Excited state quantum phase transitions and monodromy

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Abstract. Quantum phase transitions (QPT) and excited state quantum phase transitions (ESQPT) in algebraic models are briefly discussed, in particular those occurring in the U(3) model of bending vibrations of molecules. Experimental evidence in the water molecule, H₂O, is presented.

1. Introduction
Quantum phase transitions (QPT) are phase transitions that occur as a function of a coupling constant, ξ, called control parameter, that appears in the quantum Hamiltonian, $H$, that describes the system,

$$H = \xi [(1-\xi)H_1 + \xi H_2] , \quad 0 \leq \xi \leq 1 . \quad (1)$$

Associated with QPT there are quantal order parameters, the expectation values of suitable chosen operators that describe the state of the system, $\langle O \rangle$. Introduced in the 1970’s [1], they have become of great importance in a variety of systems. QPT are also called ground state phase transitions and/or zero temperature phase transitions [1]. Excited state quantum phase transitions (ESQPT) are phase transitions that occur as a function of excitation energy, $E_x$, for fixed value of the control parameter, $\xi$ [2]. ESQPT are intimately connected with quantum monodromy. ESQPT and quantum monodromy have been recently observed in molecular physics [3-5].

QPT and ESQPT can be conveniently studied within the framework of algebraic models [6]. For these models, one can do both the semi-classical and the quantal analysis, and thus study both semi-classical and quantum monodromy. Also, in many-body systems, finite size scaling (1/N expansion) can be easily investigated. The latter point is particularly important in applications to finite systems: nuclei, molecules, finite polymers, photonic crystals, optical lattices, etc.

In this contribution, after a brief review of algebraic models and their semi-classical limit, an experimental example of ESQPT and monodromy will be given. A full account of QPT and ESQPT, especially for applications to nuclear physics, is given in several review papers [7-10].

2. Algebraic models

2.1. Algebraic properties. An algebraic model is an expansion of the Hamiltonian and other operators in terms of elements, $G_{\alpha\beta}$, of an algebra (often a Lie algebra, $g$, or a contraction of it). The algebra $g$ is called the spectrum generating algebra (SGA),
\[ H = E_0 + \sum_{a,b} \varepsilon_{ab} G_{ab} + \sum_{a \neq \beta} u_{a \beta} G_{a \beta} + \ldots \]
\[ T = \lambda_0 + \sum_{a \neq \beta} J_{a \beta} G_{a \beta} + \ldots \]  

(2)

An interesting situation occurs when \( H \) does not contain all elements of \( g \), but only the invariant (Casimir) operators of a chain of algebras, \( g \supseteq g' \supseteq g'' \supseteq \ldots \)

\[ H = E_0 + \alpha \mathcal{C}(g) + \alpha' \mathcal{C}(g') + \ldots \]  

(3)
called a dynamic symmetry (DS). In this case, the energy eigenvalues can be written explicitly in terms of quantum numbers labelling the representations of \( g \)

\[ E = \langle H \rangle = E_0 + \alpha \langle \mathcal{C}(g) \rangle + \alpha' \langle \mathcal{C}(g') \rangle + \ldots \]  

(4)

It is convenient to write the elements \( G_{a \beta} \epsilon g \) as bilinear products of creation and annihilation operators (Jordan-Schwinger realization). For bosonic systems

\[ G_{a \beta} = \beta^a \beta^\dagger_{\beta} ; \quad \alpha, \beta = 1, \ldots, n \]  

(5)

From

\[ \left[ b^a_\alpha, b^\dagger_\beta \right] = \delta_{a \beta} \]  
\[ \left[ b^\dagger_\alpha, b_\beta \right] = \left[ b^a_\alpha, b^\dagger_\beta \right] = 0 \]  

(6)

One obtains the commutation relations

\[ \left[ G_{a \beta}, G_{\alpha \delta} \right] = \delta_{a \delta} G_{a \beta} - \delta_{a \beta} G_{\alpha \delta} \]  

(7)

which define the real form of \( g = u(n) \). The basis upon which the elements act is the totally symmetric representation,

\[ |N \rangle = \frac{1}{\sqrt{N!}} (b^\dagger_0)^N (b^\dagger_0)^N \ldots |0 \rangle \]  

(8)

characterized by the total number of bosons \( N \).

Fermionic systems can also be treated algebraically in terms of bilinear products of anti-commuting operators

\[ G_{ij} = a^\dagger_i a_j , \quad i,j = 1, \ldots, m \]  

(9a)

\[ \{ a_i, a_j^\dagger \} = \delta_{ij} \]  
\[ \{ a_i, a_j \} = \{ a_i^\dagger, a_j^\dagger \} = \delta_{ij} \]  

(9b)

spanning the Lie algebra \( u(m) \). Mixtures of bosonic and fermionic systems can be treated in terms of the realization

\[ \begin{pmatrix} b^\dagger_\beta b_\beta \\ a^\dagger_i a_i \end{pmatrix} \]  

(10)

spanning the graded Lie algebra (also called superalgebra) \( u(n/m) \). (Fermionic and mixed Bose-Fermi systems will not be discussed here).

**Table 1.** List of bosonic models

| \( U(2) \) | Lipkin model: Schematic model of many-body systems \([12]\)  
| 1-dim Vibron Model (VM): Stretching vibrations of molecules \([13]\) |
| \( U(3) \) | 2-dim Vibron Model (VM): Bending vibrations of molecules \([14]\) |
| \( U(4) \) | 3-dim Vibron Model (VM): Rotations-vibrations of molecules \([15]\) |
| \( U(6) \) | Interacting Boson Model (IBM): Rotations-vibrations of atomic nuclei \([16]\) |
A list [11] of algebraic models extensively investigated is given in Table 1. These provide a description of many-body systems with \( f = n - l \) degrees of freedom. A convenient realization of these models is with a scalar boson, called \( s \) and another boson \( b_m \) with \( m = 2l + 1 \) components. The integer or half-integer number \( l = 0, 1/2, 1, 3/2, 2, \ldots \) is called ‘quasi-spin’. The use of both integer and half-integer numbers allows one to treat problems in both odd and even dimensions.

2.2. Geometric properties. Geometry can be associated to algebraic models with algebra \( g \) by constructing appropriate coset spaces, obtained by splitting \( g \) into

\[
g = h \oplus p
\]

where \( h \) is a subalgebra of \( g \) called stability algebra, and \( p \) is the remainder not closed with respect to commutation. This decomposition is also called a Cartan decomposition. For models with \( u(n) \) structure the appropriate coset \( (g/h) \) is

\[
u(n) / u(n - 1) \oplus u(1)
\]

where \( u(n - 1) \) is the maximal stability subalgebra. This space is a globally symmetric Riemannian space [6, Ch.5] with dimension \( 2(n - 1) \). For bosonic models, the algebra \( h \) can be constructed by selecting one boson, \( b_1 \), and choosing

\[
h = b_1^* b_1, \quad \alpha = 2, \ldots, n
\]

Associated with the Cartan decomposition there are geometric variables \( \eta_i \) defined by

\[
|\eta_i\rangle = \exp \left[ \sum_i \eta_i p_i \right] |\Lambda_{ext}\rangle, \quad P_i \in p,
\]

where \( \Lambda_{ext} \) is called extremal state. For bosonic systems

\[
|N; \eta_\alpha\rangle = \left[ \exp \left( \eta_\alpha b_\alpha^* - \eta_\alpha^* b_\alpha \right) \right] \frac{1}{\sqrt{N!}} (b_\alpha^*)^N |0\rangle.
\]

For systems with fixed number of particles, \( N \), it is convenient to introduce projective coherent states in terms of projective variables, \( \theta_\alpha \),

\[
|N; \theta_\alpha\rangle = \frac{1}{\sqrt{N!}} \left[ b_\alpha^* + \theta_\alpha b_\alpha \right]^N |0\rangle.
\]

For algebraic models written in terms of boson operators, \( s, b_m \), it is convenient to rewrite the coherent state as

\[
|N; \alpha\rangle = \frac{1}{\sqrt{N!}} \left( s^1 + \sum_m \alpha_m b_m^1 \right)^N |0\rangle
\]

with normalization

\[
\langle N; \alpha|N; \alpha\rangle = \left( 1 + \sum_m |\alpha_m|^2 \right)^N.
\]

The semi-classical Hamiltonian associated with the quantum algebraic Hamiltonian is

\[
H_{cl}(\alpha) = \frac{\langle N; \alpha|H|N; \alpha\rangle}{\langle N; \alpha|N; \alpha\rangle}.
\]

This Hamiltonian depends on the complex coordinates \( \alpha_m \) which can be split into real coordinates, \( q_m \), and momenta, \( p_m \).

2.3. Quantum phase transitions (QPT and ESQPT). QPT and ESQPT can be studied within the framework of algebraic models both quantally and semi-classically. For QPT, in the quantum analysis, one evaluates the ground state energy, \( E_0 \), as a function of the control parameter, \( \xi \). At the same time, one studies the behavior of the order parameter as a function of \( \xi \). For bosonic systems, a convenient order parameter is the expectation value of the boson number operator \( n_b \) in the ground state,
normalized to $N, n_{\nu}/N$. The behavior of $E_0$ and $<n_{\nu}>$ determines whether or not there is a precursor of a phase transition. Since the calculation is done for a finite value of $N$, the phase transition appears as a sudden change in the quantity itself or its slope, and not as a discontinuity. For ESQPT, in the quantum analysis, one constructs the energy spectrum as a function of the control parameter $\xi$, called a correlation diagram. ESQPT appear then as an increase in level density for fixed $\xi$ as a function of excitation energy, $E_v$. For QPT in the semi-classical analysis, one evaluates the energy functional $H_\alpha(\alpha)=E(\alpha)$, Eq.(19). By minimizing $E(\alpha)$ with respect to the variable $\alpha$, one then calculates $E(\alpha_e)$ and its derivatives $\partial E(\alpha_e)/\partial \xi$, $\partial^2 E(\alpha_e)/\partial \xi^2$, ... as a function of $\xi$. These quantities may have discontinuities. The order of the phase transition, using Ehrenfest criterion, is related to the order of the derivative that is discontinuous, i.e. if $E(\alpha_e)$ is discontinuous, the transition is zeroth order, if $\partial E(\alpha_e)/\partial \xi$ is discontinuous, it is first order, and so on. For ESQPT, in the semi-classical analysis, one calculates the semi-classical action $S(\xi;E)$ and studies its behavior. ESQPT correspond to divergence of the level density $\rho(\xi;E)$ at some critical value $E=E_{sc}$. A similar semi-classical analysis can be also be done for the order parameter $n_{\nu}/N$.

3. An example of ESQPT: Bending vibrations of molecules

As an example of ESQPT, we consider here the bending vibrations of polyatomic molecules. This is a two-dimensional problem. A quantum description of this problem was given in [14]. Introducing Cartesian boson creation and annihilation operators, $\tau^+_x, \tau^+_y, \tau^-_x, \tau^-_y$ plus a scalar $\sigma^+, \sigma$ conveniently combined into circular bosons,

$$\tau^+_x = \frac{\tau^+_x + i \tau^+_y}{\sqrt{2}}, \quad \tau^+_y = \frac{\tau^+_x + i \tau^-_y}{\sqrt{2}}, \quad \tau^-_x = \frac{\tau^-_x + i \tau^-_y}{\sqrt{2}}, \quad \tau^-_y = \frac{\tau^-_x + i \tau^+_y}{\sqrt{2}}. \quad (20)$$

One can write down the elements of $u(3)$ as

$$\hat{n} = \tau^+_x \tau^-_x + \tau^+_y \tau^-_y, \quad \hat{D}_x = \sqrt{2} \left( \pm \tau^+_x \sigma + \tau^+_y \sigma^+ \right),$$
$$\hat{n}_\sigma = \sigma^+ \sigma, \quad \hat{Q}_x = \sqrt{2} \tau^+_x \tau^-_y, \quad \hat{R}_x = \sqrt{2} \left( \tau^+_x \sigma + \sigma^+ \tau^-_x \right). \quad (21)$$

The algebra of $u(3)$ has two dynamical symmetries corresponding to the breaking into subalgebras that contain the two-dimensional rotation algebra, $so(2)$.

$$u(3) \supset u(2) \supset so(2) \quad (I)$$
$$u(3) \supset so(3) \supset so(2) \quad (II) \quad (22)$$

For each of the two symmetries, states can be labelled by the quantum numbers denoting the irreducible representations of the appropriate group,

$$\left[ u(3) \supset u(2) \supset so(2) \right]$$
$$\begin{array}{c|c|c}
[N] & n & \ell \end{array} \quad (23)$$

With $n=N, N-1, \ldots, 1$ or $0$ and $l=n, n-2, \ldots, 1$ or $0$ for $n=$ odd or even, and

$$\left[ u(3) \supset so(3) \supset so(2) \right]$$
$$\begin{array}{c|c|c}
[N] & n & \ell \end{array} \quad (24)$$

With $n=0, 1, \ldots, (N-1)/2$ or $N/2$ for $N=$ odd or even, and $l=0, \pm 1, \ldots, \pm (N-2\nu)$, where $N$ is called vibron number [15].

In order to describe QPT and ESQPT in this case, one can introduce an algebraic Hamiltonian [17]
This Hamiltonian admits two exactly solvable cases, called dynamical symmetries (or phases), for which the eigenvalue problem can be solved in explicit analytic form

\[ E^{(\text{I})}(n) = E_0 + \epsilon n \]

\[ E^{(\text{II})}(v) = E_0' + 4\epsilon \left[ v \left(1 + \frac{1}{2N}\right) - \frac{1}{N} v^2 \right] \]

(26)

corresponding to symmetry (I) for \( \xi = 0 \), and to symmetry (II) for \( \xi = 1 \). Note that a single quantum number cannot be globally defined, due to the different dynamic symmetries of the two phases.

**Quantal analysis.** The correlation diagram obtained by numerical diagonalization of the Hamiltonian, Eq.(25), is shown in Figure 1.

\[
\hat{H} = \epsilon \left( (1 - \xi) \hat{n} + \frac{\xi}{N} \hat{P} \right)
\]

\[
\hat{P} = N(N+1) - \left[ \frac{1}{2} (\hat{D}_+ \hat{D}_- + \hat{D}_- \hat{D}_+) + \epsilon^2 \right]
\]

(25)

Figure 1. Correlation diagram for \( N = 40 \) and vibrational angular momentum \( l = 0 \). The normalized energy values \( E/N \) are plotted against \( \xi \) as full lines. The critical point \( \xi = 0.2 \) is marked with a vertical dotted-dashed line. The separatrix, Eq.(27), for \( N = 40 \) is shown with a dashed line.

Here the energy spectrum of \( l = 0 \) states is shown as a function of the control parameter, \( \xi \), for \( N = 40 \). One can see that for \( \xi = 0 \) the spectrum is that corresponding to the dynamic symmetry (I), \( u(2) \), with equidistant energy levels as in Eq. (26) (I), for \( \xi = 1 \) the spectrum is that corresponding to the dynamic symmetry (II), \( \text{so}(3) \), with energies given by Eq.(26) (II). If one traverses the correlation diagram at zero energy as a function of \( \xi \), one finds a change at a critical value \( \xi = \xi_c \) from one symmetry to the other. The same change appears also as a function of energy for fixed value of \( \xi \). The former change represents a QPT while the latter represents an ESQPT. The two symmetries (phases) are separated by a separatrix, with equation, in the limit \( N \to \infty \),

\[ f(\xi) = \frac{25\xi^2 - 10\xi + 1}{16\xi} \]

(27)

Also, in the limit \( N \to \infty \), the value of \( \xi_c \) is \( \xi_c = 0.2 \). For finite \( N \), a modification both in Eq.(27) and in the value of \( \xi_c \) is needed, which amount to a multiplication by a factor \((N+1)/(N-1)\).

In order to illustrate further the occurrence of ESQPT, it is convenient to plot the energy levels for fixed \( \xi \) as a function of \( l \). In Figure 2, the so called quantum monodromy diagram [18] is shown. One can see that there is a change in the behaviour with \( l \).
where \( u \) numbers the states and \( u_c \) is the value of \( u \) at which the separatrix is crossed, also called monodromy region.

\[
E^{(1)}(l) = E_0 + bl \quad u > u_c \\
E^{(2)}(l) = E_0 + al^2 \quad u < u_c
\]  

(28)

3.1. Semi-classical analysis. For the semi-classical analysis, it is convenient to go from Cartesian coordinates, \( x, y \), to polar coordinates, \( r, \theta \), and momenta \( p_r, p_\theta \). Putting all momenta equal to zero, the coherent states can be written as \( \langle |N\rangle; r, \theta | \rangle \), and the semi-classical effective potential as

\[
V(r, \theta) = \frac{\langle |N\rangle; r, \theta | H | |N\rangle; r, \theta \rangle}{\langle |N\rangle; r, \theta | |N\rangle; r, \theta \rangle}.
\]

(29)

For the Hamiltonian of Eq.(25), the effective semi-classical potential is then

\[
V(r) = e^{-\xi} \left( 1 - \xi \right) \frac{r^2}{1 + r^2} + \xi \left( 1 - \frac{r^2}{1 + r^2} \right)^2.
\]

(30)

It is instructive to plot the potential as a function of the bending angle for various values of \( \xi \), \( \xi=0 \) (linear), \( \xi=0.2 \) (quasi-linear), \( \xi=0.6 \) (quasi-bent) and \( \xi=1 \) (bent), Figure 3. One can see a progressive change from a potential with one minimum at \( \phi=0 \) degrees (linear) with a potential with two minima at \( \phi=\pm 1 \) radiant (bent). A potential of the type quadratic-quartic, \( V(r)=ar^2+br^4 \) is sometimes referred to as a “sombrero potential” or a “champagne bottle potential” [18].
Figure 3. Energy functional (potential), for linear-to-bent transition in molecules, as a function of bending angle, $\phi$, for four different values of $\xi$, (a) rigidly linear ($\xi=0.0$), (b) quasi-linear ($\xi=0.2$), (c) quasi-bent ($\xi=0.6$), and (d) rigidly bent ($\xi=1.0$).

3.2. **Experimental evidence for ESQPT and monodromy in molecules.** QPT and ESQPT have been recently observed in the bending vibrations of molecules [3-5]. The Hamiltonian used in the analysis is given in Eq.(25). There are two phases, Eq.(22), (I) linear and (II) bent. One of the best examples of ESQPT and monodromy is provided by the water molecule, H$_2$O, which is bent in the ground state and becomes linear at $E_{v_{t}} \sim 11000$cm$^{-1}$ [21]. In Figure 4, a comparison between observed and calculated energy levels is shown [4].

![Figure 3: Energy functional](image1)

![Figure 4: Birge-Spooner plot](image2)

**Figure 4.** Birge-Spooner plot as a function of $v_b$ (top left) and monodromy plot (top right) for H$_2$O. Red triangles are theory and blue circles are experiment. The bottom left panel shows the potential function and the bottom right panel shows the calculated equilibrium structure.

In the top left panel, the differences in energies $E_{v_b,K_a} - E_{v_b-1,K_a}$ are plotted versus the vibrational quantum number $v_b$ for fixed $K_a$. At the monodromy point, this quantity should go to zero, and its
inverse, related to the level density, should diverge. One observes in experiment a dip, called Dixon dip, at \(v_b=8\). The ESQPT is smoothed out by finite \(N\) effects but it still clearly appears in the figure. In the top right panel, the energies \(E_{vb,K_a}\) are plotted versus \(K_a=l\), the angular momentum. One can again see in this plot the change from quadratic to linear behaviour at \(v=8\). The bottom left panel shows the corresponding double well potential, and the bottom right part the equilibrium configuration of the ground state of the water molecule.

4. Summary and conclusions

QPT, ESQPT and monodromy have been studied in algebraic models of many-body systems both quantally and semi-classically. The case of \(u(3)\), Eq. (22), has been shown. Experimental evidence for ESQPT in the bending vibrations of the water molecule, H\(_2\)O, has been presented.

ESQPT and monodromy are related to properties of the potential. The analysis presented here applies equally well to all problems of the type

\[
\begin{align*}
\text{u(n)} &\supset \text{u(n-1)} \\
\text{u(n)} &\supset \text{so(n)}
\end{align*}
\]  

which have a 2\(^{nd}\) order phase transition from the symmetry \(u(n-1)\) to \(\text{so(n)}\). These transitions have been investigated extensively and have the same universal behaviour. For algebraic models that support 1\(^{st}\) order transitions, the structure of the spectrum and its semi-classical analysis is much more complex, since it involves several control parameters and several order parameters. The potential now depends on several coordinates. An example is the Interacting Boson Model (IBM) [16] that describes rotations and vibrations of a liquid drop with ellipsoidal shape. This model has two control parameters and three phases,

\[
\begin{align*}
\text{u(6)} &\supset \text{u(5)} \\
\text{u(6)} &\supset \text{su(3)} \\
\text{u(6)} &\supset \text{so(6)}
\end{align*}
\]  

The potential depends on two intrinsic variables, \(\beta, \gamma\). A complete analysis of classical and quantum monodromy for algebraic structures that support 1\(^{st}\) order transitions is currently being done, but it will not be reported here.

Finally, it should be noted that the dynamics of algebraic models and its behaviour around the monodromy point has been investigated [2] for all models of the type of Eq.(31). Monodromy is also a subject of great interest in mathematics. Here I have concentrated my attention on the physical applications. For a detailed account of the mathematical aspects of monodromy, see [22], and references therein.

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