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A new approach to analyse H⊗(2h⊕g) Jahn-Teller system for C_{60}

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Abstract. 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 H_u 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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1 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⊗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_xC_{60} and/or $C^{\pm n}$ 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

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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 Moate *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.

2 Symmetry aspects and coupling of states

In this section, we start by describing the Hamiltonian that generates $\mathrm{D}^\ell\otimes\mathrm{D}^\ell$ surface where D^ℓ denotes the irreducible representation. The standard Hamiltonian may be written in the form

$$\begin{aligned} H &= H_0 + H_{\mathrm{JT}} \\ H_0 &= \frac{1}{2}\hbar\omega\sum_i (P_i^2 + Q_i^2) \end{aligned} \tag{1}$$

where H_0 describes free (uncoupled) electrons/holes and vibrations, 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

$$[\mathrm{D}^\ell \otimes \mathrm{D}^\ell] = \mathrm{D}^{\ell_1} \oplus \mathrm{D}^{\ell_2} \oplus ... \oplus \mathrm{D}^{\ell_n} \tag{2}$$

where ℓ is the angular momentum quantum number. Decomposition of $[\mathrm{D}^\ell \otimes \mathrm{D}^\ell]$ implies that the JT Hamiltonian can be written in the following way

$$H_{\mathrm{JT}} = H^{\ell_1} + H^{\ell_2} + ... + H^{\ell_n} \tag{3}$$

where H^ℓ 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

$$[\mathrm{D}^2 \otimes \mathrm{D}^2] = \mathrm{D}^0 \oplus \mathrm{D}^2 \oplus \mathrm{D}^4. \tag{4}$$

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

$$[\mathrm{H}_u \otimes \mathrm{H}_u] = [\mathrm{H}_u^2] = [\mathrm{H}_g^2] = \mathrm{A}_g \oplus \mathrm{H}_g \oplus (\mathrm{G}_g \oplus \mathrm{H}_g) \tag{5}$$

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 $[\mathrm{H}_u \otimes \mathrm{H}_u]$ coupling in $O(3)$ is found using the Table 1 and is in the form

Table 1. The representations of the $O(3)$ group with $\ell < 14$ are split by the icosahedral point group.

ℓ	I_h	ℓ	I_h
0	A_g	7	T_{1u}+T_{2u}+G_u+H_u
1	T_{1u}	8	T_{2g}+G_g+H_g+ H_g
2	H_g	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_g
4	G_g+H_g	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

$$H_{\mathrm{JT}} = H^0 + H^2 + H^4 \tag{6}$$

where the superscripts 2 and 4 are ℓ values. The symmetric part contains the totally symmetric representation $H^0 = \mathrm{A}_g$ 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 $\mathrm{G}_g\oplus\mathrm{H}_g$ vibrational levels.

3 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].

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

$$C_\ell(S) = \frac{1}{S}\sum_{p\in S}\chi_z(p) \tag{7}$$

where $\chi_z(p)$ is the character of the representation p. In a zth representation of finite group, if all subgroups $S' > S$ and $C_\ell(S') < C_\ell(S)$ 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

Table 2. 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.

	D_2	D_3	D_5	T
H	$2A+B_1+B_2+B_3$	A_1+2E	$A_1+E_1+E_2$	E+T
G	$A+B_1+B_2+B_3$	A_1+A_2+E	E_1+E_2	2A+E
H⊕G	$3A+2B_1+2B_2+2B_3$	$2A_1+A_2+3E$	$A_1+2E_1+2E_2$	2A+2E+T

treated equally well in the subgroup of proper rotations of group I. The maximal little subgroups of I group have computed by using equation (7) and are given in Table 2. As seen from Table 2, the maximal little groups predict the existence of dihedral groups D_5, D_3, 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

$$\mathrm{I} \rightarrow S' \tag{8}$$

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

4 Group invariance of Jahn-Teller systems

As we stated in the previous section, the Hamiltonian of H⊗($2h \oplus g$) 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

$$U_{\ell m}(X, Q) = \sum_{i,j=1}^{2\ell+1} \sum_{k=1}^{2m+1} F_{ijk} X_i X_j Q_k. \tag{9}$$

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⊗h and H⊗($h \oplus g$) coupling. In the equation (9) the indices $2\ell+1$ and $2m+1$ stand for dimensions of electronic and active coordinates, respectively. For H⊗h coupling ℓ and m take value 2 and for H⊗($h \oplus g$) case ℓ and m take values 2 and 4 respectively.

We will focus our treatment for the computation of invariant polynomials for H⊗h and H⊗($h \oplus g$) 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 5×5 generators transform electronic coordinates X_i ($i = 1...5$) and nuclear coordinates Q_i. It can be written in the form

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

In this equation, $X'_i = \sum_{n=1}^{5} \Gamma^r_{in} X_n$ and $Q'_k = \sum_{n=1}^{5} \Gamma^r_{in} Q_n$. Γ^r_{in} is the matrix elements of 5×5 generators of I. The equation (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

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

The JT interaction matrix for H⊗h coupling is

see equation (12) below.

$$B_2 = F_1 \begin{pmatrix} 2Q_5 & 0 & -\sqrt{3}Q_3 & \sqrt{3}Q_4 & 2Q_1 \\ 0 & 2Q_5 & -\sqrt{3}Q_4 & -\sqrt{3}Q_3 & 2Q_2 \\ -\sqrt{3}Q_3 & -\sqrt{3}Q_4 & -\sqrt{3}Q_1 - Q_5 & -\sqrt{3}Q_2 & -Q_3 \\ \sqrt{3}Q_4 & -\sqrt{3}Q_3 & -\sqrt{3}Q_2 & \sqrt{3}Q_1 - Q_5 & -Q_4 \\ 2Q_1 & 2Q_2 & -Q_3 & -Q_4 & -2Q_5 \end{pmatrix}$$

$$+F_2 \begin{pmatrix} \sqrt{15}Q_1 - \frac{\sqrt{3}}{2}Q_4 + \frac{\sqrt{5}}{2}Q_5 & -\sqrt{15}Q_2 + \frac{\sqrt{3}}{2}Q_3 & \frac{\sqrt{3}}{2}Q_2 & -\frac{\sqrt{3}}{2}Q_1 - 3Q_5 & \frac{\sqrt{5}}{2}Q_1 - 3Q_4 \\ -\sqrt{15}Q_2 + \frac{\sqrt{3}}{2}Q_3 & -\sqrt{15}Q_1 + \frac{\sqrt{3}}{2}Q_4 + \frac{\sqrt{5}}{2}Q_5 & \frac{\sqrt{3}}{2}Q_1 - 3Q_5 & \frac{\sqrt{3}}{2}Q_2 & \frac{\sqrt{5}}{2}Q_2 - 3Q_3 \\ \frac{\sqrt{3}}{2}Q_2 & \frac{\sqrt{3}}{2}Q_1 - 3Q_5 & -2\sqrt{3}Q_4 - \sqrt{5}Q_5 & -2\sqrt{3}Q_3 & -3Q_2 - \sqrt{5}Q_3 \\ -\frac{\sqrt{3}}{2}Q_1 - 3Q_5 & \frac{\sqrt{3}}{2}Q_2 & -2\sqrt{3}Q_3 & 2\sqrt{3}Q_4 - \sqrt{5}Q_5 & -3Q_1 - \sqrt{5}Q_4 \\ \frac{\sqrt{5}}{2}Q_1 - 3Q_4 & \frac{\sqrt{5}}{2}Q_2 - 3Q_3 & -3Q_2 - \sqrt{5}Q_3 & -3Q_1 - \sqrt{5}Q_4 & \sqrt{5}Q_5 \end{pmatrix} \tag{12}$$

$$F_3 \begin{pmatrix} -Q_6 - 2\sqrt{5}Q_8 & 2\sqrt{5}Q_7 & \frac{5}{4}Q_7 - \frac{9\sqrt{5}}{4}Q_9 & -\frac{5\sqrt{5}}{4}Q_6 - \frac{5}{4}Q_8 & \frac{\sqrt{15}}{2}Q_8 \\ 2\sqrt{5}Q_7 & -Q_6 + 2\sqrt{5}Q_8 & -\frac{5\sqrt{5}}{4}Q_6 + \frac{5}{4}Q_8 & \frac{5}{4}Q_7 + \frac{9\sqrt{5}}{4}Q_9 & \frac{\sqrt{15}}{2}Q_7 \\ \frac{5}{4}Q_7 - \frac{9\sqrt{5}}{4}Q_9 & -\frac{5\sqrt{5}}{4}Q_6 + \frac{5}{4}Q_8 & 4Q_6 + \sqrt{5}Q_8 & \sqrt{5}Q_7 & -\frac{5\sqrt{3}}{2}Q_7 \\ -\frac{5\sqrt{5}}{4}Q_6 - \frac{5}{4}Q_8 & \frac{5}{4}Q_7 + \frac{9\sqrt{5}}{4}Q_9 & \sqrt{5}Q_7 & 4Q_6 - \sqrt{5}Q_8 & -\frac{5\sqrt{3}}{2}Q_8 \\ \frac{\sqrt{15}}{2}Q_8 & \frac{\sqrt{15}}{2}Q_7 & -\frac{5\sqrt{3}}{2}Q_7 & -\frac{5\sqrt{3}}{2}Q_8 & -6Q_6 \end{pmatrix}. \qquad (15)$$

The force elements F_1 and F_2 are given by

$$F_1 = \frac{1}{135\sqrt{3}}(-13\sqrt{5}F_{\mathrm{H1}} + 15F_{\mathrm{H2}}),$$
$$F_2 = \frac{1}{27\sqrt{15}}(\sqrt{5}F_{\mathrm{H1}} + 3F_{\mathrm{H2}}). \qquad (13)$$

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

$$\sum_{i,j=1}^{5}\sum_{k=1}^{9} F_{ijk}X_iX_jQ_k = \sum_{i,j=1}^{5}\sum_{k=1}^{9} F_{ijk}X'_iX'_jQ'_k. \qquad (14)$$

Nine dimensional H⊗$(h \oplus g)$ 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 equation (10). The nuclear coordinates Q'_k is transformed as $Q'_k = \sum_{n=1}^{9} \Lambda^{\ell}_{in} Q_n$ where Λ^{ℓ} is the direct sum of 5 and 4 dimensional irreducible matrix generators Γ and Ω given in Appendix, respectively. Solution of the equation (14) for coefficients F_{ijk} gives that three linearly independent function. In Ceulemans's paper [1], relations between polynomial coefficients F_{ijk} in equations (10, 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⊗h coupling and third one is given in:

see equation (15) above.

The sum of the B_2 given in equation (12) and JT interaction matrix given in equation (15) corresponds to the first order JT interaction matrix (B_4) for H⊗$(h \oplus g)$ coupling. It is obvious that the interaction matrix is also obtained by considering only H⊗g coupling. Force element F_3 is related by coupling parameter of G mode and is given by $F_3 = F_{\mathrm{G}}/9$. 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⊗h and H⊗$(h \oplus g)$. Combination of eigenvalues of the B_m with harmonic potential energy, in terms of little groups yield JT surface energy.

4.1 Transitions associated with H⊗h and H⊗(h⊕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

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

where Γ_{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 equation (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 $Q_4 = -\tau Q_{\mathrm{H1}}$, $Q_5 = -(\sqrt{15}/2)Q_{\mathrm{H2}}$, $Q_6 = Q_{\mathrm{G}}$, where $\tau = (1 + \sqrt{5})/2$ Under the given conditions; the energy eigenvalues of each little group are computed.

4.1.1 D₂ 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 $Q_1 \to \sqrt{5}Q_4 - \sqrt{3}Q_5$, $Q_2 \to 0$, $Q_3 \to 0$, $Q_4 \to Q_4$, $Q_5 \to Q_5$, using the equation (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

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

$$E(\mathrm{B}_1) = \frac{1}{4\sqrt{5}}(F_{\mathrm{H1}} + F_{\mathrm{H2}})(4\tau Q_{\mathrm{H1}} - 5Q_{\mathrm{H2}}) + (F_{\mathrm{H1}} - 3F_{\mathrm{H2}})\sqrt{5}Q_{\mathrm{H2}} + K_{\mathrm{H}}(Q_{\mathrm{H1}}^2 + Q_{\mathrm{H2}}^2)/2,$$

$$E(\mathrm{B}_2) = \frac{1}{4\sqrt{5}}(F_{\mathrm{H2}} - F_{\mathrm{H1}})(4\tau Q_{\mathrm{H1}} - 5Q_{\mathrm{H2}}) + (F_{\mathrm{H1}} + 3F_{\mathrm{H2}})\sqrt{5}Q_{\mathrm{H2}} + K_{\mathrm{H}}(Q_{\mathrm{H1}}^2 + Q_{\mathrm{H2}}^2)/2,$$

$$E(\mathrm{B}_3) = -\frac{1}{\sqrt{5}}2\tau F_{\mathrm{H1}}Q_{\mathrm{H1}} - \frac{1}{2}(F_{\mathrm{H1}} - \sqrt{5}F_{\mathrm{H2}})Q_{\mathrm{H2}} + K_{\mathrm{H}}(Q_{\mathrm{H1}}^2 + Q_{\mathrm{H2}}^2)/2. \qquad (17)$$

In this equation, K_{H} is the harmonic force constant. The energy values of $E(\mathrm{A})$ 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 equation (16) nine dimensional matrix generators which have been obtained by taking direct sum of five and four dimensional representations are used to assign Q_i values. It is found that $Q_1 \to \sqrt{5}Q_4 - \sqrt{3}Q_5$, $Q_2 \to 0$, $Q_3 \to 0$, $Q_4 \to Q_4$, $Q_5 \to Q_5$, $Q_6 \to Q_6$, $Q_7 \to 0$, $Q_8 \to \sqrt{5}Q_6$, $Q_9 \to 0$. In this basis, combination of eigenvalues of B_4 with harmonic potential gives us

$$\begin{aligned}E(\mathrm{A}) &= \pm\frac{1}{2\sqrt{10}}[(3F_{\mathrm{H1}}^2 + F_{\mathrm{H2}}^2)(2\tau^2 Q_{\mathrm{H1}}^2 - 5\tau Q_{\mathrm{H1}}Q_{\mathrm{H2}} \\ &\quad + 5Q_{\mathrm{H2}}^2)]^{\frac{1}{2}} + \frac{3}{8}F_{\mathrm{G}}Q_{\mathrm{G}} + \frac{1}{2}K_{\mathrm{G}}Q_{\mathrm{G}}^2 + \frac{1}{2}K_{\mathrm{H}}(Q_{\mathrm{H1}}^2 + Q_{\mathrm{H2}}^2) \\ E(\mathrm{B}_1) &= \frac{1}{4\sqrt{5}}(F_{\mathrm{H1}} + F_{\mathrm{H2}})(4\tau Q_{\mathrm{H1}} - 5Q_{\mathrm{H2}}) \\ &\quad + (F_{\mathrm{H1}} - 3F_{\mathrm{H2}})\sqrt{5}Q_{\mathrm{H2}} - \frac{1}{4}F_{\mathrm{G}}Q_{\mathrm{G}} \\ &\quad + \frac{1}{2}K_{\mathrm{G}}Q_{\mathrm{G}}^2 + \frac{1}{2}K_{\mathrm{H}}(Q_{\mathrm{H1}}^2 + Q_{\mathrm{H2}}^2) \\ E(\mathrm{B}_2) &= \frac{1}{4\sqrt{5}}(F_{\mathrm{H2}} - F_{\mathrm{H1}})(4\tau Q_{\mathrm{H1}} - 5Q_{\mathrm{H2}}) \\ &\quad + (F_{\mathrm{H1}} + 3F_{\mathrm{H2}})\sqrt{5}Q_{\mathrm{H2}} - \frac{1}{4}F_{\mathrm{G}}Q_{\mathrm{G}} \\ &\quad + \frac{1}{2}K_{\mathrm{G}}Q_{\mathrm{G}}^2 + \frac{1}{2}K_{\mathrm{H}}(Q_{\mathrm{H1}}^2 + Q_{\mathrm{H2}}^2) \\ E(\mathrm{B}_3) &= -\frac{1}{\sqrt{5}}F_{\mathrm{H1}}22Q_{\mathrm{H1}} - \frac{1}{2}(F_{\mathrm{H1}} - \sqrt{5}F_{\mathrm{H2}})Q_{\mathrm{H2}} \\ &\quad - \frac{1}{4}F_{\mathrm{G}}Q_{\mathrm{G}} + \frac{1}{2}K_{\mathrm{G}}Q_{\mathrm{G}}^2 + \frac{1}{2}K_{\mathrm{H}}(Q_{\mathrm{H1}}^2 + Q_{\mathrm{H2}}^2), \qquad (18)\end{aligned}$$

where K_{G} in the equation (18) is the harmonic force constant of G mode. It is obvious that the magnitude of splitting of energy values is increasing in $h\oplus g$ 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, $Q_1 \to 0$, $Q_2 \to 0$, $Q_3 \to 0$, $Q_4 \to 0$, $Q_5 \to Q_5$. The computed energy values are given as

$$\begin{aligned}E(\mathrm{A}_1) &= -\frac{2}{3}F_{\mathrm{H1}}Q_{\mathrm{H2}} + \frac{1}{2}K_{\mathrm{H}}Q_{\mathrm{H2}}^2, \\ E_{\mp}(\mathrm{E}) &= \frac{1}{6}F_{\mathrm{H1}}Q_{\mathrm{H2}} \mp \sqrt{\left(\frac{F_{\mathrm{H1}}}{3}\right)^2 + \left(\frac{F_{\mathrm{H2}}}{2}\right)^2}Q_{\mathrm{H2}} \\ &\quad + \frac{1}{2}K_{\mathrm{H}}Q_{\mathrm{H2}}^2. \qquad (19)\end{aligned}$$

Transformation of nuclear coordinates for $\mathrm{H}\otimes(h\oplus g)$ 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

$$\begin{aligned}E(\mathrm{A}_1) &= -\frac{2}{3}(F_{\mathrm{G}}Q_{\mathrm{G}} + F_{\mathrm{H1}}Q_{\mathrm{H2}}) + \frac{1}{2}K_{\mathrm{G}}Q_{\mathrm{G}}^2 + \frac{1}{2}K_{\mathrm{H}}Q_{\mathrm{H2}}^2, \\ E_{\mp}(\mathrm{E}) &= \frac{1}{6}(F_{\mathrm{G}}Q_{\mathrm{G}} + F_{\mathrm{H1}}Q_{\mathrm{H2}}) \\ &\quad \mp \left[\left(\frac{1}{3}F_{\mathrm{H1}}Q_{\mathrm{H2}} - \frac{5}{12}F_{\mathrm{G}}Q_{\mathrm{G}}\right)^2 + \frac{1}{4}F_{\mathrm{H2}}^2Q_{\mathrm{H2}}^2\right]^{\frac{1}{2}} \\ &\quad + \frac{1}{2}K_{\mathrm{G}}Q_{\mathrm{G}}^2 + \frac{1}{2}K_{\mathrm{H}}Q_{\mathrm{H2}}^2. \qquad (20)\end{aligned}$$

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 $Q_1 \to -Q_4/\tau^2$, $Q_2 \to 0$, $Q_3 \to 0$, $Q_4 \to 0$, $Q_5 \to (\sqrt{3}/2\tau)Q_4$. The corresponding energies are obtained as

$$\begin{aligned}E\,(\mathrm{A}_1) &= -\frac{2}{\sqrt{5}}F_{\mathrm{H2}}Q_{\mathrm{H1}} + \frac{1}{2}K_{\mathrm{H}}Q_{\mathrm{H1}}^2, \\ E\,(\mathrm{E}_1) &= \frac{1}{2}\left(-F_{\mathrm{H1}} + \frac{1}{\sqrt{5}}F_{\mathrm{H2}}\right)Q_{\mathrm{H1}} + \frac{1}{2}K_{\mathrm{H}}Q_{\mathrm{H1}}^2, \\ E\,(\mathrm{E}_2) &= \frac{1}{2}\left(F_{\mathrm{H1}} + \frac{1}{\sqrt{5}}F_{\mathrm{H2}}\right)Q_{\mathrm{H1}} + \frac{1}{2}K_{\mathrm{H}}Q_{\mathrm{H1}}^2. \qquad (21)\end{aligned}$$

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

Tetrahedral group (T) is also maximal little group of G representation of I group. In $\mathrm{H}\otimes(h\oplus g)$ coupling some energy values have been expected. (Since T is not little group of H representation. Thus in $\mathrm{H}\otimes h$ 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 $Q_9 \to -\sqrt{5/3}Q_6$, $Q_i \to 0$, $(i = 1, ...8)$. The corresponding eigenvalues of B_4 are $F_{\mathrm{G}}Q_{\mathrm{G}}$ and $(-2/3)F_{\mathrm{G}}Q_{\mathrm{G}}$, for E and T respectively.

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

5 Conclusion

In summary, we have shown how the symmetry breaking method is applied for the determination of the potential energies of the $\mathrm{H}\otimes(2h\oplus g)$ 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 $\mathrm{H}\otimes(h\oplus g)$ and $\mathrm{H}\otimes h$ state. Splitting of energy levels of icosahedral

$$\mathit{\Gamma}^1=\frac{1}{9}\begin{pmatrix}7 & 0 & 0 & 2\sqrt{5} & -2\sqrt{3}\\ 0 & 3\sqrt{5} & -6 & 0 & 0\\ 0 & -6 & -3\sqrt{5} & 0 & 0\\ 2\sqrt{5} & 0 & 0 & -1 & 2\sqrt{15}\\ -2\sqrt{3} & 0 & 0 & 2\sqrt{15} & 3\end{pmatrix}\qquad \mathit{\Gamma}^2=\frac{1}{2}\begin{pmatrix}-1 & -\sqrt{3} & 0 & 0 & 0\\ \sqrt{3} & -1 & 0 & 0 & 0\\ 0 & 0 & -1 & \sqrt{3} & 0\\ 0 & 0 & -\sqrt{3} & -1 & 0\\ 0 & 0 & 0 & 0 & 2\end{pmatrix}$$

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

$$\mathit{\Gamma}^5=\frac{1}{12\sqrt{3}}\begin{pmatrix}\frac{11}{\sqrt{3}}-\sqrt{15} & 7+\sqrt{5} & 10+2\sqrt{5} & -2\sqrt{\frac{5}{3}}+2\sqrt{3} & 2-6\sqrt{5}\\ 7+\sqrt{5} & -\sqrt{3}+\sqrt{15} & -2\sqrt{3}-2\sqrt{15} & -14+2\sqrt{5} & -2\sqrt{3}-2\sqrt{15}\\ 10+2\sqrt{5} & -2\sqrt{3}-2\sqrt{15} & 7\sqrt{3}-\sqrt{15} & -1-\sqrt{5} & -2\sqrt{3}+2\sqrt{15}\\ -2\sqrt{\frac{5}{3}}+2\sqrt{3} & -14+2\sqrt{5} & -1-\sqrt{5} & \frac{19}{\sqrt{3}}+\sqrt{15} & -6-2\sqrt{5}\\ 2-6\sqrt{5} & -2\sqrt{3}-2\sqrt{15} & -2\sqrt{3}+2\sqrt{15} & -6-2\sqrt{5} & -4\sqrt{3}\end{pmatrix}$$

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 A: Generators of I, D_2, D_3, D_5 and T groups for G and H representations

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

$$\begin{array}{ll}\mathit{\Omega}^1,\mathit{\Omega}^2,\mathit{\Gamma}^1,\mathit{\Gamma}^2\rightarrow \mathrm{I} & \mathit{\Omega}^3,\mathit{\Omega}^4,\mathit{\Gamma}^3,\mathit{\Gamma}^4\rightarrow \mathrm{D}_5\\ \mathit{\Omega}^2,\mathit{\Omega}^4,\mathit{\Gamma}^2,\mathit{\Gamma}^4\rightarrow \mathrm{D}_3 & \mathit{\Omega}^1,\mathit{\Omega}^4,\mathit{\Gamma}^1,\mathit{\Gamma}^4\rightarrow \mathrm{D}_2\\ \mathit{\Omega}^2,\mathit{\Omega}^5,\mathit{\Gamma}^2,\mathit{\Gamma}^5\rightarrow \mathrm{T} & \end{array}$$

$$\mathit{\Omega}^1=\frac{1}{3}\begin{pmatrix}-2 & 0 & \sqrt{5} & 0\\ 0 & 0 & 0 & 3\\ \sqrt{5} & 0 & 2 & 0\\ 0 & 3 & 0 & 0\end{pmatrix}\quad \mathit{\Omega}^2=\frac{1}{2}\begin{pmatrix}2 & 0 & 0 & 0\\ 0 & -1 & \sqrt{3} & 0\\ 0 & -\sqrt{3} & -1 & 0\\ 0 & 0 & 0 & 2\end{pmatrix}$$

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

$$\mathit{\Omega}^5=\frac{1}{6\sqrt{3}}\begin{pmatrix}\sqrt{3} & -3\sqrt{5} & \sqrt{15} & -3\sqrt{5}\\ -3\sqrt{5} & 0 & -6 & -3\sqrt{3}\\ \sqrt{15} & -6 & -4\sqrt{3} & 3\\ -3\sqrt{5} & -3\sqrt{3} & 3 & -3\sqrt{3}\end{pmatrix}$$

and

see equations above.

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