O}$ (equation (26)) defines a continuous set of absolute minima for the ground-state JT APES. This derivation corroborates the intuition that the displacement $\mathbf{Q}_{N-1}$ provides maximal stabilization of the electronic ground-state, while simultaneously giving a *proof* of the epikernel principle for vibronic models with continuous symmetries. Additional discussion of the latter is given in sections 3.2.3 and 3.4.

3.2.2. Topological equivalence between ground-state troughs and projective spaces. In this section, we utilize the result obtained in the previous to demonstrate the topological equivalence (homeomorphism) between the space of minima of the ground-state APES of JT models with continuous symmetries and the space of rays (lines) of real (for a spinless JT model) or quaternionic (in cases where spin–orbit coupling is strong) finite Hilbert spaces. The equivalence in the bosonic case has been previously pointed by Ceulemans [18]. In any case, we provide a derivation for both bosonic and fermionic cases, as the latter result is a simple generalization of the former. Basically, we will show that the there exists a bijective relationship between the set of physically inequivalent electronic wave functions (Kramers doublets), i.e. unrelated by multiplication by a phase (Kramers pair rotation) in the spinless (fermionic) case, and the space of molecular geometries which are minima of the electronic JT APES. Topological equivalence follows from the bijection and continuity of the maps between the electronic states (doublets) and the minimal-energy molecular geometries.

To emphasize the remarkable physical content of the statement we are about to prove, we shall paraphrase the claim. It ascertains that an arbitrary electronic wave function (Kramers pair) is guaranteed to be the electronic (Kramers) ground state at a specific molecular geometry in the minimum energy trough. Conversely, any molecular geometry in this trough is associated with a unique ground-state electronic wave function (Kramers doublet), up to a phase (SU(2) rotation). Notably, even when all possible electronic wave functions are sampled along the trough, they correspond to the same electronic energy.

Bosonic troughs. In accordance with the JT theorem, the adiabatic electronic ground-state of a molecular JT model is non-degenerate. As explained in the last sections, a continuous set $\mathcal{O}$ of global minima of the APES is guaranteed to exist in the presence of SO(N) symmetry. In particular, if $\mathbf{Q}_0 \in \mathcal{O}$, then for any $\mathbf{Q}$ in $\mathcal{O}$, there exists $T(\mathbf{Q}, \mathbf{Q}_0) \in \mathrm{SO}(N)$, such that

$$\mathbf{Q} = T(\mathbf{Q}, \mathbf{Q}_0)\mathbf{Q}_0. \tag{40}$$

In what follows, it will be important that at the space of ground-state minima $\mathcal{O}$, the electronic spectrum is assumed to be of the form derived in the previous section. The most obvious implication of this spectrum is that the electronic Hamiltonian is invariant under unitary transformations of the electronic Hilbert space that act non-trivially only on the subspace spanned by the degenerate excited states. In particular, if $|\psi_0(\mathbf{Q})\rangle$ (with $\mathbf{Q} \in \mathcal{O}$) denotes the non-degenerate electronic ground-state, and $U|\psi_0(\mathbf{Q})\rangle = \pm|\psi_0(\mathbf{Q})\rangle$, then $U \in \mathbb{Z}_2 \times O(N-1) \subset O(N)$, and $UH_{\mathrm{JT}}(\mathbf{Q})U^{-1} = H_{\mathrm{JT}}(\mathbf{Q})$. The last equation implies that the rotation of the vibrational configuration space which corresponds to U is the identity (see section 2 and equations (17) and (18)).

We again follow the convention that the Hilbert space vectors corresponding to the adiabatic electronic ground-state at $\mathbf{Q} \neq 0$ are written as *real* linear combinations of (the diabatic) electronic basis functions defined at the JT center, $\{|\psi_1\rangle, |\psi_2\rangle, ...|\psi_N\rangle\}$. Thus, a normalized electronic ground-state wave function at $\mathbf{Q}_0 \in \mathcal{O}$ can be expressed as

$$|\psi_0(\mathbf{Q}_0)\rangle = \sum_{i=1}^{N} c_{i0}(\mathbf{Q}_0)|\psi_i\rangle, c_{i0}(\mathbf{Q}_0) \in \mathbb{R},$$
$$\sum_{i=1}^{N} c_{i0}^2(\mathbf{Q}_0) = 1. \tag{41}$$

Thus, there exists a mapping of the ground-state trough to the $N-1$-dimensional sphere, $\mathbf{Q}_0 \mapsto \mathbf{c}_0(\mathbf{Q}_0) \in S^{N-1}$. However, the electronic ground-state wave function at $\mathbf{Q}_0 \in \mathcal{O}$ is only defined modulo a sign. In particular, if $|\psi_0(\mathbf{Q}_0)\rangle$ denotes a normalized eigenfunction of $H_{\mathrm{JT}}(\mathbf{Q}_0)$ with lowest eigenvalue, then so is $-|\psi_0(\mathbf{Q}_0)\rangle$. Thus, the mapping $\mathcal{O} \to S^{N-1}$ is only well-defined locally (alternatively, it may be said to be *double-valued*). However, the electronic ground-state at $\mathbf{Q}_0$ can be defined unambiguously as a rank-one projection operator $|\psi_0(\mathbf{Q}_0)\rangle\langle\psi_0(\mathbf{Q}_0)| \in \mathbb{R}P^{N-1}$. Hence, there exists a well-defined continuous function mapping the ground-state trough to the real projective space, $\Phi: \mathcal{O} \to \mathbb{R}P^{N-1}$, such that

$$\Phi(\mathbf{Q}_0) = |\psi_0(\mathbf{Q}_0)\rangle\langle\psi_0(\mathbf{Q}_0)|. \tag{42}$$

Suppose $\mathbf{Q} = T^{-1}\mathbf{Q}_0, T \in \mathrm{SO}(N)$, and let $U(T)$ denote a representative unitary transformation (e.g. $U(T)$ may be the orthogonal transformation with $\det[U(T)] = 1$) carrying the adiabatic ground-state at $\mathbf{Q}_0$ to that at $\mathbf{Q} \neq \mathbf{Q}_0$,

$$U(T)|\psi_0(\mathbf{Q}_0)\rangle = |\psi_0(T^{-1}\mathbf{Q}_0)\rangle. \tag{43}$$

The map Φ satisfies the following equivariance condition

$$\Phi(T^{-1}\mathbf{Q}_0) = U(T)\Phi(\mathbf{Q}_0)U^{-1}(T). \tag{44}$$

Thus, Φ is a continuous equivariant map of the electronic ground-state trough to $\mathbb{R}P^{N-1}$. Φ is also bijective. To show that it is injective, we assume $\Phi(\mathbf{Q}_0) = \Phi(\mathbf{Q}_1), \mathbf{Q}_0, \mathbf{Q}_1 \in \mathcal{O}$, and note that there exists $T \in \mathrm{SO}(N)$, such that $\mathbf{Q}_1 = T^{-1}\mathbf{Q}_0$,

since $\mathbf{Q}_0$ and $\mathbf{Q}_1$ belong to the ground-state trough (and thus must be related by an SO(N) transformation). It follows that

$$\Phi(\mathbf{Q}_0) = \Phi(T^{-1}\mathbf{Q}_0), \tag{45}$$

$$|\psi_0(\mathbf{Q}_0)\rangle\langle\psi_0(\mathbf{Q}_0)| = U(T)\left(|\psi_0(\mathbf{Q}_0)\rangle\langle\psi_0(\mathbf{Q}_0)|\right)U^{-1}(T). \tag{46}$$

The last equation is only satisfied if $U(T)|\psi_0(\mathbf{Q}_0)\rangle = \pm|\psi_0(\mathbf{Q}_0)\rangle$, so $U(T)$ acts non-trivially only on the degenerate orthogonal subspace to the line spanned by $|\psi_0(\mathbf{Q}_0)\rangle$. In this case, it follows from the discussion below equation (40) that $U(T)H_{\rm JT}(\mathbf{Q}_0)U^{-1}(T) = H_{\rm JT}(T^{-1}\mathbf{Q}_0) = H_{\rm JT}(\mathbf{Q}_0)$. Thus, T^{-1} acts as the identity matrix on the vibrational configuration space and $\mathbf{Q}_1 = \mathbf{Q}_0$. For the proof that Φ is surjective, let $p \in \mathbb{R}P^{N-1}$. There exists a neighborhood of p, $U_p \subset \mathbb{R}P^{N-1}$, on which a continuous section $\phi:\ U_p \to U_p \times S^{N-1}$ may be defined by

$$\phi(p) = |p\rangle_+ = \sum_{i=1}^{N} c_i(p)|\psi_i\rangle. \tag{47}$$

Let $\mathbf{Q}_0$ be the configuration in the electronic ground-state trough for which $H_{\rm JT}$ is diagonal (i.e. $\mathbf{Q}_0$ only has a non-vanishing component in the direction along which $H_{\rm JT}(\mathbf{Q}_0)$ is diagonal (in the diabatic basis)). Then, there exists a lift of $\Phi(\mathbf{Q}_0)$, denoted by $|\psi_0(\mathbf{Q}_0)\rangle$, and an SO($N$) transformation $U(T_p)$ such that

$$|p\rangle_+ = U(T_p)|\psi_0(\mathbf{Q}_0)\rangle = |\psi_0(T_p^{-1}\mathbf{Q}_0)\rangle, \tag{48}$$

where T_p is the SO(N) rotation of the vibrational configuration space corresponding to $U(T)$. This follows from the continuous symmetry conditions, as is verified by

$$\begin{aligned} H_{\rm JT}(T_p^{-1}\mathbf{Q}_0)|p\rangle_+ &= H_{\rm JT}(T_p^{-1}\mathbf{Q}_0)U(T_p)|\psi_0(\mathbf{Q}_0)\rangle \\ &= \left[U(T_p)H(\mathbf{Q}_0)U^{-1}(T_p)\right]U(T_p)|\psi_0(\mathbf{Q}_0)\rangle \\ &= E_0(\mathbf{Q}_0)|p\rangle_+, \end{aligned} \tag{49}$$

where we used equation (17). Hence, Φ is shown to be a bijective continuous map between compact manifolds (i.e. between the electronic real projective space and the vibrational configuration space trough). Therefore, it is a homeomorphism [68].

Fermionic troughs. In fermionic systems, Kramers degeneracy implies the JT distorted electronic ground-state is a doublet $|\Psi_0(\mathbf{Q}_0)\rangle \equiv \{|\psi_0(\mathbf{Q}_0)\rangle, T|\psi_0(\mathbf{Q}_0)\rangle\}$ [2]. Each normalized Kramers pair is only defined modulo multiplication by a unit quaternion $||q|| = 1$ (or equivalently, an SU(2) action) from the right (by convention) [53, 69]. Given a definition of N degenerate Kramers pairs $|\Psi_i\rangle$ at the JT center, the ground-state doublet at $\mathbf{Q} \neq 0$ may be written as

$$|\Psi_0(\mathbf{Q})\rangle = \sum_{m=1}^{N} |\Psi_m\rangle \cdot q_{0m}(\mathbf{Q}), q_{0m}(\mathbf{Q}) \in \mathbb{H}, \tag{50}$$

where $q_{0m}(\mathbf{Q}) = \sum_{j=1}^{3} q_{0mj}(-\mathrm{i}\sigma_j) + q_{0m4}\sigma_0$ is a quaternion (with imaginary units $-\mathrm{i}\sigma_i$ and 2×2 identity matrix σ_0 representing the real generator) [54, 69]. If we require $|\Psi_0(\mathbf{Q})\rangle$ to be normalized, then

$$\langle\Psi_0(\mathbf{Q})|\Psi_0(\mathbf{Q})\rangle = \sum_{m=1}^{N} ||q_{0m}(\mathbf{Q})||^2 = 1, \tag{51}$$

where $||q||^2 = \det(q^\dagger q) = q_0^2 + q_1^2 + q_2^2 + q_3^2$ is the quaternion norm. It follows that each normalized $|\Psi_0(\mathbf{Q})\rangle$ may also be viewed as a point on the sphere S^{4N-1}.

Let $\mathbf{Q}_0$ belong to the ground-state trough $\mathcal{O}$. Corresponding to it there is an infinite number of equivalent ground-state Kramers pairs related by unit quaternion multiplication, $\{|\Psi_0(\mathbf{Q}_0)\rangle \cdot q\}$. The space of equivalence classes (lines)

$$\{[\Psi] \sim [\Psi'] \text{ if } \Psi' = \Psi \cdot q | \Psi, \Psi' \in \mathbb{H}^N, q \in \mathbb{H}^* \equiv \mathbb{H} - 0\} \tag{52}$$

of $\mathbb{H}^N$ defines the quaternionic projective space $\mathbb{H}P^{N-1} \cong \mathbb{H}^N/\mathbb{H}^*$ [69]. A non-degenerate ground-state (in the quaternionic sense) for all $\mathbf{Q} \in \mathcal{O}$, implies that there exists a well-defined map Φ between the adiabatic trough $\mathcal{O}$ and $\mathbb{H}P^{N-1}$. It may be explicitly given as

$$\begin{aligned} \Phi:\ \mathcal{O} &\to \mathbb{H}P^{N-1}, \\ \Phi(\mathbf{Q}_0) &= |\Psi_0(\mathbf{Q}_0)\rangle\langle\Psi_0(\mathbf{Q}_0)|. \end{aligned} \tag{53}$$

This map is well-defined, since the projection operator is invariant under a redefinition of the basis, i.e. a gauge transformation, $|\Psi\rangle \mapsto |\Psi\rangle \cdot q$, with $q \in \mathbb{H}, ||q||^2 = 1$, as $|\Psi\rangle\langle\Psi| \to (|\Psi\rangle \cdot q)\left(q^\dagger \cdot \langle\Psi|\right) = |\Psi\rangle||q||^2\langle\Psi| = |\Psi\rangle\langle\Psi|$. Moreover, the assumed continuous invariance under USp($2N$) implies Φ satisfies an equivariance condition analogous to that discussed in the bosonic case,

$$\Phi(T^{-1}\mathbf{Q}_0) = U(T)\Phi(\mathbf{Q}_0)U^\dagger(T), \tag{54}$$

except now $U(T)$ belongs to USp($2N$). Φ can be shown to be bijective as in subsection (a). By compactness of $\mathcal{O}$ and $\mathbb{H}P^{N-1}$, Φ is a homeomorphism; this implies topological equivalence between the Kramers ground-state trough and $\mathbb{H}\mathrm{P}^{N-1}$.

We conclude this subsection by noting that the proved equivalence between projective spaces and the space of minima of JT systems with continuous symmetries implies a non-trivial topological phase for the electronic ground-state of these models (see section 3.3 and [70]). The Berry phase of JT models is robust with respect to moderate symmetry-breaking perturbations, and has observable consequences (see e.g. [13]). Thus, the Lie group condition invariance is not strictly required for the low-energy electronic APES to have the projective character proved above.

3.2.3. Generic orbits. The prior subsections provided a detailed description of the electronic ground-state equilibrium orbit of JT models carrying a maximal Lie group action. Here we will utilize the continuous symmetry property of the studied models to obtain qualitative properties of their higher-energy orbits.

Let us consider first the spinless TRI case. The equivalence between rotations of the vibrational configuration space and special orthogonal transformations of the electronic basis implies the dimensionality of the space of JT distorted structures with a given adiabatic electronic spectrum is equal to or

smaller than the dimensionality of SO(N), $N = |\Gamma|$. It may be smaller because there may be matrices in SO(N) which commute with $H_{\rm JT}(\mathbf{Q})$, in which case their action on the electronic Hamiltonian is equivalent to the identity matrix action on the vibrational configuration space, whence it follows that the nuclear configuration of the system remains invariant (equation (17)).

The subspace of $so(N)$ containing all matrices commuting with $H_{\rm JT}(\mathbf{Q})$ is called the *centralizer* of $H_{\rm JT}(\mathbf{Q})$. We denote it by $\mathcal{N}(\mathbf{Q})$,

$$\mathcal{N}(\mathbf{Q}) = \{M \in so(N) | [M, H_{\rm JT}(\mathbf{Q})] = 0\}. \tag{55}$$

It can be checked that $\mathcal{N}(\mathbf{Q})$ is a Lie subalgebra of $so(N)$ by applying the Jacobi identity,

$$[H_{\rm JT}, [N_1, N_2]] = -[N_2, [H_{\rm JT}, N_1]] - [N_1, [N_2, H_{\rm JT}]] = 0, \quad \forall\, N_1, N_2 \in \mathcal{N}. \tag{56}$$

Let $|\mathcal{N}(\mathbf{Q})|$ denote the dimensionality of $\mathcal{N}(\mathbf{Q})$. Then, the number of linearly independent JT distortions with the same adiabatic electronic spectrum $\{E(\mathbf{Q})\}$, which we denote by $|E(\mathbf{Q})|$, is given by

$$|E(\mathbf{Q})| = |so(N)| - |\mathcal{N}(\mathbf{Q})|. \tag{57}$$

Thus, the dimensionality of the space of molecular configurations with a given set of electronic energies depends on the number of degenerate eigenstates in the JT Hamiltonian when $\mathbf{Q} \neq 0$. This happens because a basis of $so(N)$ can always be constructed from antisymmetric matrices with only two non-vanishing entries [41], so that a diagonal matrix commutes with a basis vector of $so(N)$ iff the diagonal matrix elements which multiply the non-vanishing elements of the antisymmetric $so(N)$ matrices are equal.

As a simple example, we now apply equation (57) to obtain the number of dimensions of the ground-state troughs of JT models with continuous symmetries. It is instructive to rederive this result, for the same method can be easily adapted to infer the properties of higher-energy orbits. But, first, we need the dimensionality of the centralizer of $\mathbf{Q}$ at the trough, i.e. $|\mathcal{N}(\mathbf{Q})|$. It may be quickly obtained by making an assumption on the electronic spectrum at extremal regions of the JT APES, based on the epikernel principle [18, 66]. According to this, the stationary points of the ground-state APES are likely to be encountered in configuration space regions where the symmetry breaking of the molecular geometry is minimal. In the presence of the Lie group action discussed in this paper, this principle can be understood by considering the following. $\mathbf{Q} = 0$ corresponds to a maximally symmetric molecular structure. All corresponding electronic eigenvalues are equal. For any $\mathbf{Q} \neq 0$, the non-totally symmetric character of JT distortions implies the sum of the electronic eigenvalues $\lambda_i(\mathbf{Q})$ remains zero, i.e.

$$\sum_{i=1}^{N} \lambda_i(\mathbf{Q}) = 0. \tag{58}$$

A variety of possibilities exist for the splitting of the eigenvalues when $\mathbf{Q} \neq 0$, i.e. for the number of distinct degenerate multiplets which persist when the molecule undergoing JT effect is distorted along a given direction. We say that the molecular symmetry at $\mathbf{Q} = 0$ is minimally broken at $\mathbf{Q}_1$ if $\lambda_i(\mathbf{Q}) = x$, $\forall\, i \in \{1, 2, ..., N-1\}, x > 0$ and $\lambda_N(\mathbf{Q}) = -(N-1)x$. This case is typical for the stationary points of JT systems with continuous symmetries [30, 35, 49, 50]. It implies maximal stabilization of the adiabatic electronic ground-state, since all excited-states have their energy increased relative to the degenerate multiplet energy at $\mathbf{Q} = 0$ (we proved in see section 3.2.1 that the global minima of the JT models discussed here indeed satisfy this condition).

Based on the prior discussion, we now assume that for a minimal energy configuration $\mathbf{Q}_0$ of the JT system with continuous symmetry, only the lowest electronic energy eigenvalue is non-degenerate. The remaining $N-1$ are degenerate electronic excited states. Hence, a basis for $\mathcal{N}(\mathbf{Q}_0)$ consists of all matrices in $so(N)$ which mix the $N-1$ degenerate excited states at $\mathbf{Q}$ among themselves, but leave the electronic ground-state invariant. This corresponds to the number of ways of arranging $(N-1)$ distinct indices $i \in \{1, 2..., N-1\}$ into pairs ij with $i \neq j$, i.e. $(N-1)(N-2)/2$. Hence, the dimensionality of the SO(N)-invariant adiabatic electronic ground-state trough is equal to

$$|E(\mathbf{Q}_0)| = \frac{N(N-1)}{2} - \frac{(N-1)(N-2)}{2} = N-1, \tag{59}$$

which, of course, agrees with the arguments of section 3.2.1. To make a connection with the topological equivalence between electronic ground state troughs and real projective space proved in section 3.2.2, note that this result may be written equivalently as:

$$|E(\mathbf{Q}_0)| = |\mathrm{SO}(N)/\mathrm{SO}(N-1)| = |S^{N-1}| = |\mathbb{R}P^{N-1}|. \tag{60}$$

The properties of higher-energy orbits can also be obtained with relative ease. The $T \otimes (e \oplus t_2)$ model with SO(3) invariance provides again a transparent example. Recall that this system has a two-dimensional orbit space, with each point labeled by $O(r_1, r_2)$ (section 3.1), where $O(r_1, r_2)$ is a continuous subspace of the $t_2 \oplus e$ vibrational configuration space where the ground and excited-state JT APESs are flat. For a given $r_1(\mathbf{Q}) = |\mathbf{Q}|^2 \neq 0$ the epikernel principle favors the minimal energy trough to be the 2D orbit $O(Q, 1)$ by the following argument: the adiabatic electronic spectra for geometries in $O(Q, 1)$ is given by

$$\mathrm{spec}[H(O(Q,1))] = \{x, x, -2x\}, \quad x = x(Q) > 0, Q \in O(Q,1) \tag{61}$$

while in $O(Q, r_2 \neq \pm 1)$ the JT Hamiltonian eigenvalues are

$$\mathrm{spec}[H(O(Q,r_2))] = \{x', y', -x' - y'\}, \quad x' = x'(Q,r_2) > 0,\ x' > y' = y'(Q,r_2), r_2 \neq \pm 1. \tag{62}$$

Because y' is intermediate between the lowest and maximal eigenvalues, its stabilization relative to the highest-energy eigenvalue of the spectrum at $O(Q, 1)$ comes at the cost of an increased electronic ground-state energy (see equation (22)). Hence, the ground-state trough is $O(Q_0,1)$, where $Q_0 = Q_0(\omega, F_v)$ minimizes the ground-state energy [3, 50]. In section 3.1 we showed that $|O(Q_0,1)| = 2$ in accordance with application of equation (59). Note that because permutation of the eigenvalues can be effected by an SO(3) rotation, the

assumptions made regarding the order of the eigenvalues do not imply loss of generality.

For any other model and type of degeneracy splitting of $H_{\rm JT}(\mathbf{Q})$, we can apply the same methods and obtain the dimensionality and topology of the subspaces of the JT distorted structures with equal adiabatic electronic spectrum. For instance, while from previous arguments the orbit of the SO(5)-invariant model of $H \otimes (g \oplus 2h)$ with lowest ground-state energy is clearly 4D, different types of orbits (with higher electronic ground-state energies) exist with distinct dimensionalities in other parts of the configuration space, e.g. molecular geometries with a non-degenerate ground-state and two degenerate doublets [36] live in 8D orbits according to

$$|E(\mathbf{Q})| = \left|\frac{\mathrm{SO}(5)}{\mathrm{SO}(2)\times\mathrm{SO}(2)}\right| = 10-(1+1) = 8, \quad (63)$$

where we have used the fact that SO(2) is one-dimensional, and that each degenerate doublet defines an invariant electronic SO(2) subgroup of SO(5), which in turn corresponds to pseudorotational motion in a 2D plane of the vibrational configuration space as explained in sections 2 and 3. Note that it follows from equation (57) that the maximal dimension of an orbit is equal to the dimensionality of SO(N). This happens when $|\mathcal{N}(\mathbf{Q})| = 0$, i.e. in those orbits where all eigenvalues of $H_{\rm JT}(\mathbf{Q})$ are non-degenerate (see section 3.1 for the explicit verification in the case of the SO(3)-invariant $T \otimes (e \oplus t_2)$ model).

The above approach can be quickly adapted to models with strong spin–orbit coupling. The main difference is that the corresponding molecular Hamiltonians are globally invariant under the action of the unitary symplectic group USp($2N$) on spinorial and vibrational degrees of freedom. Further, independent USp(2) $\cong$ SU(2) actions on each Kramers pair commute with the Hamiltonian (since they amount to a change of basis in a Kramers pair subspace). It follows that the number of dimensions of the ground-state trough of each spinorial JT model is given by:

$$|E(\mathbf{Q}_0)| = \left|\frac{\mathrm{USp}(2N)}{\mathrm{USp}(2N-2)\times\mathrm{USp}(2)}\right|$$
$$|E(\mathbf{Q}_0)| = N(2N+1)-(N-1)(2N-1)-3 = 4(N-1), \quad (64)$$

where we used that USp($2N$) is $N(2N+1)$-dimensional [41]. As expected, this result is in agreement with previous literature on the $\Gamma_8 \otimes (e \oplus t_2)$ ($N = 2$) [30] and $\Gamma_9 \otimes (g \oplus 2h)$ ($N = 3$) [71] JT problems. The dimensionality of fermionic ground-state troughs bears a simple relationship to the spinless cases (see equation (59)). It is a consequence of the quaternionic structure of the former. As seen in section 3.2.2, while the spinless trough is topologically equivalent to a real projective space [18], fermionic time-reversal symmetry implies topological equivalence of the Kramer's trough to the *quaternionic projective space* $\mathbb{H}\mathrm{P}^{N-1}$ [69], the space of lines of $\mathbb{H}^N$.

In the case of the icosahedral $\Gamma_9 \otimes (g \oplus 2h)$, another possibility for the JT splitting is given by choosing $\mathbf{Q}$ such that all three Kramers' pairs are non-degenerate. Then, the orbit space of the USp(6) action is 12-dimensional since it can be parametrized by $\mathrm{USp}(6)/\mathrm{USp}(2)\times\mathrm{USp}(2)\times\mathrm{USp}(2)$. Here we find an interesting parallel between $\Gamma_9 \otimes (g \oplus 2h)$ and $T \otimes (e \oplus t_2)$: in both cases the orbit space is two-dimensional. The ground-state trough belongs to a 2D orbit in $T \otimes (e \oplus t_2)$, while it lives on an 8D orbit in the case of $\Gamma_9 \otimes (g \oplus 2h)$ (section 3.2). Except for a set of measure zero, higher-energy orbits of $T \otimes (e \oplus t_2)$ and $\Gamma_9 \otimes (g \oplus 2h)$ are 3D and 12D, respectively. Thus, the number of dimensions of the orbits of $\Gamma_9 \otimes (g \oplus 2h)$ is always a factor of 4 larger than those of $T \otimes (e \oplus t_2)$, which generalizes equation (64).

3.3. Geometric phase and ground-state degeneracy

The occurrence of the geometric phase [72] in JT and related models has a long history [3, 11, 19, 20, 50, 52, 56, 73–77]. It is highly relevant in the strong vibronic coupling limit, where $F_\Lambda^2/(2k_\Lambda) \gg 1$ and the adiabatic limit for the electronic ground-state nuclear dynamics is a very good approximation. In particular, it provides an unambiguous explanation for the non-generic feature (in finite physical systems) of vibronic ground-state degeneracy in some JT models [3, 49]. In this section, we discuss the Berry phases of JT models carrying a Lie group action.

The abelian Berry phase [72] characterizes the twisting of a family of 1D complex vector spaces parametrized by a configuration space C, i.e. a line bundle. It can be computed in a variety of ways [72, 74, 78]. The most significant aspect to our discussion is that for time-reversal invariant bosonic systems, the adiabatic geometric phase belongs to $O(1) = \mathbb{Z}/2\mathbb{Z} = \{+1, -1\}$. This is a consequence of the existence of a real structure in the complex Hilbert line bundle when $T^2 = 1$. In other words, a real locally continuous choice of eigenstates of a parameter-dependent Hamiltonian may be constructed for each point of the parameter space, so only ± 1 Berry phases are allowed.

In the case of fermionic systems Kramers' degeneracy implies the existence of pairs of degenerate states. A normalized pair is only defined modulo an SU(2) transformation, or equivalently, quaternion multiplication [54, 69]. As a result, the geometric phase of the ground-state of a gapped fermionic system is a (non-abelian) unit quaternion (or SU(2) matrix in the complex representation) [54, 69, 79].

JT models carrying a Lie group action are particularly susceptible to having relevant Berry phase effects. This happens because, as described in the previous subsections, the vibrational configuration space can be decomposed into topologically non-trivial orbits O_G of a Lie group G, which may admit twisted families of electronic Hilbert spaces, due to the existence of level crossing at the JT center.

3.3.1. Bosonic models. For spinless systems, the electronic ground-state of $\hat{H}_{\rm JT}(\mathbf{Q})$, with $\mathbf{Q} \neq 0$, is non-degenerate in the minimal-energy JT trough. It is homeomorphic to the space of lines in the N-dimensional real vector space, the real projective space $\mathbb{R}P^{N-1}$ (see section 3.2.2). The sphere S^{N-1} is a double cover of $\mathbb{R}P^{N-1}$, i.e. $\mathbb{R}P^{N-1} \cong S^{N-1}/\mathbb{Z}_2$. Therefore, if $N > 2$, $\mathbb{R}P^{N-1}$ has two equivalence classes of loops,

as $\pi_1(\mathbb{R}P^{N-1}) = \mathbb{Z}_2$ ($\mathbb{R}P^1$ is isomorphic to S^1, which has its loop classes distinguished by an integer, the winding number, so $\pi_1(S^1) = \mathbb{Z}$) [58]. The identity is given by the class of closed curves on S^{N-1} (as it is simply-connected when $N > 2$). Conversely, the non-trivial element of $\pi_1(\mathbb{R}P^{N-1})$ can be represented by an open continuous curve on S^{N-1} connecting antipodal points (these correspond to the same element in $\mathbb{R}P^{N-1}$). The product of two non-trivial (odd) loops (defined by performing each loop after the other [68]) gives a trivial one, but a trivial (even) path followed by a non-trivial is equivalent to the latter. Loops in the even class do not give a Berry phase for any quantum state since they can be continuously deformed into the identity path, which obviously, has no Berry phase. Conversely, the odd loops of $\mathbb{R}P^{N-1}$ *may* give rise to a nontrivial geometric phase for a non-degenerate adiabatic electronic state. In particular, this will happen if the line bundle associated to the non-degenerate electronic state is twisted, i.e. if a continuous global family of *real* adiabatic electronic wave functions $\mathbf{Q} \mapsto \psi_0(\mathbf{Q})$ does not exist. In the case of $\mathbb{R}P^1$, we may group all loops with even winding number in the trivial class, since they give rise to no geometric phase. Odd loops correspond to those with odd winding number. They give rise to a Berry phase in the case of the $E \otimes e$ model, as illustrated by figure 5.

If a Berry phase exists for a given *real* adiabatic electronic state, the vibrational wave functions are required to satisfy antiperiodic boundary conditions for the molecular wave function to be single-valued. These cannot be satisfied by vibrational wave functions transforming in the totally symmetric irrep of SO(N), for they are nodeless, i.e. even under inversion [80] (e.g. in SO(3) the totally symmetric irrep transforms like the s orbital). All other irreps of SO(N) are degenerate. Therefore, the vibronic ground-state will be degenerate whenever the adiabatic electronic ground-state admits a Berry phase. In particular, it will belong to the (fundamental) vector irrep of SO(N) when $N \geqslant 2$ [49, 50, 52, 56, 75]. This is the case, for the Schrodinger equation describing the pseudo-rotational motion in the adiabatic electronic ground-state trough has the same form as that for particle motion on an $N-1$-dimensional sphere (with the equivalence of antipodal points under the mapping to the real projective space enforced by a boundary condition), for which the set of lowest-energy eigenstates that are odd under inversion about $\mathbf{Q} = 0$ belongs to the vector irrep of SO(N) [49, 50, 52, 75].

The above picture has been shown to break down in the presence of warping of the ground-state JT APES. In a variety of examples [19, 49, 81, 82], it was found that the inclusion of sufficiently strong anisotropy in the ground-state APES resulted in the formation of a set of esis which are circulated by low-energy vibrational tunneling paths on the electronic ground-state APES. This, in turn, changes the Berry phase of the adiabatic electronic states, and modifies the symmetry of the vibronic ground-state. Thus, a rearrangement of vibronic energy levels (ground-state crossover) is seen as a function of quadratic vibronic coupling, or of difference in JT stabilization energies for vibrational modes in different irreps of the molecular point group at $\mathbf{Q} = 0$. Given the change in the symmetry and Berry phase of the electronic ground-state, this phenomenon is akin to the topological phase transitions undergone by topological insulators under variation of material properties [83, 84].

For JT systems with maximal continuous invariance under the action of a Lie group, no such ground-state crossover can happen. This has been verified for each individual case with $T^2 = 1$ of table 1 [11, 49, 50, 52, 75], and it has been traditionally understood in the following way: for any $\mathbf{Q}$ in the adiabatic electronic ground-state trough there exists a basis for which the N-dimensional electronic JT Hamiltonian is diagonal with eigenvalues $\{x, x, ..., x, -(N-1)x\}$, where $x > 0$. A closed path on the ground-state trough can be parametrized by SO(N) loops on the vibrational configuration space. By explicit computation of the phase acquired by the adiabatic ground-state upon a non-trivial loop of $\mathbb{R}P^{N-1}$,it has been shown that it *necessarily* changes sign [11, 49, 50, 52, 75]. Because the existence and properties of the trough are independent of the reduced vibronic coupling constant and vibrational frequency, the Berry phase in the spinless models of table 1 is robust with respect to both changes in the fundamental parameters of these models which preserve their fundamental symmetry, and perturbations that break the symmetry, but do not induce new ground-state esis in low-energy regions of the JT APES. More recently, we employed the theory described here to show that the Berry phase and the associated vibronic ground-state degeneracy of the JT models here discussed follow straightforwardly from the results of sections 3.2.1 and 3.2.2 without any lengthy computation [70]. Briefly, the argument relies on the fact that the trough spectrum (equation (26)) implies that the electronic ground-state at any geometry in this subspace can be mapped onto the normal vector of a sphere. This sphere provides a double-valued representation of the vibrational configuration space (which is topologically equivalent to $\mathbb{R}P^N$ as proved in section 3.2.2), such that its antipodal points correspond to the same trough geometry. Parallel transport of a normal vector at a point to its antipodal on the sphere reverses its direction, hence implying a -1 Berry phase for the electronic ground-state [70].

3.3.2. Fermionic models. In models with strong spin–orbit coupling, $H_{\mathrm{JT}}(\mathbf{Q})$ remains degenerate even when $\mathbf{Q} \neq 0$, but this ceases to be true in the quaternionic representation of the corresponding complex Hilbert space (where a quantum state and its time-reversal partner define a single vector) [2, 54]. As derived in section 3.2.3, in spinorial models with continuous symmetries, the ground-state trough is homeomorphic to the quaternionic projective space $\mathbb{H}P^{N-1} \equiv \mathbb{H}^N/\mathbb{H} - \{0\}$. The normalized ground-state Kramers' doublet is only defined modulo a local $su(2) \cong usp(2) \cong \mathbb{H}$ transformation. The impossibility of assigning a global continuous parametrization of the ground-state Kramers' doublet for all $\mathbf{Q} \in \mathbb{H}P^{N-1}$ implies the existence of a non-abelian (or, in this case, a quaternionic) Berry phase [79, 85], as it is transported according to the adiabatic theorem.

To each ground-state Kramers pair, there corresponds a quaternionic line bundle (a family of quaternion vector

spaces) over the vibrational configuration space, which completely characterizes the corresponding allowed nonabelian Berry phases. While the classification of quaternionic line bundles over $\mathbb{H}P^N$ for general N is unknown, solutions exist for the JT models of interest to our study, (a) $\Gamma_8 \otimes (e \oplus t_2)$ ($N = 1$) [30] and (b) $\Gamma_9 \otimes (g \oplus 2h)$ ($N = 2$) [71]. In case (a) the spinorial irreps can be embedded into the $J = 3/2$ irrep of SU(2), and the active JT modes are quadrupolar (they form a basis for the $J = 2$ irrep of SU(2), see section 3.1) [55]. The corresponding spinor JT Hamiltonian is equivalent to that thoroughly investigated by Avron *et al* [54]. They showed that only two topologically distinct quaternionic line bundles exist for this model, with second Chern number [58] equal to ± 1 [85]. The non-abelian Berry phase corresponds to an SU(2) transformation, as mentioned. This implies a much richer set of behaviors for Kramers' partners undergoing cyclic adiabatic evolution as the nuclear geometry pseudorotates, including e.g. the possibility of electronic state population control [34, 54, 79].

The spinorial Hamiltonian of $\Gamma_9 \otimes (g \oplus 2h)$ has only recently been constructed [38]. The electronic states form a basis for the $J = 5/2$ irrep of SU(2), while the JT modes $g \oplus h$ can be embedded into the hexadecapolar ($J = 4$) irrep of SU(2), and the remaining h vibrations are quadrupolar ($J = 2$). The extrema of the ground-state APES generate an 8D trough homeomorphic to the quaternionic projective plane $\mathbb{H}P^2$. Unfortunately, while the isomorphism $\mathbb{H}P^1 \cong S^4$ allows for a simplified analytical treatment of $\Gamma_8 \otimes (e \oplus t_2)$, the properties of $\mathbb{H}P^2$ are much more complex (though the classification of its quaternionic line bundles has also been accomplished [86]). For instance, the second Chern class [85] may be utilized to classify its 4D submanifolds, but it is not sufficient to uniquely identify the quaternionic line bundles over $\mathbb{H}P^2$ (in contrast with the $\mathbb{H}P^1$ case, for which all quaternionic line bundles are completely characterized by the second Chern class) [85]. A simpler situation arises if the hexadecapolar distortions are disallowed. Then, the spinor JT Hamiltonian is given by $\Gamma_9 \otimes h$, which is isomorphic to that of a $J = 5/2$ spin coupled to an external quadrupole field . The topological classification of the quaternionic line bundles over the space of Hamiltonians of this class was given in [54].

3.4. Symmetry breaking

In this subsection we provide brief comments on the significance of the properties of JT models carrying a Lie group action when their continuous symmetry is broken.

We have already noted that the APESs become warped in the presence of higher-order vibronic couplings and/or anisotropic JT stabilization energies/vibrational frequencies in the multimode problem. By the epikernel principle [18, 67], while a non-degenerate ground-state results from the static JT symmetry breaking, a subset of the remaining APESs are likely to be degenerate at equilibrium positions of the distorted system. The possible epikernels represent different ways to break the adiabatic electronic state degeneracy at the JT center, while preserving some non-trivial subgroup of the point group defining the JT model. This was explored in previous subsections. We also showed that radial and angular coordinates can be employed to characterize the splitting of the Lie group-invariant JT APES. In particular, each set of radial displacements specifies an orbit, the internal space of which includes molecular structures with the same electronic spectrum, that can interconvert via pseudorotation. There exists as many distinct radial coordinates as linearly independent ways to split the degenerate multiplet. For example, in $T \otimes (e \oplus t_2)$, the radial coordinates specify whether a given nuclear geometry has a degenerate electronic subspace (see figure 6). The highest-rank epikernel corresponds to molecular deformations along coordinates which remove the degeneracy at the JT center minimally (e.g. by letting $N - 1$ of the branches of the JT PES to remain degenerate). On the other hand, pseudorotational motion provides distortions which continuously map a given epikernel distortion into another that is equivalent. However, in a warped APES, pseudorotation is hindered, due to the formation of energetic barriers between the discrete set of minima. Yet, as shown by Ceulemans [18], coordinates adapted to a continuous group action provide a simple description of the set of extrema of the warped APES. Thus, radial and pseudoangular variables are also useful when the Lie group actions discussed here cease to leave the Hamiltonian invariant. In particular, under weak symmetry-breaking perturbations, pseudorotational motion will remain nearly free, while non-trivial JT motion will be to a good approximation limited to the radial motion.

4. JT models with continuous symmetries and generic conical intersections

In this section we demonstrate a common feature of molecular accidental cis [23, 87, 88] and JT systems with maximal continuous symmetries. The latter satisfy the following condition: the number of JT active displacements is *equal* to the minimal required for the intersection of a given number of APESs to happen at isolated points of the configuration space (without any assumed symmetry). We show below there exists a correspondence between accidental cis and the aforementioned JT systems with electronic multiplets consisting of 2–5 intersecting states (the SO(2), SO(3), SO(4), and SO(5) models) when spin–orbit coupling is irrelevant, and 4 and 6 states (the USp(4) and USp(6) models) when spin–orbit coupling is strong. While in this section we rederive a well-known result on the codimension of parameter spaces admitting accidental cis [89], this is done in a way that emphasizes the similarity between JT models with Lie group invariance and the behavior of a molecular system in the neighborhood of accidental cis. The significance of this result is outlined below.

Let us start with the case where $T^2 = 1$: suppose N states are degenerate at a point $\mathbf{Q} = 0$, $\mathbf{Q} \in \mathbb{R}^{P_N}$, where P_N is equal to the minimum number of parameters which need to be tuned to generate an N-state conical intersection. Let $E_1(0) = E_2(0) = ... = E_N(0) = 0$. Then, in a small neighborhood around the conical intersection,

$$H(\mathbf{Q}) = \sum_{i=1}^{P_N} Q_i M_i, \tag{65}$$

where we assume the M_i are traceless symmetric matrices. This implies iM_i belongs to the $su(N)$ Lie algebra, which has dimensionality $|su(N)| = N^2 - 1$ [63].

We can always choose a basis for $su(N)$ where $N(N+1)/2 - 1$ basis vectors are real-symmetric matrices while the remaining $N(N-1)/2$ are real-antisymmetric [63]. The latter provide an embedding of $so(N)$ into $su(N)$. The M_i do not belong to $so(N)$. Therefore, the number of independent matrices which can be employed in the linearization of $H(\mathbf{Q})$ around the conical intersection point is equal to $N(N+1)/2 - 1$, i.e.

$$P_N = \frac{N^2 + N - 2}{2}. \tag{66}$$

Note $P_1 = 0, P_2 = 2, P_3 = 5, P_4 = 9, P_5 = 14$. These are the number of free parameters which are required to vanish in order to have isolated degeneracies of $1, 2, 3, 4$ and 5 states in generic (asymmetric) systems. They agree with the number of JT active vibrational modes in each of the models of table 1.

The case where $T^2 = -1$ requires the electronic Hilbert space to be even-dimensional. Thus, the possible $iH(\mathbf{Q})$ form a subspace of the $su(2N)$ Lie algebra. The latter has $4N^2 - 1$ generators. However, the matrices in the subspace $usp(2N) \subset su(2N)$ may not be used as building blocks of $iH(\mathbf{Q})$, since $H(\mathbf{Q})$ is required to be hermitian. Hence, the dimensionality of the space of fermionic TRI Hamiltonians is given by

$$P_N = |su(2N)| - |usp(2N)| = N(2N-1) - 1. \tag{67}$$

For $N = 2$ and 3 we obtain the number of coordinates involved in the JT distortions of $\Gamma_8 \otimes (e \oplus t_2)$ and $\Gamma_9 \otimes (g \oplus 2h)$, respectively.

Just like $E \otimes e$ is a paradigmatic model for cis of two states in the presence of time-reversal symmetry and no spin–orbit coupling [11, 87, 90], we can see that the remaining JT models with continuous symmetries could also be deemed as canonical models of generic behavior near cis in cases where more than two branches of an APES intersect. They are indeed the simplest models where these appear.

The perspectives introduced by this view have at least two reasons for being relevant to the treatment of dynamics near generic cis: (i) from a practical perspective the APES near a level crossing shows the same simplifying features as the JT models carrying a Lie group action, e.g. pseudorotational directions along which the electronic spectrum is invariant; (ii) from a conceptual point of view, molecular distortions which lift the degeneracy at cis can be assigned a qualitative meaning based on the correspondence with a JT model, e.g. motions near a triplet conical intersection can be classified in terms of quadrupoles, according to their effects on the electronic spectrum and the analogy with the SO(3)-invariant $T \otimes (e \oplus t_2)$ model.

5. Epilogue

We have reviewed the theory of JT models with continuous symmetries. In particular, (1) we have introduced an alternative classification of these systems by showing that the space of electronic Hamiltonians of certain JT models invariant under a Lie group action on electronic and vibrational degrees of freedom can be identified with symmetric spaces in the orthogonal SU(N)/SO(N) and symplectic classes SU($2N$)/USp($2N$) in the spinless and fermionic cases, respectively; (ii) employed the invariance properties of the symmetric spaces to substantially reduce the complexity of the adiabatic electronic spectra of these high-dimensional models, by showing they can be decomposed into orbit spaces of SO(N) or USp($2N$) (in the spinless and fermionic models, respectively), and identified motion within each orbit with molecular pseudorotation; (iii) explained the relationship between these constructions and the abelian and non-abelian Berry phases of these models; (iv) discussed the qualitative significance of the studied systems when the continuous symmetry is broken, i.e. for more realistic systems, and (v) demonstrated that a common characteristic of the investigated systems is that they include the minimal number of parameters required to induce accidental cis involving up to 5 states of spinless models, and 6 states when spin–orbit coupling is strong. Thus, their generic features are expected to be present in systems exhibiting cis involving many states, but no molecular symmetry. We have also provided novel derivations of the topological equivalence between the ground-state trough of JT models with continuous symmetries and the real and quaternionic projective spaces in the spinless and fermionic models, respectively, and proved that the electronic adiabatic spectrum of the continuous set of minima of all JT models with maximal continuous symmetries destabilizes all states, except for the lowest which is maximally stabilized. Several questions remain to be explored, e.g. we have avoided any discussion related to non-adiabatic dynamics [91, 92], even though the corresponding couplings can be determined straightforwardly for the systems studied with the techniques discussed here. Additionally, this review provides a starting point for the investigation of the effects of the various sources of anisotropy and anharmonicity on the ideal JT problems here investigated. From the point of view of condensed matter physics, models with vibronic continuous symmetries undoubtedly provide the simplest platform for studies of systems with coupling between charge, orbital and phonon order. Importantly, while we focused on the case of isolated JT centers of relevance to solid-state and molecular physics, the vibronic JT Hamiltonians discussed here may also find realization in the fields of cold atoms and photonics.

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