Graph theory and the Jahn–Teller theorem

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The Jahn–Teller (JT) theorem predicts spontaneous symmetry breaking and lifting of degeneracy in degenerate electronic states of (nonlinear) molecular and solid-state systems. In these cases, degeneracy is lifted by geometric distortion. Molecular problems are often modelled using spectral theory for weighted graphs, and the present paper turns this process around and reformulates the JT theorem for general vertex- and edge-weighted graphs themselves. If the eigenvectors and eigenvalues of a general graph are considered as orbitals and energy levels (respectively) to be occupied by electrons, then degeneracy of states can be resolved by a non-totally symmetric re-weighting of edges and, where necessary, vertices. This leads to the conjecture that whenever the spectrum of a graph contains a set of bonding or anti-bonding degenerate eigenvalues, the roots of the Hamiltonian matrix over this set will show a linear dependence on edge distortions, which has the effect of lifting the degeneracy. When the degenerate level is non-bonding, distortions of vertex weights have to be included to obtain a full resolution of the eigenspace of the degeneracy. Explicit treatments are given for examples of the octahedral graph, where the degeneracy to be lifted is forced by symmetry, and the phenalenyl graph, where the degeneracy is accidental in terms of the automorphism group.

Keywords: Jahn–Teller effect; spectral graph theory; electronic/spectral degeneracy;
Hückel theory; group theory

1. Introduction

The Jahn–Teller (JT) theorem (Jahn & Teller 1937) predicts that degenerate electronic levels in (nonlinear) molecules and solids give rise to spontaneous symmetry-lowering distortions, which will lift the degeneracy. The purpose of the present paper is to reformulate this theorem in graph-theoretical terms, and to show that an analogous connection exists between the degeneracy of eigenvalues in the spectrum of a graph and distortion, as represented by symmetry-breaking

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patterns of edge weights. This analogy has consequences both for the molecular JT theorem and for spectral graph theory. The discussion concentrates on two examples that exhibit two different types of degeneracy: one arising from spatial symmetry, and one ‘accidental’, in the sense that it is not accounted for by the automorphism group of the graph.

2. The distortivity of graphs

Conjugated systems are inherently distortive, in that their geometric structures result from a compromise between the requirements of $\sigma$ and $\pi$ electrons, where the natural tendency of the $\sigma$ framework is towards equal bond lengths and angles, whereas the $\pi$ electrons favour bond alternation, which would often lead to broken symmetry. The distortive tendency may win the competition and lead to actual distortion, as in examples such as pentalene (Binsch et al. 1966), where the molecular framework has $C_{2h}$ point group symmetry rather than the maximum $D_{2h}$, or the reverse may happen, and the distortivity may remain unrealized, as in benzene. The history of these ideas, and in particular their relevance to the structure and spectroscopy of benzene, have been extensively reviewed elsewhere (Shaik et al. 2001). Hückel theory of $\pi$ systems is essentially a graph-theoretical model in which the orbitals and their energies correspond to eigenvectors and eigenvalues, respectively, of the adjacency matrix of the molecular graph (Coulson et al. 1978; Mallion 2009). For all-carbon frameworks, the graph is effectively unweighted, as all centres are taken to be equivalent and all edges carry equal weight, so that the role of the Hückel parameters $\alpha$ and $\beta$ is only to define the origin and unit, respectively, of the energy scale. Heilbronner wrote a famous tutorial article (Heilbronner 1989) with the title ‘Why do some molecules have symmetry different from that expected?’, in which he made it clear that the notion of $\pi$ distortivity is implied in the Hückel treatment of $\pi$ systems, and gave a simple way of incorporating it into standard calculations by re-weighting the edges of the molecular graph. This treatment was later extended to graphs in general and placed in the context of the full perturbation treatment by Fowler & Rassat (2002) and Fowler (2003).

The modes considered by Heilbronner represent alternating compression and elongation of consecutive edges in a chain or ring, and, in general, a Heilbronner vector (Fowler & Rassat 2002) is a set of weight changes added to the edges of a graph such that the sum of edge weights around every vertex with a degree greater than 1 is conserved. For an even-ring system, for example, this is certainly a JT-type distortion mode, which, for instance, will take a square into a rectangle. However, not all JT distortions are of this kind, especially in polyhedra. Moreover, pendant edges are necessarily special cases as there can be no alternation at the end vertex. The present work extends the notion of distortion/distortivity of a graph, and shows that there is a direct analogue of the JT theorem for graphs themselves. That is to say, we may define the equivalent of electronic states for general graphs, and we shall then find that if such a state is degenerate, the degeneracy can be lifted by an appropriate ‘distortion’ (i.e. re-weighting) which is spontaneous, in that it leads to a non-degenerate state with a lower energy, as defined by an appropriate sum of eigenvalues.
The extension of Hückel theory to general graphs can be specified by a set of ‘chemical’ rules. Given a pair consisting of a graph $G$ (of order $n$) and a number $N$ of electrons ($0 \leq N \leq n$), a (ground state) electronic configuration can be determined as follows (Mallion & Rouvray 1978; Mallion 2009). The eigenvalues of the weighted adjacency matrix are arranged in non-increasing order. The $N$ electrons are assigned to eigenvectors corresponding to three rules: (i) the Aufbau Principle, eigenvectors are filled in non-increasing order of eigenvalue, (ii) the Pauli Principle, each eigenvector has a maximum capacity of two electrons, and (iii) Hund’s Rule of Maximum Multiplicity, when the filling process reaches a degenerate eigenvalue, the order of filling the associated eigenvectors is such that each receives one electron before any has received two. The crucial situation for JT distortion is when the number of electrons leads to only partial filling of a degenerate eigenspace. If application of the three rules leads to two eigenvectors of a degenerate set having different occupation numbers, then this is the case of a degenerate electronic state (strictly, an orbitally degenerate state). In other words, in a non-degenerate state, every eigenspace is full (all vectors have two electrons), half-full (all vectors have one electron) or empty.

Continuing the chemical analogy, we note that the important feature for an electronic state is the total energy. Within the Hückel approximations, the Hamiltonian matrix is the sum of a diagonal matrix (the Coulomb matrix) containing the vertex weights $H_{ii}$, and a weighted version of the adjacency matrix in which pairs corresponding to edges have a weight $H_{ij}$ (the resonance matrix). The default weighting is $H_{ii} = \alpha$ and $H_{ij} = A_{ij} \beta$, where $A_{ij}$ is the entry in the adjacency matrix, equal to 1 for adjacent pairs of vertices, and zero otherwise. The energy of an orbital is the eigenvalue, $E_k$. The energy of an electronic state is the sum, $E = \Sigma n_k E_k$, where $n_k$ are the occupation numbers of the eigenvectors ($n_k = 2, 1, 0$) and $N = \Sigma n_k$. For conjugated $\pi$ systems, all vertices of the molecular graph have degree $\leq 3$, and hence a ‘chemical graph’ is taken to be one that is connected and with maximum degree $\leq 3$, but the various definitions can also be used for more general graphs and more general electronic structures.

In principle, the possible distortion modes of a graph involve all non-zero entries in the adjacency matrix; hence, not only the off-diagonal elements (‘inter-site’ or ‘hopping integrals’), but also the diagonal elements (‘on-site’ or ‘Coulomb’ integrals) should be considered. Together, they form the full distortion space of the graph: the spectrum will change if we change one of these parameters. However, these distortion modes are not all linearly independent, as we can easily show.

Let $E_k$ denote the $k$th eigenvalue of a graph ($0 \leq k \leq n$) and $c_i^k$ the corresponding eigenvalue coefficient at vertex $i$. The eigenvalue can be expressed as a double sum over the Hamiltonian matrix as

$$E_k = \frac{\sum_{i,j} c_i^k c_j^k H_{ij}}{\sum_i (c_i^k)^2}. \quad (2.1)$$

For simplicity, we assume here that all eigenvalue coefficients are real, as can always be arranged, and that overlap integrals are zero. According to the Variation Principle, the eigenvalue is optimized with respect to the coefficients,
i.e. for any vertex \(a\),
\[
\frac{\partial E_k}{\partial c^k_a} = 0. \tag{2.2}
\]

Evaluating the derivative of equation (2.1) yields
\[
\frac{\partial E_k}{\partial c^k_a} = \frac{\left(\sum_i (c^k_i)^2\right) \left(\sum_{j \neq a} c^k_j (H_{aj} + H_{ja}) + 2c^k_a H_{aa}\right) - 2c^k_a \sum_{i,j} c^k_i c^k_j H_{ij}}{\left[\sum_i (c^k_i)^2\right]^2} = 2 \frac{\sum_j c^k_j H_{aj} - c^k_a E_k}{\sum_i (c^k_i)^2}. \tag{2.3}
\]

Since this derivative vanishes, one obtains
\[
\sum_j c^k_j H_{aj} - c^k_a E_k = \sum_j c^k_j (H_{aj} - \delta_{aj} E_k) = 0. \tag{2.4}
\]

This is the matrix equation that gives rise to the eigenvalues. It is assumed that the Hamiltonian matrix is real and symmetric (real Hermitian).

The eigenvalue expression can also be used to evaluate the dependence of the energy on the on-site stabilization of a given vertex \(a\). To first order, one obtains
\[
\frac{\partial E_k}{\partial H_{aa}} = \frac{(c^k_a)^2}{\sum_i (c^k_i)^2}. \tag{2.5}
\]

This is no surprise. The sensitivity of the eigenvalue to the on-site energy depends on the density at the given site. In fact, this result was obtained more than 60 years ago, by Coulson and co-workers, who considered it to be the direct definition of the \(\pi\)-electronic charge density on a particular atom (Coulson & Rushbrooke 1940; Coulson & Longuet-Higgins 1947).

Similarly, we want to know how the energy depends on the inter-site terms (hopping matrix elements) that link site \(a\) to its neighbours
\[
\frac{\partial E_k}{\partial H_{ab}} = \frac{2c^k_a c^k_b}{\sum_i (c^k_i)^2}. \tag{2.6}
\]

As expected, in this case, the sensitivity of the energy to the inter-site hopping depends on the contribution of the \(k\)th level to the bond order, what subsequently came to be known as the Coulson bond order (Coulson 1939).

Multiplying equation (2.4) by the \(c^k_a\) coefficient, and dividing by the norm, yields
\[
\sum_{j \neq a} c^k_a c^k_j H_{aj} - (c^k_a)^2 (E_k - H_{aa}) = \frac{1}{2} \left( \sum_{j \neq a} \frac{\partial E_k}{\partial H_{aj}} H_{aj} \right) - \frac{\partial E_k}{\partial H_{aa}} (E_k - H_{aa}) = 0. \tag{2.7}
\]
We now simplify these expressions by adopting the Hückel nearest-neighbour Hamiltonian, where all on-site terms are equal to a parameter \( \alpha \) and the inter-site terms are equal to a (negative) parameter \( \beta \). Further, let \( \nu(a) \) denote the set of nearest neighbours of \( a \). Then, equation (2.7) reduces to

\[
\beta \left( \sum_{j \in \nu(a)} \frac{\partial E_k}{\partial H_{aj}} \right) = \left( E_k - \alpha \right) \frac{\partial E_k}{\partial H_{aa}}.
\]

This expression tells us that a change in on-site density can be expressed as a change in the edge interactions that connect this vertex to the network. The distortion of the vertex energy thus does not yield extra variational freedom, and the distortion space can be restricted to edge distortivity, provided that the energy level is not non-bonding, i.e. \( E_k \neq \alpha \).

As an example, take a chain of three nodes \( a\sim b\sim c \), as in the allyl radical. The ground state of this chain is given by the eigenfunction (in Dirac notation), where \( |a\rangle \) is a basis function on centre \( a \)

\[
\Phi = \frac{1}{2}(|a\rangle + \sqrt{2}|b\rangle + |c\rangle).
\]

The energy is equal to \( \alpha + \sqrt{2}\beta \), which may be rewritten in full as

\[
E_0 = \frac{1}{2}H_{bb} + \frac{1}{4}H_{aa} + \frac{1}{4}H_{cc} + \frac{1}{\sqrt{2}}H_{ab} + \frac{1}{\sqrt{2}}H_{bc}.
\]

One can verify that the slopes of the energy with respect to the different parameters confirm the expressions, e.g.

\[
\frac{\beta}{2} \left( \frac{\partial E_0}{\partial H_{bb}} + \frac{\partial E_0}{\partial H_{bc}} \right) = \left( E_0 - \alpha \right) \frac{\partial E_0}{\partial H_{bb}} = \frac{1}{\sqrt{2}} \beta.
\]

The total first-order dependence of a given energy level on the distortion of the edges is the sum over all distortions, and can be summarized as follows:

\[
\Delta E_k = \sum_{i<j} \Delta H_{ij} \frac{\partial E_k}{\partial H_{ij}}.
\]

Here, \( \Delta H_{ij} \) symbolizes a change of the hopping element of the edge-connecting vertices \( i \) and \( j \). In a chemical context, an increase of the interaction would correspond to a shortening of the bond along that edge. In fact, as the interaction element is negative, its variation correlates with a lengthening of the bond. Hence, to first approximation, a linear correspondence is expected: \( \Delta H_{ij} \sim \Delta r_{ij} \).

The combination of bond distortions that appears in equation (2.11) defines a collective distortion mode which will affect the \( k \)th level to first order. We define this mode as \( Q_k \),

\[
Q_k = \frac{1}{\sqrt{M}} \sum_{i<j} 2c_i^k c_j^k \Delta H_{ij},
\]

where \( M \) denotes a normalizer. Hence, the energy dependence on \( Q_k \) is given by

\[
\Delta E_k = \sqrt{M} Q_k.
\]
As expressed in equation (2.13), each level is coupled to a single mode. In the individual eigenvalue equations, edges that are equivalent by symmetry have the same bond order, and hence they will also be distorted to the same extent. As a result, the $Q_k$-mode is totally symmetric with respect to the automorphism group of the graph.

3. The Jahn–Teller effect

When the electron count is such that the electronic state predicted by the Aufbau, Pauli and Hund rules has partial occupation of a degenerate eigenspace, the above treatment is no longer correct on two counts. First, the interaction elements between the degenerate components of the manifold can also affect the eigenvalues to first order. Secondly, the requirement of total symmetry no longer applies to the individual eigenfunctions, but only to the average of the densities and bond-order averages over the entire degenerate manifold. The result is that the energy levels in a manifold may show a linear dependence on non-totally symmetric distortions, which will break the symmetry and remove the degeneracy. The linear terms are the so-called JT forces, which give rise to a spontaneous distortion of the molecular frame. According to the JT theorem, such distortion forces will always exist, except in the case of linear molecules (Jahn & Teller 1937). See Ceulemans & Lijnen (2010) for a group-theoretical proof of the molecular JT theorem. The molecular JT treatment can easily be translated into graph-theoretical language (Ceulemans & Lijnen 2007), but it is not known if the theorem itself will be valid for all graphs with degenerate eigenvalues.

Following the JT approach, a proper description of the distortivity of the levels requires the construction of a matrix involving all interactions within the degeneracy space. For our purpose, we consider two states, $k$ and $l$, which have the same energy. Let $\Psi_k$ and $\Psi_l$ be the corresponding eigenfunctions. They are said to be the components of a twofold degenerate manifold, and a description of the energy of the manifold requires that we set up a Hamiltonian matrix,

\[
\begin{pmatrix}
H_{kk} & H_{kl} \\
H_{lk} & H_{ll}
\end{pmatrix}.
\] (3.1)

An element of this matrix is given by

\[
H^{kl} = \langle \Psi_k | H | \Psi_l \rangle,
\] (3.2)

and the matrix is real Hermitian and therefore symmetric.

We must now consider the dependence of the matrix elements on the distortions of the edges. The diagonal elements are already given by equation (2.6). The off-diagonal element is specified by

\[
H^{kl} = \langle \sum_i c_i^k | i | \sum_j c_j^l | j \rangle = \sum_{i,j} c_i^k c_j^l H_{ij},
\] (3.3)

where normalized components are assumed. Recall that lower indices refer to vertices, and upper indices to eigenstates. Hence, the dependence on the
interaction element connecting vertices $i$ and $j$ is given by
\[
\frac{\partial H_{kl}}{\partial H_{ij}} = c_k^i c_j^i + c_i^j c_j^i. \tag{3.4}
\]

The energy dependence of the manifold on the distortion of edge $ij$ is thus to be written as a matrix. We call this the JT Hamiltonian. For normalized components, it reads
\[
H^{JT}(\Delta H_{ij}) = \Delta H_{ij} \begin{pmatrix}
2c_k^i c_j^i & c_k^i c_j^i + c_k^i c_j^i \\
(c_i^j c_j^i + c_i^j c_i^j) & 2c_i^j c_j^i
\end{pmatrix}. \tag{3.5}
\]

The full JT Hamiltonian is the sum over the entire distortion space,
\[
H^{JT} = \sum_{i<j} H^{JT}(\Delta H_{ij}). \tag{3.6}
\]

The corresponding energy variations are found by diagonalizing this Hamiltonian. In this way, one obtains an energy landscape in the space of the normal distortion modes.

### 4. Jahn–Teller-active modes

We shall continue by working out a simple example: a triangle $abc$. Its spectrum contains a twofold degenerate manifold, with eigenvalue $\alpha - \beta$, in addition to the non-degenerate eigenvalue $\alpha + 2\beta$. We shall write the levels in full as
\[
\begin{align*}
\psi_k &= \frac{1}{\sqrt{2}} (|b\rangle - |c\rangle), \\
\psi_l &= \frac{1}{\sqrt{6}} (2|a\rangle - |b\rangle - |c\rangle), \\
E_k &= \frac{1}{2} (H_{bb} + H_{cc}) - H_{bc} \\
E_l &= \frac{1}{6} (4H_{aa} + H_{bb} + H_{cc}) - \frac{2}{3} (H_{ab} + H_{ac}) + \frac{1}{3} H_{bc}.
\end{align*} \tag{4.1}
\]

The energy of the manifold is thus $\alpha - \beta$. The JT Hamiltonian reads
\[
\begin{pmatrix}
-\Delta H_{bc} & \frac{1}{\sqrt{3}} \Delta H_{ab} - \frac{1}{\sqrt{3}} \Delta H_{ac} \\
\frac{1}{\sqrt{3}} \Delta H_{ab} - \frac{1}{\sqrt{3}} \Delta H_{ac} & 1 - \frac{2}{3} \Delta H_{bc} - \frac{2}{3} \Delta H_{ab} - \frac{2}{3} \Delta H_{ac}
\end{pmatrix}. \tag{4.2}
\]

The trace of this matrix is given by
\[
\text{Tr}(H) = -\frac{2}{3} (\Delta H_{ac} + \Delta H_{ab} + \Delta H_{bc}). \tag{4.3}
\]

Simultaneous elongation or contraction of all edges will of course not lift the degeneracy, and this trace mode is thus JT inactive. We take it out by subtracting
The matrix provides us with two separate linear combinations of the edge distortions, which are called the JT-active modes. They form vectors in the distortion space of all edge distortions. In the usual JT terminology, these two (normalized) vectors are labelled as follows:

$$Q_\vartheta = \frac{1}{\sqrt{6}} (2\Delta H_{bc} - \Delta H_{ab} - \Delta H_{ac})$$
$$Q_3 = \frac{1}{\sqrt{2}} (\Delta H_{ab} - \Delta H_{ac}).$$

(4.5)

In this formalism, the first-order JT matrix (which is also called the JT force matrix) is given by

$$-\frac{\sqrt{2}}{\sqrt{3}} \begin{pmatrix} -Q_\vartheta & Q_3 \\ Q_3 & +Q_\vartheta \end{pmatrix}.$$ (4.5)

Diagonalization of this matrix yields two roots,

$$E_\pm = \pm \sqrt{\frac{2}{3}} \sqrt{Q_\vartheta^2 + Q_3^2}.$$ (4.6)

Recall that these expressions give the slope of the energy in the starting triangular configuration. Hence, on distortion of the molecule in the direction of the JT modes, the manifold will split into an upper and a lower root. Interestingly, the energy surface is to first-order circular in the distortion space. Hence, the surface looks like a conical intersection. Second-order interactions are needed to warp this cone and distinguish a preferred direction in the distortion space. Usually this is along the $\vartheta$-mode, as this is the higher epikernel subgroup of the automorphism group (Ceulemans & Vanquickenborne 1989). In the molecular world, this surface is the famous ‘Mexican hat’ surface (Bersuker & Polinger 1989).

The treatment above can of course be extended to $n$-fold degeneracies. If the level is non-bonding, one should also allow for on-site density changes. In general, for an $n$-dimensional space, the number of independent entries in the JT matrix is $n(n + 1)/2$. Subtracting the trace implies that there should be $[n(n + 1)/2] - 1$ JT-active modes. Usually, this number will be much smaller than the dimension of the non-totally symmetric distortion subspace. If $n = 1$, there is only one matrix element, and thus the only mode is an inactive one, i.e. it cannot break the symmetry group of the graph.

5. The Berry phase

Let us go one step further and consider the eigenvectors for two dimensions, for example, as a function of the distortion. First, we switch to angular coordinates.
for the distortion space,
\[ Q_\phi = \rho \cos \phi \]
and
\[ Q_\xi = \rho \sin \phi. \]

The eigenfunction as a function of these coordinates is obtained as a by-product of the diagonalization procedure,
\[ \Psi = \Psi_\xi \cos \left( \frac{\phi}{2} \right) + \Psi_\xi \sin \left( \frac{\phi}{2} \right). \]

This expression has a topological meaning. It links (by a fibre) the position in the distortion space with a direction in the electronic function space, formed by the components of the manifold. The distortion is seen to rotate at twice the rate of the electronic vector. The ratio of 2 between the angle dependences in equations (5.1) and (5.2) is the Chern number (Shapere & Wilczek 1989). Hence, after completing one full turn around the conical intersection, we are back at the same structure in distortion space, but the wave function has changed from \( \Psi_k \) to \(-\Psi_k\), and two turns will be needed before we return to the starting point in the function space. This is the famous Berry phase (Berry 1984), implied in the work of Longuet-Higgins (Longuet-Higgins 1975). It has important consequences for the dynamics of the system in the neighbourhood of the conical intersection, but this is outside the scope of the present graph-theoretical approach.

In the following section, we shall apply this treatment to two examples of particular graphs: the octahedral graph, with a non-bonding JT level, and the phenalenyl graph, with an accidental degeneracy.

### 6. Examples

(a) The octahedral graph

The spectrum \{4, 0\textsuperscript{3}, -2\textsuperscript{2}\} of the octahedral graph (figure 1) has a threefold degenerate non-bonding level that is only partially occupied by four electrons (Mallion & Rouvray 1978). In chemistry, this is a classical case of the JT effect in an orbital triplet. It is denoted as the \( T \otimes (e + t_2) \) problem. We shall treat it from the graph-theoretical point of view. The vertices are labelled as in the figure. A convenient presentation of the three components of the orbital triplet is

\[
\Psi_x = \frac{1}{\sqrt{2}}(|a\rangle - |d\rangle), \\
\Psi_y = \frac{1}{\sqrt{2}}(|b\rangle - |e\rangle), \\
\Psi_z = \frac{1}{\sqrt{2}}(|c\rangle - |f\rangle).
\]

Clearly, the density distribution in these components is very anisotropic, being localized on only two antipodal vertices. The octahedral equivalence can be restored only by taking the average over the three components. Parenthetically, we note that, for this particular case, it is possible to transform these functions...
into a basis where all vertices carry the same density (Ceulemans et al. 1998) if we are prepared to use complex combinations

$$\psi_0 = \frac{1}{\sqrt{3}} (\psi_x + \psi_y + \psi_z) = \frac{1}{\sqrt{6}} (|a\rangle + |b\rangle + |c\rangle - |d\rangle - |e\rangle - |f\rangle),$$

$$\psi_{+1} = \frac{1}{\sqrt{3}} (\psi_x + \varepsilon \psi_y + \varepsilon^2 \psi_z) = \frac{1}{\sqrt{6}} (|a\rangle + \varepsilon |b\rangle + \varepsilon^2 |c\rangle - |d\rangle - \varepsilon |e\rangle - \varepsilon^2 |f\rangle),$$

and

$$\psi_{-1} = \frac{1}{\sqrt{3}} (\psi_x + \varepsilon^2 \psi_y + \varepsilon \psi_z) = \frac{1}{\sqrt{6}} (|a\rangle + \varepsilon^2 |b\rangle + \varepsilon |c\rangle - |d\rangle - \varepsilon^2 |e\rangle - \varepsilon |f\rangle),$$

where $\varepsilon = e^{2\pi i/3}$. These individual components are ‘equi-distributive’ in the sense that, according to this choice, all equivalent vertices carry the same density.

As this is a triple degeneracy, we expect coupling with five active modes. However, this triplet is non-bonding. In fact, only three active edge-distortion modes can be obtained. The remaining two degrees of freedom require distortions of the Coulomb terms. This confirms the general result in equation (2.8) for a non-bonding level. There are thus two independent contributions to the JT force matrix. The one coming from edge distortions is given by

$$H(Q) = \begin{pmatrix} 0 & Q_\xi & Q_\eta \\ Q_\xi & 0 & Q_\xi \\ Q_\eta & Q_\xi & 0 \end{pmatrix},$$

with

$$Q_\xi = \frac{1}{2}(\Delta H_{bc} + \Delta H_{ef} - \Delta H_{bf} - \Delta H_{ce}),$$

$$Q_\eta = \frac{1}{2}(\Delta H_{ac} + \Delta H_{df} - \Delta H_{af} - \Delta H_{cd})$$

and

$$Q_\zeta = \frac{1}{2}(\Delta H_{ab} + \Delta H_{ed} - \Delta H_{ae} - \Delta H_{bd}).$$

These modes are always restricted to four vertices forming one square. They represent the so-called scissoring modes that distort the square to a rectangle. In octahedral symmetry, these modes follow the $b_{2g}$ irreducible representation.
The contribution owing to changes of the Coulomb terms is found on the diagonal. One has

\[
H_0(\Delta \alpha) = \begin{pmatrix}
\frac{1}{2}(\Delta \alpha_a + \Delta \alpha_d) & 0 & 0 \\
0 & \frac{1}{2}(\Delta \alpha_b + \Delta \alpha_e) & 0 \\
0 & 0 & \frac{1}{2}(\Delta \alpha_c + \Delta \alpha_f)
\end{pmatrix}.
\] (6.4)

When the trace is taken out, two modes survive. They are labelled as \(P_\phi\) and \(P_\epsilon\), and form the \(e_\sigma\) distortion mode in octahedral symmetry,

\[
\begin{aligned}
\text{Tr}(H_0) &= \frac{1}{\sqrt{2}}(\Delta \alpha_a + \Delta \alpha_b + \Delta \alpha_c + \Delta \alpha_d + \Delta \alpha_e + \Delta \alpha_f), \\
\frac{1}{\sqrt{12}}(2\Delta \alpha_c + 2\Delta \alpha_f - \Delta \alpha_a - \Delta \alpha_d - \Delta \alpha_b - \Delta \alpha_e) \\
\frac{1}{2}(\Delta \alpha_a + \Delta \alpha_d - \Delta \alpha_b - \Delta \alpha_e).
\end{aligned}
\] (6.5)

The zero-trace form of the Coulomb matrix then reads

\[
H(P) = \frac{1}{\sqrt{3}} \begin{pmatrix}
-\frac{1}{2}P_\phi + \frac{\sqrt{3}}{2}P_\epsilon & 0 & 0 \\
0 & -\frac{1}{2}P_\phi - \frac{\sqrt{3}}{2}P_\epsilon & 0 \\
0 & 0 & P_\phi
\end{pmatrix}.
\] (6.6)

The full JT Hamiltonian is then given by the sum \(H(Q) + H(P)\). This yields a \(3 \times 3\) matrix in a five-dimensional parameter space: \(P_\phi\), \(P_\epsilon\), \(Q_x\), \(Q_y\), \(Q_z\). Diagonalization of this matrix has been studied extensively in the JT literature. As \(H\) consists of two terms depending on intrinsically different parameters, on-site versus inter-site, different regimes of solutions can be considered.

We shall summarize here the main conclusions (Bersuker & Polinger 1989). If the Coulomb-force elements are dominant, distortions will be in the \(P\)-space. The energy surface in this space is not conical, but shows three so-called tetragonal wells, characterized by increasing attraction at two antipodal nodes, at the expense of the four remaining ones. As an example, following the \(P_\phi\)-mode in the negative direction, the Coulomb attraction is enhanced at sites \(c\) and \(f\), at the expense of sites \(a\), \(b\), \(d\) and \(e\). This mode will stabilize the \(\Psi_x\) component, which is localized on \(c\) and \(f\), relative to \(\Psi_x\) and \(\Psi_y\). As a result, under this distortion, the original triplet will split into a singlet and a doublet. In order to accommodate four electrons in a closed shell, one would have to invert the direction of the distortion in such a way that the doublet component becomes the lowest. The root, \(-\frac{1}{2}P_\phi + \frac{\sqrt{3}}{2}P_\epsilon\), is characterized by an entirely similar distortion pattern, but this time, the \(a\) and \(d\) nodes are stabilized at the expense of \(b\), \(c\), \(e\) and \(f\). This reflects the composition of the \(\Psi_x\) component. A similar relationship holds between the remaining root, \(-\frac{1}{2}P_\phi - \frac{\sqrt{3}}{2}P_\epsilon\), and the \(\Psi_y\) component.
On the other hand, if the forces resulting from edge distortions win, one should consider the solutions of the $H(Q)$ Hamiltonian. Again, in this case, the surface is not conical, but warped. The lowest roots correspond to the so-called trigonal modes. In this case, the octahedron is distorted to a trigonal antiprism. There are four equivalent ways to do that. The one in which the $\Delta_{abc}$ and $\Delta_{def}$ antipodal triangles are elongated, and the edges in between are compressed, is given by

$$\frac{1}{\sqrt{3}}(Q_x + Q_y + Q_z).$$

(6.7)

Again, along this distortion, the triplet splits into a singlet and a doublet, which is appropriate to accommodate either two or four electrons.

Finally, there is also the exceptional case, where the Coulomb and edge contributions are accidentally equal. In this case, a true conical structure is recovered, consisting of three sheets in a five-dimensional distortion space.

From the present perspective, the example of the octahedron is interesting because it illustrates the need to combine on-site and inter-site distortions in the case of a non-bonding level. This is really a consequence of the nearest-neighbour Hamiltonian. Since the $\Psi$ functions in equation (6.1) contain only nodes that are not connected in the graph, we cannot change their energies by varying the connections. This is not the case in a real octahedral molecule. An octahedron is a deltahedron (all faces are triangular), which implies that its edge stretches describe the full flexibility of the structure, and thus will also cover the tetragonal modes (Ceulemans & Fowler 1991). It is also interesting to note that the trigonal modes are at variance with the Heilbronner (1989) distortivity concept. The individual scissoring distortions in equation (6.3) are indeed alternating deformations of a four-ring, but they are not the optimal solution. The optimal trigonal solution is a linear combination of three Heilbronner modes, as indicated in equation (6.7).

In a real molecule, increasing or reducing the on-site Coulomb attraction can be mimicked only by replacing, for instance, a carbon by an atom with a higher or lower electronegativity. The splitting effect of such a substitution is indeed known as the ‘substitutional JT effect’, but it is outside the scope of a variational treatment, as it implies discrete changes.

(b) The phenalenyl graph

Phenalenyl is a conjugated radical, which is represented by a 13-vertex graph (figure 2a), consisting of three fused hexagons. The automorphism group of this graph is $S_3$, the symmetric group of three objects. This group is isomorphic to the in-plane molecular point group $C_{3v}$. The spectrum of this graph $\{\sqrt{6}, \sqrt{3^2}, 1^3, 0, -1^3, -\sqrt{3^2}, -\sqrt{6}\}$ is characterized by a non-bonding semi-occupied level, in between two triplets at $\alpha \pm \beta$. (It might be noted in passing that the spectrum just listed for the bipartite graph/alternant hydrocarbon phenalenyl is symmetrical about zero and thus conforms to the theorem of Coulson & Rushbrooke (1940) about ‘pairing’ of the eigenvalues of such graphs about the zero value; furthermore, the zero eigenvalue encountered in the spectrum of phenalenyl is to be expected because a bipartite graph/alternant hydrocarbon

Graph theory and the Jahn–Teller theorem

Figure 2. (a) Phenalenyl graph with indication of the edge distortions leading to the \( \epsilon_1 \) minimum of the \( (A_1 + E) \otimes (a + 2e) \) problem. (b) Projective planar representation of the topology of the dynamic \( (A_1 + E) \otimes (a + 2e) \) problem. Minima are indicated by black points, maxima by open circles and transition states by crosses. The full lines indicate possible tunnelling trajectories.

with an odd number of vertices/carbon atoms is bound (by virtue of the Coulson–Rushbrooke theorem) to have at least one zero-eigenvalue.) There is no apparent symmetry operation that can explain the existence of such a threefold degeneracy. The irreducible representations of the automorphism group have dimensions one or two; hence, only non-degenerate or twofold degenerate spectral levels are expected on the basis of symmetry. This graph thus represents a case of ‘accidental’ or ‘excessive’ degeneracy (Burdett et al. 1985) when compared with the previous octahedral graph, where the threefold degeneracy was a ‘legal’ symmetry degeneracy.

The question arises whether this accidental degeneracy will also be reflected in a full conical distortivity. The corresponding molecular problem is the JT activity of the dication, where the bonding triplet would host five electrons and one hole. The eigenvectors of the triplet will be labelled as \( a_1, e_\beta \) and \( e_\epsilon \). These labels refer to the usual designations of the molecular symmetry group: \( a_1 \) denotes a totally symmetric non-degenerate level, and the \( e \)-components refer to a twofold degeneracy. The orbital triplet is the direct sum, \( a_1 + e \).

The three components of the triplet can be expressed as normalized linear combinations of the 13 nodes, as follows:

\[
\begin{align*}
|a_1\rangle &= \frac{1}{\sqrt{30}}(-2|a\rangle - 2|b\rangle - 2|c\rangle + |d\rangle + |e\rangle + |f\rangle - |g\rangle - |h\rangle - |i\rangle - |j\rangle) \\
&\quad - |k\rangle - |l\rangle + 3|x\rangle), \\
|e_\beta\rangle &= \frac{1}{2\sqrt{6}}(-2|a\rangle + |b\rangle + |c\rangle - 2|d\rangle + |e\rangle + |f\rangle - |g\rangle - |h\rangle + 2|i\rangle - |j\rangle) \\
&\quad - |k\rangle + 2|l\rangle) \\
\text{and} \quad |e_\epsilon\rangle &= \frac{1}{2\sqrt{2}}(|b\rangle - |c\rangle + |e\rangle - |f\rangle - |g\rangle + |h\rangle - |j\rangle + |k\rangle).
\end{align*}
\]

(6.8)
Table 1. Normalized JT-active modes for the $(A_1 + E) \otimes (a + 2e)$ problem.

<table>
<thead>
<tr>
<th>ag</th>
<th>bk</th>
<th>ci</th>
<th>ah</th>
<th>cj</th>
<th>bl</th>
<th>fy</th>
<th>dk</th>
<th>ei</th>
<th>eh</th>
<th>dj</th>
<th>fl</th>
<th>ex</th>
<th>dx</th>
<th>fx</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6\sqrt{3} \times Q_0$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-3</td>
<td>-3</td>
<td>-3</td>
<td>-3</td>
<td>-3</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$2\sqrt{6} \times Q_0$</td>
<td>1</td>
<td>-2</td>
<td>1</td>
<td>-2</td>
<td>1</td>
<td>1</td>
<td>-2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$2\sqrt{2} \times Q_0$</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$2\sqrt{66} \times Q_3$</td>
<td>5</td>
<td>2</td>
<td>-7</td>
<td>5</td>
<td>2</td>
<td>-7</td>
<td>-2</td>
<td>1</td>
<td>1</td>
<td>-2</td>
<td>1</td>
<td>4</td>
<td>-8</td>
<td>4</td>
</tr>
<tr>
<td>$2\sqrt{22} \times Q_4$</td>
<td>3</td>
<td>-4</td>
<td>1</td>
<td>-3</td>
<td>4</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>4</td>
<td>0</td>
<td>-4</td>
</tr>
</tbody>
</table>

The JT Hamiltonian for this level can be limited to changes of the interactions corresponding to the 15 edges. Since this is a $3 \times 3$ problem, the traceless JT matrix will contain five linearly independent active modes. Normalized expressions for these modes as a function of the edge distortions are given in Table 1.

The Hamiltonian reads

$$
\begin{align*}
\langle e_\vartheta \rangle & \quad -\frac{\sqrt{3}}{10} Q_0 + \frac{1}{\sqrt{6}} Q_\vartheta \\
\langle e_\varepsilon \rangle & \quad \frac{1}{\sqrt{6}} Q_\varepsilon \\
\langle a_1 \rangle & \quad \frac{1}{4\sqrt{30}} Q_\vartheta + \frac{\sqrt{66}}{8\sqrt{5}} Q_3
\end{align*}
\right) \cdot
\begin{align*}
\frac{1}{4\sqrt{30}} Q_\varepsilon + \frac{\sqrt{66}}{8\sqrt{5}} Q_4 + \frac{\sqrt{3}}{5} Q_0
\end{align*}
\right). \quad (6.9)

It should be realized that this Hamiltonian does not contain any parameters. Hence, the distortions of the triplet level in the space of the five active modes are entirely described by the numerical coupling coefficients multiplying the $Q$ symbols. We also note that the matrix contains an upper $2 \times 2$ block that corresponds to the normal JT distortion of the $e$-sublevel in the $(Q_\vartheta, Q_\varepsilon)$ subspace, as in the example of the triangle.

In order to find the directions of maximal distortion, we shall follow the method of the isostationary function (Ceulemans 1987). This method avoids the cumbersome diagonalization of the matrix and immediately leads to the directions of maximal distortion. One first adds to the Hamiltonian an isotropic term, which is proportional to the square of the radius of the active space and, in a molecular context, is called the harmonic restoring potential, $V$,

$$
V = \frac{1}{2}(Q_0^2 + Q_\vartheta^2 + Q_\varepsilon^2 + Q_3^2). \quad (6.10)
$$

An eigenstate of the Hamiltonian is represented as

$$
|\Psi\rangle = c_\vartheta |e_\vartheta \rangle + c_\varepsilon |e_\varepsilon \rangle + c_a |a_1 \rangle, \quad (6.11)
$$

where $c_\vartheta$, $c_\varepsilon$ and $c_a$ are normalized coefficients. The corresponding eigenenergy is given by

$$
E(Q) = V(Q) + \sum_{i,j} c_i c_j H_{ij}(Q). \quad (6.12)
$$
The first term in this equation has a quadratic dependence on $Q$, while the second term has a linear dependence. By minimizing $E$ with respect to the $Q$-quantities, we thus obtain expressions for the stationary coordinates, $\|Q\|$, as a function of the $c$-coefficients,

$$
\begin{align*}
\|Q_0\| &= \frac{\sqrt{3}}{10} c_\phi^2 + \frac{\sqrt{3}}{10} c_\epsilon^2 - \frac{\sqrt{3}}{5} c_a^2, \\
\|Q_\phi\| &= -\frac{1}{\sqrt{6}} c_\phi^2 - \frac{1}{2\sqrt{30}} c_\phi c_a + \frac{1}{\sqrt{6}} c_\epsilon^2, \\
\|Q_\epsilon\| &= -\frac{\sqrt{2}}{3} c_\phi c_\epsilon + \frac{1}{2\sqrt{30}} c_\epsilon c_a, \\
\|Q_3\| &= -\frac{1}{2} \sqrt{\frac{33}{10}} c_\phi c_a, \\
\|Q_4\| &= -\frac{1}{2} \sqrt{\frac{33}{10}} c_\epsilon c_a.
\end{align*}
$$

These expressions are reinserted into equation (6.12). As a result, the $Q$-space is projected into the $c$-space and the energy becomes a quartic function of the $c$-coefficients only: $E(Q(c))$,

$$
E(Q(c)) = \frac{59}{600} (c_\phi^4 + 2c_\phi^2 c_\epsilon^2 + c_\epsilon^4) - \frac{3}{50} c_a^4 - \frac{1}{12\sqrt{5}} (c_\phi^3 c_a - 3c_\phi c_\epsilon^2 c_a)$$

$$
- \frac{107}{300} (c_\phi^2 c_a^2 + c_\epsilon^2 c_a^2).$$

This function in $c$-space is called the isostationary function. It has the same extrema as the JT energy landscape, but has the benefit of a reduced dimensionality. The stationary points may be found by minimizing the expression in equation (6.14) subject to the eigenvector normalization condition: $c_\phi^2 + c_\epsilon^2 + c_a^2 = 1$. The use of Lagrange multipliers yields 26 extremal eigenvectors that, since $E(Q(c))$ is an even function under spatial inversion, come in 13 pairs with opposite sign. As the stationary coordinates, $\|Q\|$ in equation (6.13), are also invariant under inversion in $c$-space, both members of a given antipodal pair will correspond with the same extremal point in $Q$-space, leading to a perfect 2-to-1 mapping between the $c$- and $Q$-spaces. The 13 non-trivial extremal eigenvectors (one of each pair) of the isostationary function can be further distributed over five distinct orbits ($\alpha - \epsilon$), which are listed in table 2.

The exact nature of the extrema was checked by an evaluation of the Hessian matrix at these locations, subject to the eigenvector normalization condition. In the current case, the low dimensionality of the problem allows us to visualize the full isostationary function on the 2-sphere (figure 3). The observed equipotential line around the equator ($c_a = 0$) is reminiscent of the $E \otimes e$ type JT problem, but these points no longer form a continuous minimal energy trough as in the case of the Mexican hat. In fact, the coupling between the accidentally degenerate $e$ and $a_1$ modes leads to three isolated minima forming the $\epsilon$ orbit of table 2. To obtain the actual configurations of these minima, one first identifies their location in $Q$-space by feeding in the electronic coefficients into the extremal coordinate
Figure 3. Contour plots showing the full isostationary function for the \((A_1 + E) \otimes (a + 2e)\) problem. (a) Top view showing the maximum of type \(a\) surrounded by three \(e\) minima. (b, c) Side views focusing, respectively, on the \(\delta\) and \(\gamma\) transition states between two \(e\) minima. (Online version in colour.)

Table 2. Energy, symmetry and nature of the five stationary orbits of eigenvectors.

<table>
<thead>
<tr>
<th>orbit</th>
<th>dim</th>
<th>sym</th>
<th>eigenvectors ((c_\phi, c_\varepsilon, c_a))</th>
<th>energy</th>
<th>Hessian eigenvalues</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)</td>
<td>1</td>
<td>(C_{3v})</td>
<td>(\alpha_1 = (0, 0, 1))</td>
<td>(-0.06 = -3/50)</td>
<td>(-0.0473333/) (-0.0473333)</td>
</tr>
<tr>
<td>(\beta)</td>
<td>3</td>
<td>(C_s)</td>
<td>(\beta_1 = (0.496776, 0.860442, 0.113375), \beta_2 = (-0.993552, 0, 0.113375), \beta_3 = (0.496776, -0.860442, 0.113375))</td>
<td>(-0.096213)</td>
<td>(-0.322822/) (-0.037782)</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>3</td>
<td>(C_2)</td>
<td>(\gamma_1 = \frac{1}{2}(\sqrt{3}, -1, 0)), (\gamma_2 = (0, 1, 0)), (\gamma_3 = \frac{1}{2}(\sqrt{3}, 1, 0))</td>
<td>(-0.098333 = -59/600)</td>
<td>(-0.355192/) (0.035519)</td>
</tr>
<tr>
<td>(\delta)</td>
<td>3</td>
<td>(C_s)</td>
<td>(\delta_1 = (0.372768, 0.645653, 0.666466), \delta_2 = (-0.745535, 0, 0.666466), \delta_3 = (0.372768, -0.645653, 0.666466))</td>
<td>(-0.119979)</td>
<td>(0.341763/) (-0.166657)</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>3</td>
<td>(C_s)</td>
<td>(\varepsilon_1 = (0.791621, 0, 0.611012), \varepsilon_2 = (-0.395811, 0.685564, 0.611012), \varepsilon_3 = (-0.395811, -0.685564, 0.611012))</td>
<td>(-0.141720)</td>
<td>(0.437760/) (0.162235)</td>
</tr>
</tbody>
</table>

conditions of equation (6.13) and subsequently translating these coordinates back to edge distortions with the help of table 1. As an example, in figure 2, we depict the configuration corresponding with the minimum \(\varepsilon_1\). The signs and weights of the edge distortions, \(\Delta H_{ij}\), are, respectively, indicated by the plus and minus signs on the edges and the numbers next to them. A typical feature of minimal-energy JT distortions is that the automorphism group is not reduced to the trivial group. The remaining subgroup is an epikernel of the full symmetry group (Ceulemans & Vanquickenborne 1989). In the present case, the epikernel corresponds to the reflection symmetry in figure 2. Also note the exact equality of edge distortions \(\delta j\) and \(\varepsilon i\). This reflects the properties of the particular subspace formed by the JT-active modes.

Tunnelling between the minima can occur via two types of transition states ($\gamma$ or $\delta$). The discussion of the topological Berry phases attained by different closed tunnelling regimes will be based on figure 2, which sketches the projective planar topology of the JT surface. The energetically most preferred tunnelling regime is the one mediated by transition states of type $\delta$. In this way, the closed path $(\varepsilon_1-\delta_1-\varepsilon_2-\delta_2-\varepsilon_3-\delta_3-\varepsilon_1)$ can be formed for which phase tracking in $Q$-space shows that the wave function acquires no Berry phase. However, the alternative tunnelling regime, which uses the $\gamma$-type transition states to form the closed path $(\varepsilon_1-\gamma_1-\varepsilon_2-\gamma_2-\varepsilon_3-\gamma_3-\varepsilon_1)$, will result in the wave functions acquiring a Berry phase of $\pi$. A more general analysis shows that the Berry phase acquired by a closed tunnelling path depends on the number of times the path crosses the boundary in figure 2 or, equivalently, on the number of times that a $\gamma$-type transition state is used to tunnel between minima. For those closed paths that cross the border an even number of times, the loop will be topologically contractible and the eigenvector attains no Berry phase, whereas non-contractible loops that cross the boundary an odd number of times will be characterized by a Berry phase of $\pi$.

7. Discussion

The JT theorem predicts the existence of a symmetry-lowering effect in chemistry and condensed-matter physics: a system in a degenerate state will show a spontaneous distortion that removes the initial degeneracy. At the origin of this symmetry lowering is the non-vanishing energy gradient of the state in the space of the non-totally symmetric geometrical distortion coordinates.

We claim that this result can be transposed to graph theory. This conjecture states that whenever the spectrum of a graph contains a set of bonding or anti-bonding degenerate eigenvalues, the roots of the Hamiltonian matrix over this set will show a linear dependence on edge distortions, which has the effect of lifting the degeneracy. The derivatives with respect to the distortion modes are the essential coupling parameters. These parameters are intrinsic characteristics of a graph. The graph-theoretical analogue of the JT theorem will hold if these parameters are different from zero.

Non-bonding degenerate manifolds are more subtle. In this case, there will be edge distortions in the active space that cannot couple to the degeneracy. A case in point is the non-bonding triplet level in the octahedral graph. The active space contains an $e$-type edge distortion that cannot couple to the triplet level. Distortions of the vertex weights have to be included as well, in order to complete the JT Hamiltonian.

The conjecture also has an intriguing dimensional consequence. As an example, the complete graph, $K_5$, has only 10 edges, so its distortion space cannot accommodate all active modes for a quintuple degeneracy, which would require a 14-dimensional active space. However, while the automorphism group of $K_5$ is the symmetric group $S_5$, which contains fivefold and sixfold degenerate irreducible representations, the actual spectrum of $K_5$ has no degeneracy larger than 4. Hence, a possible dimensional conflict with the theorem is avoided. A similar JT treatment can be carried out for the Petersen graph, the automorphism group of which is also isomorphic to $S_5$. This graph has 15 edges, which is sufficient to cover...
the active space for a fivefold degeneracy, but insufficient for the 20-dimensional active space that would be required to lift a sixfold degeneracy. In support of our conjecture, the spectrum of the Petersen graph indeed has no degeneracy larger than 5. The distortions of this fivefold level in the Petersen graph mimic the JT instability of the icosahedral quintuplet problem (Ceulemans & Fowler 1990).

The graph-theoretical analogy also has a chemical relevance. The coupling of electronic states with vibrational distortion modes has recently been analysed by Sato et al. (2006, 2010) in terms of a vibronic coupling density, which separately identifies bond (inter-site) and atom (on-site) contributions to the vibronic coupling parameters. For many examples, this scheme reveals the dominant role of the underlying molecular graph in the JT effect.

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References


