A NEW APPROACH to ANALYSE $H \otimes (2h \oplus g)$ JAHN-TELLER SYSTEM for $C_{60}$

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It is now well known that electron (hole)-vibron coupling and hence Jahn-Teller (JT) effect is important understanding the properties of $C_{60}$ and related molecules. In this paper, we study $H \otimes (2h \oplus g)$ coupling case to find the potential energy surfaces for the positively charged $C_{60}$ molecule due to distortion. The $H \otimes (2h \oplus g)$ Jahn-Teller system is of particular importance as this will be the JT effect displayed by $C_{60}$ molecules removed with an electron. $C_{60}^{+}$ is obtained by removing one electron from fivefold degenerate Hu highest occupied molecular orbital (HOMO) and a hole in HOMO interacts with the vibrational modes of $C_{60}$ and symmetry is broken. We apply the method of symmetry breaking mechanism to obtain expressions for the potential energy surface.

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INTRODUCTION

Except at absolute zero in temperature, all atoms and molecules have energy and vibrate. The electrons in $C_{60}$ molecule will be sensitive to these vibrations. It is believed that this vibronic coupling plays an important role in determining the behaviour of $C_{60}$ molecules and related fullerene compounds.

The symmetry group of $C_{60}$ molecule is icosahedral ($I_h$). This symmetry group implies large representations, thus large degeneracies of the interacting electronic and vibrational states of isolated ion. Icosahedral symmetry is extremely rare in nature, vibronic coupling effects have not been investigated in this symmetry until very recently. Many interesting effects due to vibronic coupling are possible from a theoretical point of view due to quantum-mechanical four and five-fold degenerate states. The ground state of pure $C_{60}$ molecule is singlet $A_g$ state, so it is not very sensitive to JT effect. However, the ground state of $C_{60}^{+}$ and $C_{60}^{-}$ states do potentially strong effects. Ionic form of $C_{60}$ molecule is subject to the Dynamical Jahn-Teller effect (DJT). The Dynamical Jahn-Teller effect is closely related to, but should be distinguished from the static Jahn-Teller effect, where there is a permanent symmetry breaking molecular distortion or instability to one of the potential-well minima, removing all or part of orbital degeneracy. JT effect is also important from experimental point of view. Most workers agree that electron-vibron interactions are very important for many properties of fullerenes and may explain superconductivity. It is known that origin of superconducting pairing in $C_{60}$ compounds is due to interaction of electrons with vibronic modes of $C_{60}$ molecule.

In the general formalism of the JT effect, a degenerate electronic state corresponding to a representation of $D$ of symmetry group $G$ of the molecule can interact with the vibrational modes corresponding to representations contained in the symmetric part of the direct product $D \otimes D$ (excluding the identical representation which is trivial). As it is well known, the molecular symmetry reduced by the JT distortion with splitting of the electronic-state degeneracy. The distorting forces acting along a certain non-totally vibrational modes carry the nuclei over into distorted configurations. Distorted configuration of a molecule can be characterised by subgroup symmetries of parent molecular group.

In general, a physical system may pass from a symmetric to less symmetric state, during its evolution. This symmetry transition is known as spontaneously symmetry breaking [6,7]. The process of symmetry breaking applies to all domains described by expectation values of operators. This common mathematical technique can be applied successfully to different domains of physics because they all share in the occurrence of broken symmetry.

In order to study the JT structure of $A_2C_{60}$ and/or $C_{60}^{\pm}$ various theoretical approaches have been used. Ceuleman has proposed on analytical treatment of JT distortion in the general case of a fivefold degenerate state of an $I_h$ molecule. The extreme points were identified by using the isostationary function and epikernel methods [1,2]. First order JT interaction and its continuous group invariance were discussed and the energies were found for JT coupling with and without splitting [3]. The ground state Berry phase of some JT systems were calculated in the five dimensional rotation group SO(5) [4]. Classical and semi-classical models were introduced about JT manifold for electron vibron interactions, by Auerback, Manini and Tosatti [5]. The $H \otimes (h \oplus g)$ problem is investigated analytically using a unitary transformation by C.P Moate, J.L Dunn et al. [12].

The present paper provides a group theoretical treatment of JT distortion in general case of a fivefold degenerate
state of \(I_h\) molecule. The JT surface energies have been obtained by breaking symmetries of \(I_h\) group into its maximal little group. This is never done before.

**SYMMETRY ASPECTS AND COUPLING OF STATES**

In this section, we start by describing the Hamiltonian that generates DD surface where D denotes the irreducible representation. The standard Hamiltonian may be written in the form

\[
H = H_0 + H_{JT}; \quad H_0 = \frac{1}{2} \hbar \sum_i (P_i^2 + Q_i^2)
\]

where \(H_0\) describes free (uncoupled) electrons/holes and vibrations and \(Q_i\) is the distortion coordinate and \(P_i\) is the conjugate momentum. In general, \(H_{JT}\) introduces a rotationally invariant linear coupling between the electronic state and the vibrational mode. It is known that the Hamiltonian for a linear JT coupling of \(H \otimes (2h \oplus g)\) system is invariant under the rotational operations of \(I_h\) group. If either the restriction of linear coupling or harmonic forces is relaxed, the symmetry of Hamiltonian is reduces to point group \(G\).

As we have mentioned above, totally symmetric part of direct product of an irreducible representation of a finite group, which describes the properties of JT surfaces, is written in the form of

\[
[D^\ell \otimes D^\ell] = D^{\ell_1} \oplus D^{\ell_2} \oplus \cdots \oplus D^{\ell_n}
\]

where \(\ell\) is the angular momentum quantum number. Decomposition of \([D^\ell \otimes D^\ell]\) implies that the JT Hamiltonian can be written in the following way

\[
H_{JT} = H^{\ell_1} + H^{\ell_2} + \cdots + H^{\ell_n}
\]

where \(H^{\ell}\) is the JT Hamiltonian and it is invariant under the symmetry operations of corresponding finite group, for the \(2\ell+1\) dimensional representation. Since the \(I_h\) group is subgroup of \(O(3)\), decomposition of coupling of two states should be written in terms of

\[
[D^2 \otimes D^2] = D^0 \oplus D^2 \oplus D^4
\]

Therefore, symmetric part of the five dimensional direct product for \(I_h\) group can be written in the notation of icosahedral molecule:

\[
[H_u \otimes H_u] = [H_u^2] = [H_g^2] = A_g \oplus H_g \oplus (G_g \oplus H_g)
\]

where \(A_g, G_g\) and \(H_g\) are one, four and five dimensional irreducible representations of \(I_h\), respectively. The decomposition of direct product of \([H_u \otimes H_u]\) coupling in \(O(3)\) is found using the Table 1 and is in the form

\[
H_{JT} = H^0 + H^2 + H^4
\]

where the superscripts 2 and 4 are \(\ell\) values. The symmetric part contains the totally symmetric representation \(H_0 = A_g\) that is trivial polaronic problem \([9,10]\) and it can be solved, exactly. The \(H_0\) vibration shift energies but it does not cause splitting. Remaining vibrations subtend the configuration space, which contains all distorted configurations, may be reached by JT active coordinates. As shown from Table 1, the Hamiltonian \(H_2\) corresponds five dimensional representations \(H_g\) and \(H_4\) corresponds to the direct sum of \(G_gH_g\) vibrational levels.

**DETERMINATION OF STATIONARY POINTS ON JT SURFACE USING LITTLE GROUPS OF ICOSAHEDRAL**

The second important aspect of invariant polynomial functions, in addition to, linear Jahn-Teller matrices, concerns the extremum points on JT surface. Since our interest are the minimal points and the saddle points, the present section is devoted to the determining of extremum points on JT surface by breaking symmetries of icosahedral group into its maximal little groups. The problem has been studied by Ceulemans by using the isostationary function \([1]\).
TABLE I: The representations of the $O(3)$ group with $\ell <$14 are split by the icosahedral point group.

| $I_h$ | $I_h$ |
|-----------------|-----------------|
| $0 \, A_g$ | $7 \, T_{1u} + T_{2u} + G_u + H_u$ |
| $1 \, T_{1u}$ | $8 \, T_{2g} + G_u + H_y + H_y$ |
| $2 \, H_u$ | $9 \, T_{1u} + T_{2u} + G_u + G_u + H_u$ |
| $3 \, G_u + T_{2u}$ | $10 \, A_g + T_{1g} + T_{2g} + G_g + 2H_y$ |
| $4 \, G_g + H_y$ | $11 \, 2T_{1u} + T_{2u} + G_u + 2H_u$ |
| $5 \, T_{1u} + T_{2u} + H_u$ | $12 \, A_g + T_{1g} + T_{2g} + 2G_g + 2H_g$ |
| $6 \, A_g + T_{1g} + G_g + H_g$ | $13 \, T_{1u} + 2T_{2u} + 2G_u + 2H_u$ |

TABLE II: Maximal Little groups of $H$ and $G$ representations. Decomposition implies that $T$ is not maximal little group of $H$ state, and $D_5$ is not maximal little group for $G$ state.

The little group is the new symmetry group of distorted molecule as a result of coupling. A real representation of any subgroup $S < G$; the degree of subduction can be computed by the relation

$$C_\ell(S) = \frac{1}{S} \sum_{p \in S} \chi_z(p)$$

(7)

where $\chi_z(p)$ is the character of the representation $p$. In a $z$th representation of finite group, if all subgroups $S > S$ and $C(S) < C(S)$ then $S$ is little group of $G$. For finite groups converse of this definition is also true. In order to simplify the notation, we shall switch from $O(3)$ to the $SO(3)$ notation, omitting therefore the $g/u$ symbol for inversion. Then, the electronic–vibrational coupling is symbolized as $H \otimes (2h \oplus g)$ where capital letter shows electronic and small letters show the vibrational levels. Without loss of generality the problem for $I_h$ group can be treated equally well in the subgroup of proper rotations of group $I$. The maximal little subgroups of $I$ group have computed by using Eqn.(7) and are given in Table 2. As seen from Table 2, the maximal little groups predict the existence of dihedral groups $D_3, D_5$, and $D_2$ minima on the icosahedral molecular cage. In the coordinate space the distortion that is the result of JT instability should conserve all maximal little group symmetry.

In our perspective the structure of Jahn-Teller surfaces have been identified by the symmetry breaking of the continuous symmetry to the true finite point group of the representation space and its maximal little groups. This may be represented as follows

$$I \rightarrow S'$$

(8)

where $S'$ are little groups of $I$ group given in Table 2.

GROUP INVARIANCE OF JAHN-TELLER SYSTEMS

As we stated in the previous section, the Hamiltonian of $H \otimes (2h \oplus g)$ coupling have three parts $H^0, H^2$ and $H^4$, which must be separately invariant under $I$ symmetry. In this section, we want to construct a polynomial function in electronic and nuclear configuration space, to examine symmetry properties of potential energy surface. A polynomial function which have been produced for this purpose is in the form

$$U_{lm}(X, Q) = \sum_{i,j=1}^{2\ell+1} \sum_{k=1}^{2m+1} F_{ijk}X_iX_jQ_k.$$  

(9)

In this expression $X_i$ and $X_j$ correspond to electronic coordinates $Q_k$ corresponds to nuclear coordinates. The force elements or coupling coefficients should be chosen appropriately for each $H \otimes h$ and $H \otimes (h \oplus g)$ coupling. In the
Eqn.(9) the indices $2\ell + 1$ and $2m + 1$ stand for dimensions electronic and active coordinates, respectively. For $H \otimes h$ coupling $\ell$ and $m$ take value 2 and for $H \otimes (h \oplus g)$ case $\ell$ and $m$ take values 2 and 4 respectively.

We will focus our treatment for the computation of invariant polynomials for $H \otimes h$ and $H \otimes (h \oplus g)$ problems. The invariant polynomial function for $\ell = 2$, in real basis has been computed using the matrix representations of $H$ state which are given in Appendix. The $5 \times 5$ generators transform electronic coordinates $X_i (i = 1, \cdots, 5)$ and nuclear coordinates $Q_j$. It can be written in the form

$$\sum_{i,j=1}^{5} \sum_{k=1}^{5} F_{ijk} X_i X_j Q_k = \sum_{i,j=1}^{5} \sum_{k=1}^{5} F_{ijk} X'_i X'_j Q'_k. \quad (10)$$

In this equation, $X_i = \sum_{n=1}^{5} \Gamma^r_{in} X_n$ and $Q'_k = \sum_{n=1}^{5} \Gamma^r_{in} Q_n$. $\Gamma^r_{in}$ is the matrix elements of $5 \times 5$ generators of $I$. The Eqn.(10) is solved for $F_{ijk}$ and two linearly independent polynomial function have been obtained. One of our main goal that first order JT interaction matrices can be derived by working out invariant polynomial function. The double differentiation of $U_{22}(X,Q)$ with respect to electronic coordinates $X_i$ and $X_j$ produce linear JT interaction matrix.

In general, we can write

$$\left( B_m \right)_{ij} = \frac{\partial^2 U_{2m}}{\partial X_i \partial X_j}, \quad (i, j = 1, 2 \cdots 5). \quad (11)$$

The JT interaction matrix for $H \otimes h$ coupling is

$$B_2 = F_1 \begin{pmatrix} 2Q_5 & 0 & -\sqrt{3}Q_3 & \sqrt{3}Q_4 & 2Q_1 \\ 0 & 2Q_5 & -\sqrt{3}Q_4 & -\sqrt{3}Q_3 & 2Q_2 \\ -\sqrt{3}Q_4 & -\sqrt{3}Q_3 & -\sqrt{3}Q_2 & \sqrt{3}Q_1 & -Q_5 & -Q_4 & -Q_3 \\ 2Q_1 & 2Q_2 & -Q_3 & -Q_4 & -Q_5 \end{pmatrix} + \begin{pmatrix} \sqrt{15}Q_1 - \frac{\sqrt{3}}{2}Q_4 + \frac{\sqrt{5}}{2}Q_5 \\ -\sqrt{15}Q_1 + \frac{\sqrt{3}}{2}Q_4 + \frac{\sqrt{5}}{2}Q_5 \\ -\sqrt{3}Q_1 - 3Q_5 \\ \frac{\sqrt{3}}{2}Q_1 - 3Q_4 \\ \frac{\sqrt{3}}{2}Q_2 - 3Q_3 \end{pmatrix} \begin{pmatrix} \sqrt{15}Q_2 & -\sqrt{15}Q_2 \sqrt{3}Q_5 & \sqrt{3}Q_1 & -3Q_5 & \sqrt{3}Q_2 & -3Q_2 - 3Q_3 & \sqrt{3}Q_1 - 3Q_4 \\ \frac{\sqrt{3}}{2}Q_1 - 3Q_4 & \sqrt{3}Q_2 - 3Q_3 & -2\sqrt{3}Q_4 - \sqrt{5}Q_5 & -2\sqrt{3}Q_3 & -2\sqrt{3}Q_3 & -2\sqrt{3}Q_3 & -3Q_2 - \sqrt{3}Q_5 \end{pmatrix} \begin{pmatrix} \sqrt{15}Q_2 & -\sqrt{15}Q_2 \sqrt{3}Q_5 & \sqrt{3}Q_1 & -3Q_5 & \sqrt{3}Q_2 & -3Q_2 - 3Q_3 & \sqrt{3}Q_1 - 3Q_4 \\ \frac{\sqrt{3}}{2}Q_1 - 3Q_4 & \sqrt{3}Q_2 - 3Q_3 & -2\sqrt{3}Q_4 - \sqrt{5}Q_5 & -2\sqrt{3}Q_3 & -2\sqrt{3}Q_3 & -2\sqrt{3}Q_3 & -3Q_2 - \sqrt{3}Q_5 \end{pmatrix} \quad (12)$$

The force elements $F_1$ and $F_2$ are given by

$$F_1 = \frac{1}{135\sqrt{3}}(-13\sqrt{5}F_{H1} + 15F_{H2}); \quad F_2 = \frac{1}{27\sqrt{15}}(\sqrt{5}F_{H1} + 3F_{H2}) \quad (13)$$

In this equation $F_{H1}$ and $F_{H2}$ are coupling parameters of $H$ mode. The invariant polynomial function is derived for $H \otimes (h \oplus g)$ as in the same way $H \otimes h$. In this case Eqn.(10) takes form

$$\sum_{i,j=1}^{5} \sum_{k=1}^{5} F_{ijk} X_i X_j Q_k = \sum_{i,j=1}^{5} \sum_{k=1}^{5} F_{ijk} X'_i X'_j Q'_k. \quad (14)$$

Nine dimensional $H \otimes (h \oplus g)$ state consists of one $H$ mode with components $\{Q_1, Q_2, Q_3, Q_4, Q_5\}$ and $G$ mode with components $\{Q_6, Q_7, Q_8, Q_9\}$. The icosahedral generators transform the electronic and nuclear coordinates. Transformation $X_i$ and $X_j$ are same as given in Eqn.(10). The nuclear coordinates $Q_k$ is transformed as $Q'_k = \sum_{n=1}^{9} \Lambda^r_{in} Q_n$, where $\Lambda^r$ is the direct sum of $5$ and $4$ dimensional irreducible matrix generators $\Gamma$ and $\Lambda$ given in Appendix, respectively. Solution of the Eqn.(14) for coefficients $F_{ijk}$ gives that three linearly independent function. In Ceulemans’s paper [1], relations between polynomial coefficients $F_{ijk}$ in Eqn(10) and Eqn(14) are expressed in terms of Clebsch Gordon series for the icosahedral point group [13]. The linear JT interaction matrices for this coupling are derived
from the relation (11). The two of them are same with matrices of $H \otimes h$ coupling and third one is

$$F_3 = \begin{pmatrix} -Q_6 - 2\sqrt{5}Q_8 & 2\sqrt{5}Q_7 & \frac{2}{\sqrt{5}}Q_7 - \frac{9\sqrt{5}}{2}Q_9 & -\frac{5\sqrt{5}}{2}Q_6 - \frac{1}{2}Q_8 & -\frac{3\sqrt{5}}{2}Q_8 \\ 2\sqrt{5}Q_7 & Q_0 + 2\sqrt{5}Q_8 & -\frac{5\sqrt{5}}{2}Q_6 + \frac{1}{2}Q_8 & \frac{4}{\sqrt{5}}Q_7 + \frac{3\sqrt{5}}{2}Q_9 & \frac{5\sqrt{5}}{2}Q_7 \\ \frac{2}{\sqrt{5}}Q_7 - \frac{9\sqrt{5}}{2}Q_9 & -\frac{5\sqrt{5}}{2}Q_6 + \frac{1}{2}Q_8 & \sqrt{5}Q_7 & 4Q_6 + \sqrt{5}Q_8 & \sqrt{5}Q_7 \\ -\frac{3\sqrt{5}}{2}Q_8 & \frac{4}{\sqrt{5}}Q_7 + \frac{3\sqrt{5}}{2}Q_9 & \frac{5\sqrt{5}}{2}Q_7 & 4Q_6 - \sqrt{5}Q_8 & -\frac{3\sqrt{5}}{2}Q_8 \\ \sqrt{5}Q_8 & 4Q_6 + \sqrt{5}Q_8 & -\frac{5\sqrt{5}}{2}Q_7 & \sqrt{5}Q_8 & \sqrt{5}Q_8 \end{pmatrix}.$$ (15)

The sum of the $B_2$ given in Eqn.(12) and JT interaction matrix given in Eqn.(15) corresponds to the first order JT interaction matrix ($B_4$) for $H \otimes (h \oplus g)$ coupling. It is obvious that the interaction matrix is also obtained by considering only $H \otimes g$ coupling. Force element $F_3$ is related by coupling parameter of $G$ mode and is given by $F_3 = F_G/9$. The first order linear JT interaction matrices for $H$ state have been found in [14] and are in agreement with our results. We guess that the higher order JT interaction matrices may be obtained by constructing higher order icosahedral invariant polynomials.

In section 4.1, symmetry of icosahedral is broken into its little groups for $H \otimes h$ and $H \otimes (h \oplus g)$. Combination of eigenvalues of the $B_m$ with harmonic potential energy, in terms of little groups yield JT surface energy.

**TRANSITIONS ASSOCIATED WITH H \otimes h AND H \otimes (h \oplus g) COUPLINGS**

The five dimensional irreducible representation of I group has three maximal little group named $D_2$, $D_3$ and $D_5$. In order to break symmetry of a parent group into its little groups, one should assign an appropriate $Q_i$ which can be computed by constructing set of equations such that

$$Q_i = \sum_{j=1}^{2\ell+1} \Gamma_{ij}Q_j \quad (16)$$

where $\Gamma_{ij}$ is the matrix elements of generator of the corresponding little group. The method of symmetry breaking predicts the existence of saddle points, trigonal and pentagonal turning points on JT surfaces associated with $D_2$, $D_3$ and $D_5$ groups. From the solution of Eqn.(16) it is found that two $H$ type coordinates $Q_{H1}, Q_{H2}$ and one $G$ type coordinate $Q_{G}$. The $H$ and $G$ type coordinates are constrained to $Q_4 = -\tau Q_{H1}, \quad Q_5 = -\sqrt{\frac{5}{3}}Q_{H2}, \quad Q_6 = Q_{G}$, where $\tau = \frac{1}{2}(1 + \sqrt{5})$. Under the given conditions; the energy eigenvalues of each little group are computed.

**4.1.1 D_2 TRANSITION**

Decomposition of five dimensional representations in $D_2$ group is $2A + B_1 + B_2 + B_3$. The symmetry of the group $I$ is broken into $D_2$, assigning as $Q_1 \rightarrow \sqrt{5}Q_4 - \sqrt{3}Q_5, \quad Q_2 \rightarrow 0, \quad Q_3 \rightarrow 0, \quad Q_4 \rightarrow Q_4, \quad Q_5 \rightarrow Q_5$, using the Eqn.(16). After substituting values of $Q_i$ into $B_2$, the eigenvalues of $B_2$ are carried out. Combinations of eigenvalues of $B_2$ with harmonic restoring potentials for the distortional coordinates $Q_{H1}$, and $Q_{H2}$ gives JT surface energy values.

$$E(A) = \pm \frac{1}{2}\sqrt{10} [ (3F_{H1}^2 + F_{H2}^2)(2\tau^2Q_{H1}^2 - 5\tau Q_{H1}Q_{H2} + 5Q_{H2}^2) ] + \frac{1}{2}K_H(Q_{H1}^2 + Q_{H2}^2)$$

$$E(B_1) = \frac{1}{4\sqrt{5}}(F_{H1} + F_{H2})(4\tau Q_{H1} - 5Q_{H2}) + (F_{H1} - 3F_{H2})\sqrt{5}Q_{H2} + \frac{1}{2}K_H(Q_{H1}^2 + Q_{H2}^2)$$

$$E(B_2) = \frac{1}{4\sqrt{5}}(F_{H2} - F_{H1})(4\tau Q_{H1} - 5Q_{H2}) + (F_{H1} + 3F_{H2})\sqrt{5}Q_{H2} + \frac{1}{2}K_H(Q_{H1}^2 + Q_{H2}^2)$$

$$E(B_3) = \frac{1}{\sqrt{5}}(2\tau F_{H1}Q_{H1} - \frac{1}{2}(F_{H1} - \sqrt{5}F_{H2})Q_{H2} + \frac{1}{2}K_H(Q_{H1}^2 + Q_{H2}^2).$$ (17)

In this equation, $K_H$ is the harmonic force constant. The energy values of $E(A)$ predicts the existence of saddle points.

The direct sum of $g$ and $h$ states consists of both $G$-type and $H$-type nuclear coordinates. For this reason, computations are more complicated than the $h$ state. In this case, there are three distortional coordinates that are invariant under $D_2$. In Eqn.(16) nine dimensional matrix generators which have been obtained by taking direct sum
of five and four dimensional representations are used to assign \( Q \) values. It is found that \( Q_1 \to \sqrt{5}Q_4 - \sqrt{3}Q_5, Q_2 \to 0, Q_3 \to 0, Q_4 \to Q_1, Q_5 \to Q_5, Q_6 \to Q_6, Q_7 \to 0, Q_8 \to \sqrt{5}Q_6, Q_9 \to 0 \). In this basis, combination of eigenvalues of \( B_4 \) with harmonic potential gives us

\[
E(A) = \pm \frac{1}{2\sqrt{10}} \left[ (3F^2_{H1} + F^2_{H2})(2\tau^2Q^2_{H1} - 5\tau Q_{H1}Q_{H2} + 5Q^2_{H2}) \right]^{\frac{1}{2}} + \frac{3}{8}F_GQ_G + \frac{1}{2}K_GQ_G^2 + \frac{1}{2}K_H(Q^2_{H1} + Q^2_{H2})
\]

\[
E(B_1) = \frac{1}{4\sqrt{5}}(F_{H1} + F_{H2})(4\tau Q_{H1} - 5Q_{H2}) + (F_{H1} - 3F_{H2})\sqrt{5}Q_{H2} - \frac{1}{4}F_GQ_G + \frac{1}{2}K_GQ_G^2 + \frac{1}{2}K_H(Q_{H1}^2 + Q_{H2}^2)
\]

\[
E(B_2) = \frac{1}{4\sqrt{5}}(F_{H2} - F_{H1})(4\tau Q_{H1} - 5Q_{H2}) + (F_{H1} + 3F_{H2})\sqrt{5}Q_{H2} - \frac{1}{4}F_GQ_G + \frac{1}{2}K_GQ_G^2 + \frac{1}{2}K_H(Q_{H1}^2 + Q_{H2}^2)
\]

\[
E(B_3) = -\frac{1}{\sqrt{5}}(F_{H1}22Q_{H1} - \frac{1}{2}(F_{H1} - \sqrt{5}F_{H2})Q_{H2} - \frac{1}{4}F_GQ_G + \frac{1}{2}K_GQ_G^2 + \frac{1}{2}K_H(Q^2_{H1} + Q^2_{H2}),
\]  

(18)

where \( K_G \) in the Eqn.(18) is the harmonic force constant of \( G \) mode. It is obvious that the magnitude of splitting of energy values is increasing in \( hg \) state compared to \( h \) state.

### 4.1.2 \( D_3 \) TRANSITION

In this case decomposition of \( H \) representation of irreducible representations of \( D_3 \) is \( A_1 + 2E \) in \( D_3 \). Following the same procedure given in 4.1.1, symmetry of \( I \) group can be broken into \( D_3 \), in the directions, \( Q_1 \to 0, Q_2 \to 0, Q_3 \to 0, Q_4 \to 0, Q_5 \to Q_5, Q_6 \to Q_6, Q_7 \to 0, Q_8 \to 0, Q_9 \to 0 \). The computed energy values are given as

\[
E(A_1) = -\frac{2}{3}F_{H1}Q_{H2} + \frac{1}{2}K_HQ_{H2}^2
\]

\[
E_{\pm}(E) = \frac{1}{6}F_{H1}Q_{H2} \mp \sqrt{\left( \frac{F_{H1}}{3} \right)^2 + \left( \frac{F_{H2}}{2} \right)^2} Q_{H2} + \frac{1}{2}K_HQ_{H2}^2.
\]  

(19)

Transformation of nuclear coordinates for \( H \otimes (h \oplus g) \) state gives that \( Q_1 \to 0, Q_2 \to 0, Q_3 \to 0, Q_4 \to 0, Q_5 \to Q_5, Q_6 \to Q_6, Q_7 \to 0, Q_8 \to 0, Q_9 \to 0 \). The energy values consists of the two distortional coordinates, and therefore

\[
E(A_1) = -\frac{2}{3}(F_GQ_G + F_{H1}Q_{H2}) + \frac{1}{2}K_GQ_G^2 + \frac{1}{2}K_HQ_{H2}^2
\]

\[
E_{\pm}(E) = \frac{1}{6}(F_GQ_G + F_{H1}Q_{H2}) \mp \left[ \left( \frac{3}{2}F_{H1}Q_{H2} - \frac{5}{12}F_GQ_G \right)^2 + \frac{1}{4}F_{H2}Q_{H2}^2 \right]^{\frac{1}{2}} + \frac{1}{2}K_GQ_G^2 + \frac{1}{2}K_HQ_{H2}^2.
\]  

(20)

These energy values are in agreement with the energy values given in [1].

### 4.1.3 \( D_5 \) TRANSITION

In \( D_5 \) the quintet irreducible representation state reduces to \( A_1 + E_1 + E_2 \). Applying the same procedure as in the previous section, \( Q_i \) values are found as \( Q_1 \to -\frac{Q_4}{\sqrt{5}}, Q_2 \to 0, Q_3 \to 0, Q_4 \to 0, Q_5 \to \sqrt{5}Q_4 \). The corresponding energies are obtained as

\[
E(A_1) = -\frac{2}{\sqrt{5}}F_{H2}Q_{H1} + \frac{1}{2}K_HQ_{H1}^2
\]

\[
E(E_1) = \frac{1}{2}(-F_{H1} + \frac{1}{\sqrt{5}}F_{H2})Q_{H1} + \frac{1}{2}K_HQ_{H1}^2
\]

\[
E(E_2) = \frac{1}{2}(F_{H1} + \frac{1}{\sqrt{5}}F_{H2})Q_{H1} + \frac{1}{2}K_HQ_{H1}^2.
\]  

(21)

The calculations have been carried out for \( H \otimes (h \oplus g) \) coupling and same results have been obtained as expected.

Tetrahedral group (\( T \)) is also maximal little group of \( G \) representation of I group. In \( H \otimes (h \oplus g) \) coupling some energy values have been expected. Since (\( T \) is not little group of \( H \) representation. Thus in \( H \otimes h \) coupling energy
eigenvalues of $B_2$ is zero.\) Decomposition of $H$ state in $T$ group is $E + T$, and symmetry is broken according to the directions $Q_i \rightarrow -\sqrt{3}Q_i$, $Q_i \rightarrow 0$, $(i = 1, \ldots, 8)$. The corresponding eigenvalues of $B_4$ are $F_6Q_6$ and $-\frac{2}{3}F_6Q_6$, for $E$ and $T$ respectively.

In general, minimal energy values for each little group can be obtained from the given energy expressions.

## CONCLUSION

In summary, we have shown how the symmetry breaking method is applied for the determination of the potential energies of the $H \otimes (2h \otimes g)$ surface. In Ceulemans’ paper [1], these energies were found by the method of isostationary function and potential energies of $D_3$ and $D_5$ groups were investigated. In our work, all maximal little groups of icosahedral group are studied for the $H \otimes (h \otimes g)$ and $H \otimes h$ state. Splitting of energy levels of icosahedral system due to distortion is analysed and amazingly interesting that, there is a proper contribution on the connection between our method and method of isostationary function. This method can also be used for other distorted systems.

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## APPENDIX

Generators of $I$, $D_2$, $D_3$, $D_5$ and $T$ groups for $G_{a7}$ and $H$ representations

Four and five dimensional irreducible matrix generators of $I$ and its little groups can be generated from the matrices:

$\Omega^1, \Omega^2, \Gamma^1, \Gamma^2 \rightarrow I$,  $\Omega^3, \Omega^4, \Gamma^3, \Gamma^4 \rightarrow D_5$,  $\Omega^2, \Omega^1, \Gamma^2, \Gamma^4 \rightarrow D_3$  $\Omega^1, \Omega^4, \Gamma^1, \Gamma^4 \rightarrow D_2$,  $\Omega^2, \Omega^5, \Gamma^2, \Gamma^5 \rightarrow T$

\[
\Omega^1 = \frac{1}{3} \begin{pmatrix}
-2 & 0 & \sqrt{3} & 0 \\
0 & 0 & 0 & 3 \\
\sqrt{3} & 0 & 2 & 0 \\
0 & 3 & 0 & 0
\end{pmatrix}; \quad \Omega^2 = \frac{1}{2} \begin{pmatrix}
2 & 0 & 0 & 0 \\
0 & -1 & \sqrt{3} & 0 \\
0 & -\sqrt{3} & -1 & 0 \\
0 & 0 & 0 & 2
\end{pmatrix}
\]

\[
\Omega^3 = \frac{1}{6} \begin{pmatrix}
-4 & \sqrt{15} & -\sqrt{5} & 0 \\
-\sqrt{15} & -3 & \sqrt{3} & -3 \\
-\sqrt{5} & -\sqrt{3} & 1 & 3\sqrt{3} \\
0 & -3 & -3\sqrt{5} & 0
\end{pmatrix}; \quad \Omega^4 = \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & -1
\end{pmatrix}
\]

\[
\Omega^5 = \frac{1}{6\sqrt{3}} \begin{pmatrix}
\sqrt{3} & -3\sqrt{5} & \sqrt{15} & -3\sqrt{5} \\
-3\sqrt{5} & 0 & -6 & -3\sqrt{3} \\
\sqrt{15} & -6 & -4\sqrt{3} & 3 \\
-3\sqrt{3} & -3\sqrt{3} & 3 & -3\sqrt{5}
\end{pmatrix}; \quad \Gamma^1 = \frac{1}{9} \begin{pmatrix}
7 & 0 & 0 & 2\sqrt{5} & -2\sqrt{3} \\
0 & 3\sqrt{5} & -6 & 0 & 0 \\
0 & -6 & -3\sqrt{5} & 0 & 0 \\
2\sqrt{5} & 0 & 0 & -1 & 2\sqrt{15} \\
-2\sqrt{3} & 0 & 0 & 2\sqrt{15} & 3
\end{pmatrix}
\]

\[
\Gamma^2 = \frac{1}{2} \begin{pmatrix}
-1 & -\sqrt{3} & 0 & 0 & 0 \\
\sqrt{3} & -1 & 0 & 0 & 0 \\
0 & 0 & -1 & \sqrt{3} & 0 \\
0 & 0 & -\sqrt{3} & -1 & 0 \\
0 & 0 & 0 & 0 & 2
\end{pmatrix}
\]

\[
\Gamma^3 = \frac{1}{36} \begin{pmatrix}
7 - 9\sqrt{5} & -7\sqrt{3} - 3\sqrt{15} & 6\sqrt{3} - 2\sqrt{15} & 18 + 2\sqrt{5} & 4\sqrt{3} \\
7\sqrt{3} + 3\sqrt{15} & -21 + 3\sqrt{5} & -6 - 6\sqrt{3} & -6\sqrt{3} + 2\sqrt{15} & 12 \\
-6\sqrt{3} + 2\sqrt{15} & -6 - 6\sqrt{3} & 3 - 3\sqrt{3} & -6\sqrt{3} - 3\sqrt{15} & -12\sqrt{3} \\
18 + 2\sqrt{5} & 6\sqrt{3} - 2\sqrt{15} & \sqrt{3} + 3\sqrt{15} & -1 + 9\sqrt{5} & -4\sqrt{15} \\
4\sqrt{3} & -12 & 12\sqrt{3} & -4\sqrt{15} & 12
\end{pmatrix}
\]
\[ \Gamma^4 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \]

\[ \Gamma^5 = \frac{1}{12\sqrt{3}} \begin{pmatrix} \frac{11}{\sqrt{3}} - \sqrt{15} & 7 + \sqrt{5} & 10 + 2\sqrt{5} & -2\sqrt{\frac{5}{3}} + 2\sqrt{3} & 2 - 6\sqrt{3} \\ 7 + \sqrt{5} & -\sqrt{3} + \sqrt{15} & -2\sqrt{3} - 2\sqrt{15} & -14 + 2\sqrt{5} & -2\sqrt{3} - 2\sqrt{15} \\ 10 + 2\sqrt{5} & -2\sqrt{3} - 2\sqrt{15} & 7\sqrt{3} - \sqrt{15} & -1 - \sqrt{5} & -2\sqrt{3} + 2\sqrt{15} \\ -2\sqrt{\frac{5}{3}} + 2\sqrt{3} & -14 + 2\sqrt{5} & -1 - \sqrt{5} & \frac{10}{\sqrt{3}} + \sqrt{15} & -6 - 2\sqrt{5} \\ 2 - 6\sqrt{3} & -2\sqrt{3} - 2\sqrt{15} & -2\sqrt{3} + 2\sqrt{15} & -6 - 2\sqrt{5} & -4\sqrt{3} \end{pmatrix} \]

REFERENCES
1. A. Ceulemans, P.W. Fowler, J. Chem. Phys. 93, 1221 (1990).
2. A. Ceulemans, J. Chem. Phys. 87, 5374 (1987)
3. D. R. Pooler, J. Phys. C: Solid St. Phys. 13, 1029 (1980).
4. S.E. Apsel, C.C. Chancey, M.C.M O’Brien Phys. Rev. B 45, 5251 (1992).
5. N. Manini, E. Tosatti, A. Auerbach, Phys. Rev. B 49, 13008 (1994).
6. L. Michel, Rev. Mod. Phys. 52, 617 (1980).
7. M. Koca, R. Koç, M. Al-Barwani, J. Phys. A: Math. Gen. 30, 2109 (1997).
8. R. Englman, The Jahn-Teller Effect in Molecules and Crystals (Wiley –Interscience 1972).
9. P.L. Rios, N. Manini, E. Tosatti, Phys. Rev. B 54, 7157 (1996).
10. J. Ihm, Phys. Rev. B 49, 10726 (1994).
11. M.C.M. O’Brien, Phys. Rev. B 53, 3775 (1996).
12. C.P. Moate, J.L. Dunn, C.A. Bates and Y.M. Liu, Zeitschrift fur Physikalische Chemie 200, 137 (1997).
13. P.W. Fowler, A. Ceulemans, Molecular Physics 54, 767 (1985).
14. C.C. Chancey and M.C.M O’Brien, The Jahn-Teller Effect in C60 and Other Icosahedral Complexes (Princeton University Press, 1997).

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