BERRY-PHASE AND SYMMETRY OF THE GROUND STATE IN DYNAMICAL JAHN-TELLER SYSTEMS

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Abstract

We show through selected examples, relevant to the physics of fullerene ions, that the presence of a Berry phase in dynamical Jahn-Teller systems does not guarantee the degeneracy of the ground state, contrary to what previously believed. Moreover, we introduce a new class of Jahn-Teller systems with no Berry phase, as a generalization of the basic icosahedral $H \otimes h$ case.

I. INTRODUCTION

The interest on degenerate electron-lattice interaction (Jahn-Teller effect) in molecules and impurity centers in solids started in the ’30s and found large fields of application in the ’60s. In recent years the interest is coming back, excited by the realization of new systems of this type calling for a revision of a number of commonly accepted beliefs. One of these systems, fullerene, is an highly symmetric icosahedral molecule: this symmetry group implies large representations, thus large degeneracies of the interacting electronic and vibrational states of the isolated ion. New Jahn-Teller (JT) systems have therefore been studied, and they have been shown to imply new exciting properties. A particularly new and surprising one has been demonstrated recently: the possibility of a change in symmetry of the ground state.
The molecular symmetry reduction associated to the splitting of the electronic state degeneracy is restored, as it is known for longtime, in the vibronic ground state thanks to the dynamical JT effect (DJT), i.e. the coherent tunneling among equivalent distortions. In all JT systems known till few years ago, for single-electron occupancy, it was generally accepted an empiric “symmetry conservation rule”, sometimes known as “Ham’s theorem”, stating that the symmetry of the vibronic DJT ground state, at any coupling strength, remains the same as that of the electronic multiplet prior to coupling [1]. This phenomenon, not required by any general constraint in the JT physics can be seen as the fingerprint of a Berry phase in the entangled electronic-phononic dynamics, in turn an apparently general feature. New excitement sprung from the discovery of the first dynamical JT system where the ground state is not degenerate in the strong coupling limit, thus a system which is Berry-phase free [2, 3]. This is the model that in spherical symmetry is indicated as $(L = 2) \otimes (l = 2)$, where electrons of angular momentum $L = 2$ interact with vibrations also belonging to an $l = 2$ representation. This system is relevant to the physics of fullerene ions $C_{60}^+$, where the 5-fold degenerate electronic state has $H$ icosahedral label and the quadrupolar distortions correspond to some of the $h$ modes [3]. It has been shown both analytically and numerically that a nondegenerate state in the vibronic spectrum moves down for increasing coupling, to cross the 5-fold ground state at some finite value of the coupling parameter, thus becoming the ground state at strong coupling.

In this paper we consider more in general the possibility of nondegenerate vibronic ground states, and their compatibility with the presence of a Berry phase in the coupled dynamics.

II. SYMMETRY AND TOPOLOGY CONSIDERATIONS

According to the general theory of the JT effect, an $N$-fold degenerate electronic level corresponding to a representation $\Gamma$ of the symmetry group of the molecule can interact with the vibrational modes corresponding to representations $\{\Lambda\}$ contained in the symmetric part of $\Gamma \otimes \Gamma$ (excluding the identical representation which is trivial). The Hamiltonian for the case where exactly one mode $\omega_\Lambda$ of each symmetry label $\Lambda$ is present and interacts linearly with strength $g_\Lambda$ with the $N$-fold degenerate electronic level is

$$H = \frac{1}{2} \sum_\Lambda \hbar \omega_\Lambda \sum_{i=1}^{[\Lambda]} (p_{\Lambda i}^2 + q_{\Lambda i}^2) +$$
\[
\sum_{\Lambda} g_{\Lambda} \sum_{i=1}^{\vert\Lambda\vert} \sum_{j,k=1}^{\vert\Gamma\vert} q_{\Lambda i} c_{\Gamma j}^\dagger c_{\Gamma k} <\Lambda i|\Gamma j\Gamma k>,
\]

(1)

where \(|\Lambda|\) is the dimension of the \(\Lambda\) representation (and analogously for \(|\Gamma|\)) and \(<\Lambda i|\Gamma j\Gamma k>\) are the Clebsch-Gordan coefficients for the symmetry group \(G\) of the molecule. In (1) we choose the real representation for the vibrational degrees of freedom, and a second-quantized notation for the electrons.

In the special case where all frequencies \(\omega_\Lambda\) and couplings \(g_\Lambda\) are equal, the symmetry group of (1) is raised to \(SO(N)\) and the problem reduces to a single-mode JT coupling between two representations of that group [4]. Within this context it has been shown [3] that the set of minima of the Born-Oppenheimer (BO) potential, corresponding to the most convenient classical distortions, constitute a continuous manifold, referred to as Jahn-Teller manifold (JTM). In particular, due to the smooth adiabatic mapping from the vibrational to the electronic sphere (meaning that to every point on the JTM there corresponds a precise electronic eigenstate of the electron-vibron interaction operator), the JTM shares the same symmetry and topological properties of the electronic Hilbert space. Since the Hamiltonian for the JT problems we consider is real, the electronic space is a sphere \(S^{N-1}\) in the \(N\)-dimensional real vector space. This sphere has \(SO(N)\) symmetry and, because of the mapping, the JTM is also invariant for transformation under the group \(SO(N)\), and not just \(G\). Moreover, the points on the electronic sphere are defined modulo a sign (identification of the antipodes, representing the same electronic state). Consequently, from the topological point of view, the electronic sphere is a multiply connected manifold. Due once more to the smooth mapping, the JTM is also multiply connected. When the system goes along a closed path on the JTM and the electronic state follows adiabatically, it may happen that the final electronic state differs from the initial state by a change of sign. In the most general case of a multiply connected JTM, there are no smooth deformations of the closed path in vibrational space such that this anomaly can be eliminated. This is the essence of the Berry phase in DJT systems: the electronic state, in the adiabatic approximation, induces non trivial phases onto the vibrational dynamics.

III. RESULTS

In the perspective of moving to the general case of different couplings \(g_\Lambda\)'s, it is instructive to first consider the extreme case where only one of the couplings \(g_\Lambda\) is nonzero. Problems of this kind are, for example, \(T \otimes t\) in cubic symmetry and
$H \otimes h$ in icosahedral symmetry. In particular the latter case is of interest because the icosahedral group is non-simply reducible, so that there are two different coupling schemes for the $H \otimes h$ problem \cite{2,3,6}. While one of them is unique to the discrete-group features of the icosahedral group, the other coupling may be chosen to coincide with the $(L = 2) \otimes (l = 2)$ JT system introduced above.

In this very special case, due to the symmetry properties of the Clebsch-Gordan coefficients of $SO(3)$, even if the Hamiltonian has $SO(3)$ symmetry only, the JTM shares the same symmetry properties of the electronic sphere, which here is the four-dimensional unit sphere $S^4$ in the five-dimensional electronic space (with opposite points identified). The JTM of the $(L = 2) \otimes (l = 2)$ system is therefore also a four-dimensional manifold, immersed in the five-dimensional space of distortions, enjoying complete $SO(5)$ symmetry. The only possible manifold satisfying these requirements, is isomorphic to another sphere $S^4$. Yet a sphere $S^4$ in a five dimensional space is a simply-connected object, whereas the electronic sphere is not. Therefore some pathology is to be expected in the adiabatic mapping from the vibrational space to the electronic one. In particular, there must exist at least one loop on the electronic sphere which maps to a single point in vibrational space: under this condition, it is possible to drag and deform smoothly any path connecting a point to its antipode on the electronic sphere (corresponding to a closed path in vibrational space) to this pathological path, which is equivalent to one point in the distortion sphere. This mechanism eliminates the Berry phase anomaly for this problem. As a consequence, as anticipated above, the strong-coupling ground state is non-degenerate.

The main reasons for the elimination of the Berry phase in the $(L = 2) \otimes (l = 2)$ model are therefore the symmetry of the Clebsch-Gordan coefficients and the exact matching of the dimensions of the electronic and vibrational spaces: together they force the JTM to become a plain (simply-connected) sphere. In larger spaces of distortions, the JTM can be both $SO(N)$-symmetric and multiply connected, and in all known cases it really is. This mechanism being clear, we predict that all the $SO(3)$ coupling schemes of the type $L \otimes l$, with even $l = L$ are DJT systems with no Berry-phase entanglement. In particular, the strong-coupling ground state for this whole class of systems is non-degenerate. We verified by numerical diagonalization that this is indeed the case for the $(L = 4) \otimes (l = 4)$ case: an $L = 0$ state originating (at weak coupling) from the one-quantum multiplet, at $g_4 \sim 8$ crosses down below the $L = 4$ vibronic state which was the weak-coupling ground state. Such kind of highly-symmetric systems may have applications for small to medium-sized atomic clusters, or in odd-$A$ nuclei.

This result has a great relevance to the cases of coupling to a single mode,
but it is necessary to be careful in drawing general conclusions from it. One of the main results of this work is indeed that in a many-mode situation, the presence of a Berry phase does not automatically guarantee the degeneracy of the ground state of the system.

This point is made very clear in the \((L = 2) \otimes (l = 2 \oplus l = 4)\) case (an \((L = 2)\) electronic state linearly coupled to two spherical modes of symmetry \(l = 2\) and \(l = 4\) respectively). In that case, for equal frequencies and couplings of the two modes, it was shown \([2,4]\) that the overall underlying symmetry of the model is \(SO(5)\). For this special case, the presence of a Berry phase has been explicitly demonstrated, as well as its consequences for the allowed levels. In the general case \(g_2 \neq g_4\), the symmetry is reduced to the original \(SO(3)\) and the large \(SO(5)\) representations split into the \(SO(3)\) ones. In particular, in the limit \(g_4 \to 0\), the vibronic spectrum of \((L = 2) \otimes (l = 2)\) model is recovered. For \(g_4 \equiv 0\) there is no Berry phase, and for \(g_2 \gtrsim 8\) the ground state is a vibronic nondegenerate \(L = 0\) state separated by a finite energy gap from the first 5-fold degenerate \(L = 2\) excited state \([2,3]\). The continuous lowering of \(g_4\) from \(g_4 = g_2\) to \(g_4 = 0\) describes a smooth mapping of a situation with a Berry phase entanglement (and a degenerate ground state) to a case where this entanglement disappears (nondegenerate ground state). This implies a new case of level crossing, at some intermediate value of \(g_4\). In particular we have a crossover value of \(g_4\) for which the \(L = 0\) and \(L = 2\) states become degenerate. At strong coupling the energy gap \(E[L = 2] - E[L = 0] = c_2\omega_2/g_2^2 + O(g_2^{-4})\) for \(g_4 = 0\) and \(E[L = 2] - E[L = 0] = -c_4\omega_4/g_4^2 + O(g_4^{-4})\) for \(g_2 = 0\), where \(c_2\) and \(c_4\) are positive constants. The curve of crossover points in the \((g_2, g_4)\) plane must get therefore asymptotically close to the straight line \(g_4/g_2 = \sqrt{c_4\omega_4/c_2\omega_2}\) at strong coupling. These considerations permit to draw the zero-temperature “phase diagram” represented in Fig. 1.

This intuitive picture captures the correct physics of the system, and it is noteworthy for describing a whole region of the phase diagram where the presence of a Berry phase coexists with a nondegenerate \(L = 0\) ground state. We need to reconcile the gradual, smooth effect of turning on the coupling to the \((l = 4)\) mode, with the abrupt appearance of a Berry phase, which is a topological effect, intrinsically non-perturbative, as soon as \(g_4 \neq 0\). In actuality, for any \(g_4 \neq g_2\), the 30-fold degenerate first-excited state (labeled \([3,0]\) according to \(SO(5)\)) of the \(g_4 = g_2\) “hypersymmetric” spectrum is split \([2]\) into its \(L = 0, 3, 4, 6\) components (\(SO(3)\) representations). In particular the \(L = 0\) fragment is the lowest one when \(g_4/g_2 < 1\). For small enough \(g_4/g_2\), this nondegenerate state has the opportunity to localize as much as possible in the (hyper)spherical potential well in the \(l = 2\) vibron space, therefore becoming the ground state. Even in this limit, however, the Berry phase prescription is globally
respected, since the \( L = 0 \) (nondegenerate) ground state is really a fragment of an odd \([3,0]\) level selected by the Berry phase: the ground state still fulfills the parity constraint imposed to the low-energy \( SO(5) \) representations by the Berry phase in the global \( (l = 2 \oplus l = 4) \) space. Note however that the same \( L = 0 \) state, if seen restricted to the \( l = 2 \) vibration space, is naturally classified as an \([0,0]\) state for the symmetry group \( (SO(5) \) again) of the JTM.

IV. DISCUSSION

Throughout our discussion we implicitly assumed a linear JT coupling scheme as described by (1). The introduction of quadratic terms has usually effects similar to those produced by different linear coupling \( g_E \neq g_T \) in cubic symmetry, i.e. of “warping” the JTM. The symmetry of the Hamiltonian, as a consequence, is reduced to the symmetry group \( G \) of the molecule, and so is that of the JTM. Yet, the properties of connectedness are topological properties, being therefore robust against perturbations such as the warping: even if the symmetry is reduced, the consequence of the presence/absence of the Berry phase on the ground-state symmetry are unchanged. Ham [8] has shown in particular, for the \( e \otimes E \) coupling scheme, that the introduction of quadratic terms in the Hamiltonian, although splitting specific degeneracies of excited states, does not substantially change the picture as far as the Berry phase and the degeneracy of the ground state are concerned.

In summary, we have shown that the presence/absence of the Berry phase is not a sufficient criterion to decide whether the ground state is degenerate or not at strong coupling. However, the absence of a Berry phase in at least one of the subsystem seems to be a necessary condition for having a non-degenerate ground state. We also illustrate the relevance of the actual values of the coupling strengths between electrons and vibrations, that only can really decide about the symmetry of the ground state. In this perspective, the experimental or \textit{ab-initio} determination of the actual values of such couplings is of the utmost importance for practical systems such as those based on positive fullerene ions. Finally, we propose evidence for a whole family, following the \( (L = 2) \otimes (l = 2) \), of Berry-phase–free dynamical JT systems whose strong-coupling ground state is, as a consequence, nondegenerate.

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FIG. 1. The zero-temperature “phase diagram” of the \((L = 2) \otimes (l = 2 \oplus l = 4)\) JT system in the space of the coupling parameters \(g_2\) and \(g_4\), for fixed frequencies \(\omega_2\) and \(\omega_4\). The solid line marks the crossing between the five-fold (left) and the nondegenerate (right) ground states. The dashed line indicates the asymptotic behavior of the crossover line at strong coupling.