Lie Algebraic approach to molecular spectroscopy: Diatomic to polyatomic molecules

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Abstract

Interacting dipole ($p$) bosons along with scalar ($s$) bosons, based on the ideas drawn from the interacting boson model of atomic nuclei, led to the development of the vibron model based on $U(4)$ spectrum generating algebra for diatomic molecules. The $U(4) \supset SO(4) \supset SO(3)$ algebra generates rotation-vibration spectra. Extending this to two coupled $SO(4)$ algebras and three $SO(4)$ algebras describe triatomic and four-atomic molecules respectively. Similarly, appropriately coupled $U(2) \supset SO(2)$ algebras will describe the stretching vibrations, with proper point group symmetries, in polyatomic molecules. In addition, coupled $U(3)$ algebras describe coupled benders. The Lie algebraic approach to molecular spectroscopy is briefly described along with a list giving future directions and presented in three appendices results for: (i) $U(3)$ algebra for bending vibrations and coupled benders; (ii) symmetry mixing Hamiltonians generating regular spectra; (iii) partition functions for diatomic and triatomic molecules.

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I. INTRODUCTION

Quantizing the relative co-ordinate in a diatomic molecules gives raise to a description of vibrational-rotational spectra in terms of interacting dipole (π) bosons with \( \ell = 1^- \). The π bosons along with scalar (s) bosons, based on the ideas drawn from the interacting boson model of atomic nuclei [1, 2], led to the development of the vibron model for diatomic molecules with \( U(4) \) spectrum generating algebra (SGA) [3, 4]. The \( SO(4) \) sub-algebra in \( U(4) \supset SO(4) \supset SO(3) \) generates rotation-vibration spectra; \( SO(3) \) generates angular momentum. Extension with two coupled \( U(4) \supset SO(4) \) algebras describe stretching and bending vibrations in triatomic molecules. Similarly, three coupled \( U(4) \supset SO(4) \) algebras describe four-atomic molecules. Continuing this to several coupled \( SO(4) \) algebras will in principle describe polyatomic molecules but these algebras will become unwieldy for molecules with 5 or more atoms. Then, an alternative is to use coupled \( U(2) \supset SO(2) \) algebras [it is also possible to use the more complicated, but simpler than \( U(4) \supset SO(4) \), coupled \( U(3) \supset SO(3) \) algebras [5–7] as described in Appendix-A]. This, along with a Majorana force will allow for incorporating the point group symmetries of polyatomic molecules within the Lie algebraic approach and describe for example stretching vibrations in a variety of polyatomic molecules [8, 9]. Going beyond these and using the ideas from the interacting boson-fermion model of atomic nuclei [10–12], Lie algebraic approach is also shown to describe molecular electronic spectra [13]. In this article we will give an overview of these developments in the Lie algebraic approach to molecular spectroscopy with emphasis on group theoretical aspects. Now we will give a preview.

Section 2 gives the results of \( SO(4) \) algebra for diatomic molecules. Similarly, Section 3 gives the results of coupled \( SO(4) \) algebras for triatomic and four-atomic molecules. Section 4 is on coupled \( SU(2) \supset SO(2) \) algebras for polyatomic molecules. Section 5 gives conclusions along with a list giving future directions. These are supplemented with three appendices describing the following in some detail: (i) \( U(3) \) algebra for bending vibrations and coupled benders and their application to quantum phase transitions (QPT) and excited state quantum phase transitions (EQPT); (ii) symmetry mixing Hamiltonians generating regular spectra using \( U(4) \) subalgebras; (iii) partition functions for diatomic and triatomic molecules.
II. SO(4) ALGEBRA FOR DIATOMIC MOLECULES

Quantizing the relative co-ordinate \( \vec{r} \) between the two atoms of a diatomic molecule we have the vector boson (\( \pi \) boson) with \( \ell = 1^- \); \( \pi_\mu^\dagger = (r_\mu - ip_\mu)/\sqrt{2} \) and \( \pi_\mu = (r_\mu + ip_\mu)/\sqrt{2} \). Now, introducing \( s \) bosons (\( \ell = 0^+ \)) and demanding that the total number \( (N) \) of \( \pi \) and \( s \) bosons is conserved, we have the vibron model based with \( U(4) \) spectrum generating algebra (SGA). The \( U(4) \) is generated by the 16 one-body operators \( \pi_\mu^\dagger \pi_{\mu',}s^\dagger s, \pi_\mu^\dagger s^\dagger \pi_{\mu'} \).

In angular momentum coupled representation, introducing \( \tilde{\pi} \) algebra (SGA). The \( U(4) \) any further in this article except in Appendix B. The quantum numbers [called irreducible representations (irreps) in the representation theory of Lie algebras] of \( U(4), \) \( SO(4) \) and \( SO(3) \) are \( N, \omega \) and \( L \) respectively. The \( M \) quantum number of \( SO(2) \) is trivial and it is dropped from now on as we deal with only \( L \) scalar Hamiltonians. The \( N \rightarrow \omega \rightarrow L \) irrep reductions are easy to identify using pairing algebra in nuclear physics and also using many other approaches [3, 4, 14]. Then we have, \( N \rightarrow \omega = N, N - 2, \) \( N - 4, \ldots, 0 \) or \( 1 \) and \( \omega \rightarrow L = 0, 1, 2, \ldots, \omega \). Using only the quadratic Casimir invariants, the \( U(4) \) Hamiltonian [assuming one plus two-body in nature and preserving \( N \) and \( L \)] for diatomic molecules \( (H_{d-m}) \) is

\[
H_{d-m} = E_0 + \alpha C_2(SO(4)) + \beta C_2(SO(3)) \\
= E_0 + \alpha [L^2 + D^2] + \beta L^2 .
\]

Here \( E_0 \) is a function of \( N \). Using the well known formulas for the Casimir invariants will give \( E = E_0 + \alpha \omega(\omega + 2) + \beta L(L + 1) \); note that \( \langle C_2(SO(4)) \rangle_{N,\omega,L}^{N,\omega,L} = \omega(\omega + 2) \) [2]. Changing \( \omega \) into the vibrational quantum number \( v = (N - \omega)/2 \) will give the energy formula to be

\[
E = E'_0 - 4\alpha(N + 2)(v + \frac{1}{2}) + 4\alpha(v + \frac{1}{2})^2 + \beta L(L + 1) ; \\
v = (N - \omega)/2 = 0, 1, 2, \ldots, \left[\frac{N}{2}\right] \text{ or } \left[\frac{N-1}{2}\right] ,
\]

\[
v \rightarrow L = 0, 1, 2, \ldots, (N - 2v) .
\]
Therefore, with \( N \) large, \( \alpha < 0 \) and \( \beta > 0 \), the \( SO(4) \) algebra generates rotation-vibration spectrum as seen clearly for example in \( \text{H}_2 \) molecule in its electronic ground state (here \( N \sim 31 \) and this follows from the observed \( v_{\text{max}} \) value). In fact \( SO(4) \) represents rigid molecules (this can be derived from the Morse oscillator) and the other limit \( U(4) \supset [SU(3) \supset SO(3)] \oplus U(1) \) is for non-rigid molecules [3]; see Appendix B. It is important to recognize that Eq. (2) is similar to the well known Dunham expansion [15].

III. COUPLED \( SO(4) \) ALGEBRAS FOR TRIATOMIC AND FOUR-ATOMIC MOLECULES

Let us start with triatomic molecules. Now there are two relative co-ordinates and associating \( U(4) \) SGA to each of these, the SGA for triatomic molecules is \( U_1(4) \oplus U_2(4) \). This SGA admits large number of subalgebras but the most important are: (i) local basis generated by \( U_1(4) \oplus U_2(4) \supset SO_1(4) \oplus SO_2(4) \supset SO_{12}(4) \supset SO(3) \); (ii) normal basis generated by \( U_1(4) \oplus U_2(4) \supset U_{12}(4) \supset SO_{12}(4) \supset SO(3) \). In the local basis, the two \( U_{i=1,2}(4) \) algebras give boson numbers \( N_1 \) and \( N_2 \) and similarly the two \( SO_{i=1,2}(4) \) give \( \omega_1 \) [or \( v_1 = (N_1 - \omega_1)/2 \)] from \( N_1 \) and \( \omega_2 \) [or \( v_3 = (N_2 - \omega_2)/2 \)] from \( N_2 \) respectively. The \( SO_{12}(4) \) irreps are \( (\tau_1, \tau_2) \) and they are generated by the so called Kronecker product of \( \omega_1 \) and \( \omega_2 \). This then gives (see for example [3, 14] for the Kronecker products),

\[
(\tau_1, \tau_2) = \sum_{\alpha, \beta} (\omega_1 + \omega_2 - \alpha - \beta, \alpha - \beta); \quad \alpha = 0, 1, \ldots, \min(\omega_1, \omega_2), \quad \beta = 0, 1, \ldots, \alpha .
\]

Similarly, the reduction of \((\tau_1, \tau_2) \rightarrow L \) follows from the recognition that \( SO(4) \) is isomorphic to \( SO(3) \otimes SO(3) \) and the two \( SO(3) \)'s are labeled by \( J_1 = (\tau_1 + \tau_2)/2 \) and \( J_2 = (\tau_1 - \tau_2)/2 \); \( \tau_1 \geq \tau_2 \). Then, the simple angular momentum coupling rule gives \( J_1 \times J_2 \rightarrow L \). The final result is

\[
L = 0^+, 1^-, 2^+, \ldots, \tau_1^\pi; \quad \text{for } \tau_2 = 0 \quad \text{and } \pi = (-1)^{\tau_1}
\]

\[
L = \tau_2^\pm, (\tau_2 + 1)^\pm, \ldots, (\tau_1)^\pm; \quad \text{for } \tau_2 \neq 0 .
\]

More conventional notation for \((\tau_1, \tau_2)\) is to use \( v_2^{\ell_2} \) with \( v_2 = N_1 + N_2 - 2v_1 - 2v_3 - \tau_1 \) and \( \ell_2 = \tau_2 \). Using Eq. (3) we have, \( v_2 = 0, 1, 2, \ldots \), \( 2^\ast \min(N_1 - 2v_1, N_2 - 2v_3) \) and \( \ell_2 = v_2, v_2 - 2, \ldots 0 \) or 1. Note that \( \ell_2 = 0, 1, 2, 3, 4, \ldots \) are in spectroscopic notation \( \Sigma, \Pi, \Delta, \Phi, \Gamma \) and so on. Adding the \( L \) and \( D \) operators from the two \( SO(4) \)'s will give the quadratic
Casimir invariant $L_{12}^2 + D_{12}^2$ of $SO_{12}(4)$ and its eigenvalue in $(\tau_1, \tau_2)$ irrep are $[\tau_1(\tau_1+2)+\tau_2^2]$. Now, using $H_{t-m} = E_0 + a_1 C_2(SO_4(4)) + a_2 C_2(SO_2(4)) + a_4 C_2(SO_{12}(4)) + a_3 L_{12}^2$ will give a formula exactly similar to Dunham expression,

$$E(v_1 v_2^0 v_3 L) = E_0' + \sum_i \alpha_i (v_i + d_i) + \sum_i \beta_i (v_i + d_i)^2 + \sum_{i<j} \gamma_{ij} (v_i + d_i)(v_j + d_j) + g_{12}^2 L^2 + h L(L+1).$$

(5)

where $d_i = 1/2$ for $v_1$ and $v_3$ and 1 for $v_2$. For linear triatomic molecules Eq. (5) is good. However, for bent molecules the projection quantum number $k$ (same as $\ell_2$ but $\ell_2$ is used for linear molecules) can take any value and different $k$ states are expected to be degenerate. Here, we define $(v_i', k)$ via $\tau_1 = N_1 + N_2 - 2v_1 - 2v_3 - 2v_2' - k$ and $\tau_2 = k$. Then, $v_2' = 0, 1, 2, \ldots$ and $k = 0, 1, 2, 3, \ldots$ for any $v_2'$. To obtain $k$ degeneracy, we need to consider $C_2(SO_{12}(4)) = \sqrt{|L \cdot D|^2}$ and its eigenvalues in the $(\tau_1 \tau_2)$ irrep are $\tau_2(\tau_1 + 1)$. Therefore, adding $2a_{12} C_2(SO_{12}(4))$ to $H_{t-m}$ will give $a_{12}(\tau_1 + \tau_2)(\tau_1 + \tau_2 + 2)$ and then $E$ is independent of the $k$ quantum number.

Turning to the normal mode basis, it is easy to identify that the $U_{12}(4)$ irreps will be \{Na, Nb\} = \{N_1 + N_2 - n, n\} where $n = 0, 1, 2, \ldots, \min(N_1, N_2)$. The \{Na, Nb\} $\to (\tau_1, \tau_2)$ reductions can be written down but they involve the more complicated 'multiplicity' label; see for example [3, 14]. One usefulness of $U_{12}(4)$ is that it can be used to mix local basis states and in reality, for describing linear or bent molecules some mixing is essential. The Majorana interaction $M_{12}$, which is related to $C_2(SU_{12}(4))$ in a simple manner and has a proper physical meaning [2], is added to $H$ for generating mixing. Inclusion of $M_{12}$ term in $H_{t-m}$ is similar to Darling-Dennison coupling between the local modes $v_1$ and $v_3$ [3]. In addition, also a Fermi coupling term $F_{12}$ and higher order terms in Casimir operators are added to $H$. With these good agreements with data (within 1-5 cm$^{-1}$) are obtained for many triatomic molecules such as H$_2$O, SO$_2$, CO$_2$, HCN, OCS, H$_2$S, D$_2$O, N$_2$O and in some with different isotopes (ex: C$^{12}$O$_2$, C$^{15}$O$_2$, H$_2$O$^{16}$, H$_2$O$^{18}$). Depending on the molecule, $N_1 = N_2$ or $N_1 \neq N_2$. Also, in all the cases the value of $N_i$ is quite large. Besides comparing spectra, the algebraic approach also allows for calculating intensities of vibrational excitations; see [3, 16, 17] for details. All these extend to four-atomic molecules as shown by Iachello et al., by coupling three $SO(4)$ algebras, in a series of papers analyzing for example spectroscopic properties of the molecules C$_2$H$_2$, C$_2$D$_2$, C$_2$HD and HCCF [18]. Note that, here the coupling of the first two $SO(4)$ algebras will give $(\tau_1, \tau_2)$ irreps and then these are coupled to the $(\omega_3, 0)$
irreps of the third $SO(4)$ algebra. As $SO(4) \sim SO(3) \otimes SO(3)$, all the algebra here also is carried out by exploiting angular momentum algebra.

IV. COUPLED $U(2)$ ALGEBRAS FOR VIBRATIONAL MODES IN POLYATOMIC MOLECULES

Study of the vibrational excited states in medium and large molecules is an important current area of research. Based on the fact that $U(2) \supset SU(2) \supset SO(2)$ [with boson number $N$ denoting $U(2)$ irreps, $\frac{N}{2}$ the irreps of $SU(2)$ and $\frac{N}{2} - v$ the irreps of $SO(2)$] is the algebra of one-dimensional Morse oscillator, a coupled $U(2)$ model for vibrational states in polyatomic molecules has been introduced by Iachello and Oss [8] by attaching a $U_i(2)$ algebra to each bond of a polyatomic molecule. Then, the SGA for stretching vibrations is $\sum_i U_i(2) \oplus$. The interaction between any two bonds $i$ and $j$ is then generated by (I) local $U_i(2) \oplus U_j(2) \supset SO_i(2) \oplus SO_j(2) \supset SO_{ij}(2)$ algebra and (II) normal $U_i(2) \oplus U_j(2) \supset U_{ij}(2) \supset SO_{ij}(2)$ algebra. Note that for simplicity the $SU(2)$ is dropped everywhere but one need to remember that $SU(2) \supset SO(2)$ algebra is the simple angular momentum algebra with the $J$ quantum number being $\frac{N}{2}$ and the $J_z$ quantum number being $m = \frac{N}{2} - v$. Then, the local basis is $|N_i, v_i, N_j, v_j, \rangle$. Each bond energy is generated by $C_i = [2J_z(i)]^2 - N_i^2$ with

$$\langle C_i \rangle |_{N_i, v_i} = -4(N_i v_i - v_i^2).$$  \hspace{1cm} (6)
It is important to note that the one dimensional Morse oscillator is given by \( h_m = p^2/2\mu + D[1 - \exp(-ax)]^2 = a_0 + a_1 C \). Similarly the pair energy operator preserving (I) is \( C_{ij} = [2J_z(i) + 2J_z(j)]^2 - (N_i + N_j)^2 \) and its matrix elements are,

\[
\langle C_{ij} \rangle^{N_i,v_i,N_j,v_j} = -4 \left[ (N_i + N_j)(v_i + v_j) - (v_i + v_j)^2 \right] .
\] (7)

The interaction between the bonds \( i \) and \( j \) will mix the local (I) basis states. A simple operator for this purpose is the Majorana operator \( M_{ij} \) that is related to the Casimir operator of \( SU_{ij}(2) \). The \( M_{ij} \) operator and its matrix elements (they will follow easily from the angular momentum algebra),

\[
M_{ij} = -\left\{ 2 \left[ J_z(i)J_z(j) - \frac{N_iN_j}{2} \right] + J_+(i)J_-(j) + J_-(i)J_+(j) \right\}
\]

\[
\langle N_i v_i N_j v_j \mid M_{ij} \mid N_i v_i N_j v_j \rangle = (N_i v_j + N_j v_i - 2v_i v_j)
\]

\[
\langle N_i v_i - 1 N_j v_j + 1 \mid M_{ij} \mid N_i v_i N_j v_j \rangle = -\sqrt{(N_j - v_j)(N_i - v_i + 1)v_i(v_j + 1)}
\]

\[
\langle N_i v_i + 1 N_j v_j - 1 \mid M_{ij} \mid N_i v_i N_j v_j \rangle = -\sqrt{(N_i - v_i)(N_j - v_j + 1)v_j(v_i + 1)}
\]

Now, diagonalizing the following Hamiltonian

\[
H = E_0 + \sum_i^{n} A_i C_i + \sum_{i<j}^{n} A_{ij}' C_{ij} + \sum_{i<j}^{n} \lambda_{ij} M_{ij}
\] (9)

in the local basis \( \prod_i \mid N_i v_i \rangle \) will give the vibrational energies. However, molecules carry point group symmetries (ex: octahedral \( O_h \) for \( XY_6 \), \( D_{6h} \) for \( C_6H_6 \)) and they need to be incorporated in Eq. (9). It is recognized that this can be done easily by imposing restrictions on the parameters \( A, A' \) and more importantly on \( \lambda_{ij} \).

Let us consider the Benzene molecule \( C_6H_6 \) as shown in Fig. 1. There are six bonds and they are all equal imposing the conditions \( N_i = N, A_i = A \) and \( A_{ij}' = A' \). The \( \sum_{i<j}^6 \lambda_{ij} M_{ij} \) term is constrained by \( D_{6h} \) symmetry depending on \( (i, j) \) nearest neighbors, next nearest neighbors and so on. Simplest choice is \( S = \sum_{i<j}^6 \lambda_{ij} M_{ij} \) with \( \lambda_{ij} = 1 \). Next is \( S' = \sum_{i<j}^6 \lambda_{ij} M_{ij} \) with \( \lambda_{ij} = 1 \) for nearest neighbors and zero otherwise. The nearest neighbors are with \( (ij) = (12), (16), (23), (34), (45) \) and (56). Third choice is \( S'' = \sum_{i<j}^6 \lambda_{ij} M_{ij} \) with \( \lambda_{ij} = 1 \) for next nearest neighbors and zero otherwise. The next nearest neighbors are
with \((ij) = (13), (15), (24), (26), (35)\) and \((46)\). With these, the \(H\) that generates states with \(D_{6h}\) symmetry is \(H = E_0 + AC + A'C' + \lambda S + \lambda' S' + \lambda'' S''\) where \(C = \sum C_i\) and \(C' = \sum_{i<j} C_{ij}\). Instead of constructing the \(H\) and diagonalizing it in the local basis, it is also possible to directly construct the symmetry adopted basis [19]. The algebraic method is applied successfully to stretching overtones of \(SF_6\), \(WF_6\) and \(UF_6\) molecules, \(C-H\) stretching and \(C-H\) bending vibration levels in \(C_6H_6\) (also \(C_6D_6\)), \(CH\) stretches in \(n\)-alkane molecules and so on; see [8, 9, 20] and references therein.

V. CONCLUSIONS AND FUTURE OUTLOOK

Starting with the \(U(4) \supset SO(4) \supset SO(3)\) Lie algebra chain for rotation-vibration levels in diatomic molecules, a brief account of the Lie algebraic approach to triatomic molecules using two coupled \(SO(4)\) algebras, for four-atomic molecules three coupled algebras and coupled \(SU(2)\) algebras for poly-atomic molecules is given in Sections II-IV. The Lie algebra approach is not too complex and yet it is powerful as seen from the applications carried out till now. In this short review, all mathematical details are kept to a minimum and for detailed comparisons between theory and experimental data, the reference given at the end should be consulted. There are several new directions enlarging the scope of the Lie algebra approach and some of these are as follows. (i) Analysis of two coupled benders (in four-atomic molecules) using coupled \(U(3)\) algebras [5–7] and its extensions to three or more benders. In two dimensions, necessary for describing bending vibrations, \(U(4)\) algebra reduces to \(U(3)\) algebra and some details of the \(U(3)\) algebra are given in Appendix A. (ii) Algebraic approach for simultaneous description of electronic, vibrational and rotational energy levels. For example, with electrons in \(s\) and \(p\) orbitals the SGA for electrons is \(U(8) \supset U(4) \otimes SU(2)\) with \(U(4)\) for the spatial part and \(SU(2)\) generating spin. The key point now is that the spatial \(U(4)\) can be combined with the \(U(4)\) generated by \((\pi, s)\) bosons to give a Bose-Fermi (BF) coupling scheme [13]. Let us add that BF schemes are well studied in nuclear structure [10, 11]. (iii) Development of the Lie algebra approach and its applications to polyatomic molecules with very large number of atoms (also to macromolecules, polymers etc.) [8, 20, 21]. (iv) Shape phase transitions that correspond to quantum phase transition (QPT) and excited state quantum phase transitions (EQPT) can be studied using classical analysis of the Lie algebraic models and with this it is possible to address quantum monodromy
FIG. 2. (a) Spectra as a function of the mixing parameter $\xi$ in $H$ interpolating the symmetry limits (S1) and (S2) mentioned in Appendix A. Results are shown for: (i) $(n_1, n_2) = (9,6)$ and $(15,3)$ with number of bosons $N = 50$; (ii) $(n_1, n_2) = (50,50)$ with $N = 50$; (iii) $(n_1, n_2) = (30,30)$ with $N = 30$. All results are shown for $(\omega_1, \omega_2) = (0,0)$ irrep where $\omega_1$ is the irrep of $SO(n_1)$ and $\omega_2$ is the irrep of $SO(n_2)$. (b) Excitation energies as a function of the mixing parameter $\xi$ for $(n_1, n_2) = (6,6)$, $N = 60$ and $(\omega_1, \omega_2) = (0,0)$. Figures show that there will be QPT only when the boson number $N$ is much greater than $n_1 + n_2$. Figures are taken from [28] and see this reference for further details.

in molecules [6, 22, 23]. In fact quantum monodromy is see recently in some molecules [24]. Some aspects of QPT and EQPT are mentioned in Appendix A. (v) Applications of the algebraic coupling schemes discussed in Sections II-IV and Appendix-A in the study of order chaos transitions and random matrix theory; see Appendix B and Ref. [25]. (vi) Level densities, partition functions and other thermodynamic quantities for polyatomic molecules
can be studied using the algebraic models; some analytical results for diatomic and triatomic molecules are available as presented in Appendix C.

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APPENDIX A

$U(3)$ algebra chains for bending vibrations and coupled benders

In Sections II and III the full three dimensional $U(4)$ and coupled $U(4)$ algebras for diatomic to polyatomic molecules are briefly described and Section IV coupled one dimensional $U(2)$ algebras for stretching vibrations are described. However, even if one separates rotations and vibrations, one dimensional description will not suffice for bending vibrations as these require two dimensions, say $x$ and $y$. Introducing boson creation operators $\tau_x^\dagger$ and $\tau_y^\dagger$ together with a scalar boson creation operator $\sigma^\dagger$, we have three boson creation (call them $b_i^\dagger$, $i = 1, 2$ and 3 respectively) and three annihilation ($b_i$, $i = 1, 2$ and 3) operators. Then, clearly the SGA is $U(3)$ generated by the 9 operators $b_i^\dagger b_j$, $i, j = 1, 2, 3$. In order to find the subalgebras in $U(3)$, it is more convenient to consider circular bosons,

$$\tau_\pm = \frac{1}{\sqrt{2}} (\tau_x^\dagger \pm i\tau_y^\dagger), \quad \tau_{\pm} = \frac{1}{\sqrt{2}} (\tau_x \mp i\tau_y)$$

and they satisfy the commutation relations $[\tau_i^\dagger, \tau_j^\dagger] = 0$, $[\tau_i, \tau_j] = 0$ and $[\tau_i, \tau_j^\dagger] = \delta_{ij}$. With these, the number operator $\hat{n}$ giving number ($n$) of circular bosons is

$$\hat{n} = \tau_x^\dagger \tau_x + \tau_y^\dagger \tau_y = \tau_+^\dagger \tau_+ + \tau_-^\dagger \tau_- = \hat{n}_+ + \hat{n}_-.$$  

Similarly, $\hat{n}_s = \sigma^\dagger \sigma$ gives number of scalar bosons. The total boson number $N = n + n_s$ is generated by $\hat{N} = \hat{n} + \hat{n}_s$. Given $N$ bosons, it is easy to recognize that all the $N$ boson states belong to the totally symmetric irrep $\{N\}$ of $U(3)$. Also, It is well known that $U(3)$ admits two subalgebras [12]: (I) $U(3) \supset SO(3) \supset SO(2)$; (II) $U(3) \supset [U(2) \supset SU(2) \supset SO'(2)] \otimes U(1)$. Let us now identify the generators of the various algebras in (I) and (II) and the associated irrep reductions [5, 6].
FIG. 3. Energy spectra for 50 bosons in $s$, $d$ and $g$ orbits with $(\omega^B_{sd}, \omega^B_g) = (0, 0)$ in with the Hamiltonian $H_{sdg}(\xi, x) = [(1 - \xi)/N^B] \hat{n}_g + [((\xi/(N^B))^2) [4(S^d_+ + xS^g_+)(S^d_- + xS^g_-) - N^B(N^B + 13)]$ interpolating the symmetry limits (S1) and (S2) mentioned in Appendix A with $n_1 = 6$ and $n_2 = 9$. Note that $S^d_\pm$ is the pair creation operator for the $sd$ boson system and $S^g_\pm$ for the $g$ boson system. Similarly, $N^B$ is boson number operator, $\omega^B_{sd}$ is the $SO_{sd}(6)$ irrep and $\omega^B_g$ is the $SO_g(9)$ irrep. In each panel, energy spectra are shown as a function of the parameter $\xi$ taking values from 0 to 1. Results are shown in the figures for $x = 1, 0.8, 0.5, 0.2, 0, -0.2, -0.5, -0.8$ and $-1$; $x = 1$ and $-1$ correspond to the two $SU(1,1)$ algebras in the model. In the figures, energies are not in any units. Figure is taken from [30].

Starting with (I), the $SO(3)$ algebra is generated by the three operators $D_+$, $D_-$ and $D_0 = \hat{\ell}$,

$$D_+ = \sqrt{2} \left( \tau^+_+ \sigma - \tau^-_- \sigma^\dagger \right), \quad D_- = \sqrt{2} \left( \tau^+_+ \sigma^\dagger - \tau^-_- \sigma \right), \quad D_0 = \hat{\ell} = \hat{n}_+ - \hat{n}_- .$$  

This is established by proving easily that $[D_+, D_-] = 2D_0$ and $[D_0, D_+] = D_+$. The
associated angular momentum quantum number is denoted by \( \omega \) and the eigenvalues of
\[
\hat{W}^2 = D_+ D_- + \ell^2 - \ell = \frac{1}{2} (D_+ + D_-) + \ell^2
\] (A-4)
are \( \omega(\omega + 1) \). Then, the symmetry limit I is,
\[
\begin{bmatrix}
U(3) & \supset & SO(3) & \supset & SO(2) \\
\{N\} & \omega & \ell & \left(D_+, D_-, \ell\right) & \hat{\ell}
\end{bmatrix}
\] (A-5)

\[
N \to \omega = N, N - 2, \ldots, 0 \text{ or } 1 \\
\omega \to \ell = -\omega, -\omega + 1, \ldots, 0, \ldots, \omega - 1, \omega .
\]

As discussed ahead, \( \omega \) quantum number is also related to pairing. As in Section II, introducing the vibrational quantum number \( v = (N - \omega)/2 \) will give \( v = 0, 1, 2, \ldots, (N/2) \) or \( (N - 1)/2 \) and \( \ell = 0, \pm 1, \pm 2, \ldots, \pm (N-2v) \). Now, the basis states are \( |N, v, \ell\rangle \) and a Hamiltonian (including at most quadratic Casimir invariants \( C_r, r \leq 2 \)) preserving the symmetry limit I is \( H = E_0 + \alpha C_1(U(3)) + AC_2(SO(3)) + B[C_1(SO(2))]^2 \) giving \( E = E_0 + \alpha N + AN(N + 1) - 4A[N + \frac{1}{2})v - v^2] + BL^2 \).

In \( U(N) \supset SO(N) \) for bosons, the \( SO(N) \) is related to pairing [26]. This result applies to \( SO(3) \) in \( U(3) \supset SO(3) \). With \( \tau_\pm \) and \( \sigma \) bosons, the pair creation operator \( \hat{P} \) is
\[
\hat{P} = 2 \tau_+ \tau_- + \sigma^\dagger \sigma^\dagger .
\] (A-6)

Then, the pairing Hamiltonian, a two-body operator, is \( H_p = \hat{P}(\hat{P})^\dagger \); note that \( (\hat{P})^\dagger = (2\tau_+ \tau_- + \sigma \sigma) \). Simple algebra gives the important relation
\[
H_p = \hat{P} (\hat{P})^\dagger = \hat{N} (\hat{N} + 1) - (\hat{W})^2
\] (A-7)

establishing the relation between pairing and the \( SO(3) \) algebra. It is also important to point out that there is a second \( SO(3) \) subalgebra in \( U(3) \) and we will denote this by \( \overline{SO(3)} \).

Its generators and the corresponding pairing operator \( H'_p \) are
\[
\overline{SO(3)} : \left( R_+, R_-, \hat{\ell} \right) ,
\]
\[
\begin{align*}
R_+ &= \sqrt{2} \left( \tau_+^\dagger \sigma + \tau_-^\dagger \sigma^\dagger \right) , \\
R_- &= \sqrt{2} \left( \tau_-^\dagger \sigma + \tau_+^\dagger \sigma^\dagger \right) , \\
[R_+, R_-] &= 2 \hat{\ell} , \\
[\hat{\ell}, R_+] &= R_+ ,
\end{align*}
\]
\[
\hat{R}^2 = R_+ R_- + (\hat{\ell})^2 - \ell \rightarrow \langle \hat{R}^2 \rangle^N_{\omega, \ell} = \omega(\omega + 1) ,
\]
\[
P' = 2 \tau_+^\dagger \tau_-^\dagger - \sigma^\dagger \sigma^\dagger , \\
H'_p = P' (P')^\dagger = \hat{N} (\hat{N} + 1) - \hat{R}^2 .
\] (A-8)
For the significance of $U(3) \supset SO(3) \supset SO(2)$ see Appendix B.

Turning to limit II, it is easy to recognize that we can divide the space into the one with $\tau$ bosons and other with $\sigma$ bosons giving $U(3) \supset U_\tau(2) \oplus U_\sigma(1)$ with $U(2)$ generating $n$ and $U(1)$ generating $n_s$ so that $N = n + n_s$. As we always consider states with a fixed $N$ value, given $n$ the value of $n_s$ is uniquely $N - n$ and therefore we will not mention $U(1)$ hereafter.

The $U(2)$ algebra is generated by the 4 operators

$$Q_+ = \tau_+^\dagger \tau_-, \quad Q_- = \tau_-^\dagger \tau_+, \quad Q_0 = \frac{\hat{n}_+ - \hat{n}_-}{2} = \frac{\hat{\ell}}{2}, \quad \hat{n}.$$  \hspace{1cm} (A-9)

More importantly, the operators $\{Q_+, Q_-, Q_0\}$ form angular momentum algebra $SU(2)$ with $m$ quantum number $\ell/2$. It is easy to show that $[Q_+, Q_-] = 2Q_0$ and $[Q_0, Q_+] = Q_+$. Given $n$ bosons, the $SU(2)$ irrep is spin $n/2$. Then,

$$\frac{\ell}{2} = -\frac{n}{2}, -\frac{n}{2} + 1, \ldots, \frac{n}{2} - 1, \frac{n}{2} \Rightarrow \ell = \pm n, \pm(n - 2), \ldots, 0 \text{ or } 1.$$  \hspace{1cm} (A-10)

Putting all these together, the symmetry limit II is,

$$\begin{pmatrix}
U(3) \supset U(2) & \supset SO(2) \\
\{N\} & n \\
\left(Q_+, Q_-, \hat{\ell}/2, \hat{n}\right) & \hat{\ell}
\end{pmatrix}$$  \hspace{1cm} (A-11)

$$N \to n = N, N - 1, \ldots, 0,$$

$$n \to \ell = \pm n, \pm(n - 2), \ldots, 0 \text{ or } 1.$$  

Now, the basis states are $|N, n, \ell\rangle$ and a Hamiltonian (including at most quadratic Casimir invariants $C_r$, $r \leq 2$) preserving the symmetry limit II is $H = E_0 + \alpha C_1(U(2)) + \beta C_2(U(2)) + B[C_1(SO(2))]^2$ giving $E = E_0 + \alpha n + \beta n(n + 1) + B\ell^2$.

Most general $U(3)$ Hamiltonian preserving $N$ and $\ell$ can be written as a polynomial in the nine $U(3)$ generators $\hat{N}, \hat{n}, \hat{\ell}, D_\pm, R_\pm$ and $Q_\pm$. Note that $D$ and $R$ operators change $\ell$ by one unit and $Q$ by two units. It is easy to write the matrix elements of $H$ (i.e. construct $H$ matrix) in the $|N, n, \ell\rangle$ basis; $n_s = N - n$, $n_+ = (n + \ell)/2$ and $n_- = (n - \ell)/2$. Both second degree and higher degree polynomials are used in the applications to bending motion in many triatomic molecules [6, 22]. Another important aspect of the $U(3)$ model is that the simple interpolating Hamiltonian

$$H_{\text{mix}} = (1 - \xi) \hat{n} + \frac{\xi}{N - 1} H_P$$  \hspace{1cm} (A-12)
Hamiltonian describing the various structures is of the form $H$ same as discussed above for one bender and $V$ (A-7) and its matrix elements in the $|N, n, \ell\rangle$ basis follow easily from its definition,

$$
\langle N, n', \ell | H_P | N, n, \ell \rangle = [(N - n)(N - n - 1) + n^2 - \ell^2] \delta_{n', n} + \sqrt{(N - n + 2)(N - n + 1)(n + \ell)(n - \ell)} \delta_{n', n - 2} + \sqrt{(N - n)(N - n - 1)(n + \ell + 2)(n - \ell + 2)} \delta_{n', n + 2}.
$$

(A-13)

As shown in [6], with $\xi$ varying from 0 to 1 the Hamiltonian changes the structure from rigidly linear ($\xi = 0$) to rigidly bent ($\xi = 1$) structure. More importantly, for $0 < \xi \leq 2$, the molecule will be quasi-linear and for $0.2 < \xi < 1$ quasi-bent. Moreover, at $\xi = 0.2$ the system exhibits QPT (change in ground state structure) and it is a second order phase transition. Also, at $\xi = 0.6$ the system with $H$ defined by Eq. (A-12) exhibits EQPT [22]. Let us stress that the $U(3)$ model is a simple two-level model ($3 = 2 + 1$) and the QPT and EQPT are typical of general two level models [23, 27]. For bosons in two levels with $n_1$ and $n_2$ number of degenerate single particle levels, the SGA is $U(n_1 + n_2)$ and then there are two symmetry limits, S1: $U(n_1 + n_2) \supset U(n_1) \oplus U(n_2) \supset SO(n_1) \oplus SO(n_2) \supset K$ and S2: $U(n_1 + n_2) \supset SO(n_1 + n_2) \supset SO(n_1) \oplus SO(n_2) \supset K$. In generating the spectrum for a fixed $SO(n_1) \oplus SO(n_2)$ irrep, the Lie algebra $K$ will not play any role. Numerical examples for QPT (also EQPT) are shown in Figs. 2 and 3 for some general two level models. See [28–30] for details of the results in the figures.

Besides describing single benders, using coupled $U(3)$ algebras it is possible to study various structures generated by coupled benders in tetra-atomic molecules. Associating a $U(3)$ for each bender we have $U_1(3) \oplus U_2(3)$ SGA with large number of subalgebra chains preserving boson numbers $N_1$ and $N_2$ and the total $\ell = \ell_1 + \ell_2$ quantum number. At the first level, the subalgebras are $U_1(2) \oplus U_2(2)$, $SO_1(3) \oplus SO_2(3)$, $U_{12}(3)$ and $U_1(2) \oplus SO_2(3)$. The $U_1(2) \oplus U_2(2)$ admits $U_{12}(2)$ and $SO_1(2) \oplus SO_2(2)$ subalgebras, $SO_1(3) \oplus SO_2(3)$ admits $SO_{12}(3)$ and $SO_1(2) \oplus SO_2(2)$ subalgebra [the later also appears in $U_1(2) \oplus SO_2(3)$] and finally $U_{12}(3)$ admits $U_{12}(2)$ and $SO_{12}(3)$ subalgebras. All these will have the final subalgebra $SO_{12}(2)$. It is possible to write the generators of all these algebras and also one and two-body operators that preserve $N$ and $\ell$. Extending the algebras described before for one bender, it is possible to construct the $H$ matrix for the coupled benders systems. However, a simple Hamiltonian describing the various structures is of the form $H = H_1 + H_2 + V_{12}$ with $H_i$ same as discussed above for one bender and $V_{12}$ contains, $(P_{12})(P_{12})^\dagger$, $\hat{W}_1 \cdot \hat{W}_2$, the quadratic
Casimir invariant of $SU_{12}(3)$ or equivalently the Majorana operator $M_{12}$ and so on. See [7, 31] for further mathematical details and applications to $C_2H_2$ and $H_2CO$ molecules.

**APPENDIX B**

Symmetry mixing Hamiltonians generating regular spectra

Given the two symmetry limits (i) $U(4) \supset SO(4) \supset SO(3)$ and (ii) $U(4) \supset [SU(3) \supset SO(3)] \oplus U(1)$ for diatomic molecules, general two-body Hamiltonian mixing these two symmetry limits is,

$$H_{mix} = \alpha_0(N) + \alpha_1 C_1(U(1)) + \alpha_2 C_2(SO(4)) + \alpha_3 C_2(SU(3)) + \alpha_4 C_2(SO(3)).$$  \hspace{1cm} (B-1)

Note that $\alpha_0(N)$ is a quadratic polynomial in $N$. More importantly, $\alpha_2 = 0$ will give limit (ii) and $\alpha_1 = \alpha_3 = 0$ will give limit (i). However, even when $\alpha_1, \alpha_2, \alpha_3 \neq 0$, it is possible to produce a regular spectrum. This is due to the existence of $SO(4)$ generated by $L^1_q$ and $D^1_\mu = (\pi^\dagger s - s^\dagger \tilde{\pi})^1_\mu$ mentioned in Section II. Note that both $C_2(SO(4))$ and $C_2(SO(4))$ generate the same spectrum with eigenvalues $\omega(\omega + 2)$. These operators are given by,

$$C_2(SO(4)) = 4 (\pi^\dagger \tilde{\pi})^1 \cdot (\pi^\dagger \tilde{\pi})^1 - 2 [\pi^\dagger s \cdot s^\dagger \tilde{\pi} + s^\dagger \tilde{\pi} \cdot \pi^\dagger s].$$ \hspace{1cm} (B-2)

Using the results that $ss^\dagger = (n_s + 1)$ and $\tilde{\pi} \cdot \pi^\dagger = -(3 + n_\pi)$ we have,

$$C_2(\overline{SO(4)}) = -C_2(SO(4)) + 4(N - 1)n_\pi - 4n_\pi^2 + 6N + 2C_2(SO(3)).$$ \hspace{1cm} (B-3)

As $C_1(U(1)) = n_s = N - n_\pi$ and $C_2(SU(3)) = n_\pi(n_\pi + 3)$, clearly for a particular choice of the parameters in Eq. (B-1), $H_{mix}$ can be reduced to $C_2(\overline{SO(4)})$ and hence solvable (generates a regular spectrum). For details of the significance of this result for order-chaos transitions and quantum phase transitions, see [23, 32]. It is also important to add that the occurrence of multiple pairing algebras, as seen from the $U(3)$ model discussed in Appendix A, is a general feature of both fermion and boson systems with two or more levels or orbits and they play an important role in QPT and EQPT; see [30].
APPENDIX C

Partition functions for diatomic and triatomic molecules

Starting with the energy formula given by Eq. (2), it is possible to derive a simple formula for the partition function \( Z(\beta) = Tr(\exp{\beta E}) \) for diatomic molecules in the \( SO(4) \) \([U(4) \supset SO(4) \supset SO(3) \supset SO(2)]\) limit. Using Eq. (2) for the eigenvalues and the allowed quantum numbers, we have

\[
Z_{SO(4)}(\beta) = Z_0 \sum_{v=0}^{[N/2]} \sum_{L=0}^{N-2v} (2L + 1) \exp{ -\beta \{ A(N + 1)v - Av^2 + BL(L + 1) \} } .
\]

(C-1)

Note that \( A = -4\alpha \) and \( B = \beta; \alpha \) and \( \beta \) are defined in Eq. (2). In addition, \( Z_0 \) is a constant. Clearly, with \( A > 0 \) and \( B > 0 \) the ground state is \( |N, v = 0, L = 0\rangle \). With \( N \to \infty \) and \( \sigma = 1/(2\beta B)^{1/2} >> 1 \), \( Z(\beta) \) takes the simpler form

\[
Z_{SO(4)}(\beta) \xrightarrow{N \to \infty, \sigma >> 1} Z_0 (2\sigma^2) (1 - \exp{ -\beta(AN)})^{-1} = Z_0 Z_{rot}(\beta) Z_{vib}(\beta) .
\]

(C-2)

Note that \( Z_{rot}(\beta) = 2\sigma^2, Z_{vib}(\beta) = (1 - \exp{ -\beta(AN)})^{-1} \) and \( \sigma^2 = 1/(2\beta B) \). The decomposition of \( Z_{SO(4)}(\beta) \) into a product of \( Z \)'s for the rotational and vibrational parts is similar to the decomposition obtained before in the interacting boson model of atomic nuclei [33].

A different formula, in the limit \( \beta \to 0 \), is given by

\[
Z_{SO(4)}(\beta) \xrightarrow{\beta \to 0} Z_0 \int_0^{N/2} dv \int_0^{N-2v} dL(2L + 1) \exp{ -\beta \{ A(N + 1)v - Av^2 + BL(L + 1) \} } = Z_0 \frac{1}{B\beta} \int_0^{N/2} dv \left[ 1 - \exp{ -\beta B(N - 2v)(N - 2v + 1) } \right] \exp{ -\beta \{ A(N + 1)v - Av^2 \} } .
\]

(C-3)

The last integral here can be written in terms of error functions; see also [34]. Let us add that more accurate formulas for \( Z_{SO(4)}(\beta) \) can be derived using Euler-Maclaurin summation formula.

The other symmetry limit, for diatomic molecules, starting with \( U(4) \) is \( U(4) \supset [SU(3) \supset SO(3) \supset SO(2)] \oplus U(1) \) with basis states \(|N, n_\pi, L, M\rangle \) where \( N \to n_\pi = 0, 1, \ldots, N \) and \( n_\pi \to L = n_\pi, n_\pi - 2, \ldots, 0 \) or 1. Now, the Hamiltonian and the partition function in this
$SU(3)$ limit are

\[
H = E_0'' + A_1 C_1(U(3)) + A_2 C_2(SU(3)) + A_3 L(L+1),
\]

\[
Z_{SU(3)}(\beta) = Z_0 \sum_{\pi=0}^{N} \sum_{L=\pi}^{N} (2L + 1) \exp - \beta \{ A_1 n_\pi + A_2 n_\pi (n_\pi + 3) + A_3 L(L+1) \}.
\]  

(C-4)

Note that with $A_1 > 0$, $A_2 << A_3$ and $A_3 > 0$, the ground state is $|N, n_\pi = 0, L = 0\rangle$. In the symmetry limit it is a good approximation to assume $A_2, A_3 \simeq 0$. Then we have,

\[
Z_{SU(3)}(\beta) = Z_0 \sum_{\pi=0}^{N} \frac{(n_\pi + 1)(n_\pi + 2)}{2} \exp - \beta(A_1 n_\pi) = Z_0 (1 - \exp - \beta A_1)^{-2}.
\]  

(C-5)

In addition, it is also possible to derive a formula for $Z_{SU(3)}(\beta)$ in the $\beta \to 0$ limit in terms of error functions.

Turning to tri-atomic molecules, using the energy formula given by Eq. (5) and the associated quantum numbers (see Section III), it is possible to derive a formula for the partition function $Z_{\text{local-}SO_{12}(4)}(\beta)$ in the local basis symmetry limit $U_1(4) \oplus U_2(4) \supset SO_1(4) \oplus SO_2(4) \supset SO_{12}(4) \supset SO(3)$. In the limit $N_1 \to \infty$, $N_2 \to \infty$, $a_{12} \sim 0$ and $\sigma >> 1$ ($a_{12}$ is the strength of $C_2(SO_{12}(4))$ and $\sigma^2 = 1/2 \beta d$ where $d$ is the strength of $L(L+1)$ term), the energy formula given by Eq. (5) reduces to the form $E(N_1, N_2, v_1, v_2, v_3, L) = e_0 + e_1 v_1 + e_2 v_2 + e_3 v_3 + dL(L+1)$. Then $Z(\beta)$ is,

\[
Z_{\text{local-}SO_{12}(4)}(\beta) = Z_0 \sum_{v_1, v_2, v_3=0}^{\infty} \sum_{\ell_2 \in \ell_2} \sum_{L} (2L + 1) \exp - \beta \{ e_1 v_1 + e_2 v_2 + e_3 v_3 + dL(L+1) \}.
\]  

(C-6)

The $L$ integration gives $2\sigma^2$ for $\ell_2 = 0$ and $2(2\sigma^2)$ for $\ell_2 \neq 0$; see Eq. (4) for $\tau_2 = \ell_2 \to L$ and the doubling for $\ell_2 \neq 0$. Combining this with the $v_2 \to \ell_2$ reductions ($v_2 = 0 \to \ell_2 = 0$, $v_2 = 1 \to \ell_2 = 1$, $v_2 = 2 \to \ell_2 = 0, 2$, $v_2 = 3 \to \ell_2 = 1, 3$, $v_2 = 4 \to \ell_2 = 0, 2, 4, \ldots$) will allow us to carry out the $\ell_2$ summation in Eq. (C-6) giving,

\[
Z_{\text{local-}SO_{12}(4)}(\beta) = (2\sigma^2) \sum_{v_1, v_2, v_3=0}^{\infty} (v_2 + 1) \exp - \beta(e_1 v_1 + e_2 v_2 + e_3 v_3)
\]  

(C-7)

\[
= (2\sigma^2) (1 - \exp - \beta e_1)^{-1} (1 - \exp - \beta e_3)^{-1} (1 - \exp - \beta e_2)^{-2}.
\]

Further improvements of the formula for $Z_{\text{local-}SO_{12}(4)}(\beta)$ are possible. Also, in future it is important to derive the formulas for $Z(\beta)$ for the other symmetry limits of the $U_1(4) \oplus U_2(4)$
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