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# TOPOLOGICAL ASPECTS OF SYMMETRIC MOLECULES

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Topological problems have been extensively discussed for π-electron systems. The topology of a molecule is given by the point symmetry of the nuclear configuration and by the connections which are drawn between these points (connectedness). A separation of topological effects from a general variational treatment of a symmetric molecule may serve to classify questions about the physical origin of some molecular properties observed. The symmetry and linkage properties of the molecule determine the orbital energy scheme and other properties derived from one electron treatments, like for example bond orders and charge densities. In semi-empirical theories the solution of the topological part is, in general, sufficient for a satisfactory theoretical treatment of electronic structures, where the integrals remain as parameters in the equations.

In the Hückel–Wheland molecular orbital approximation of π-electron systems, such a separation of topological effects is easily obtained from the secular equation

$$|\boldsymbol{H}-E\boldsymbol{S}| = 0 \tag{1}$$

by resolving the energy and overlap matrix, respectively, into

$$\boldsymbol{H} = \alpha\mathbf{1}+\beta\boldsymbol{M}$$

and

$$\boldsymbol{S} = \mathbf{1}+S\boldsymbol{M},$$

where $\mathbf{1}$ is the unit matrix, $\alpha$ and $\beta$ the Hückel Coulomb and resonance integrals, and $\boldsymbol{M}$ is the incidence[1], topological[2] or structural[3] matrix defined by

$$M_{ij} = \begin{cases} \theta \text{ if } i = j \\ 1 \text{ if } i, j \text{ are neighbours} \\ 0 \text{ if } i, j \text{ are non-neighbours.} \end{cases}$$

Inserting (2) into (1) yields

$$|\alpha\mathbf{1}+\beta\boldsymbol{M}-E(\mathbf{1}+S\boldsymbol{M})| = |\boldsymbol{M}(\beta-ES)+\mathbf{1}(\alpha-E)| =$$
$$= |\boldsymbol{M}-\frac{E-\alpha}{\beta-ES}\mathbf{1}| = |\boldsymbol{M}-\rho\mathbf{1}| = 0 \tag{3}$$

if $\beta - ES \neq 0$ and

$$\rho = \frac{E-\alpha}{\beta - ES}$$

are the Hückel numbers leading to the well known expression

$$E = \frac{\alpha+\rho\beta}{1+\rho\beta} \tag{4}$$

Thus a separation of the topological part of the problem is obtained. The diagonalization of the secular equation is simplified by solving the eigenvalue condition (3). Since $\boldsymbol{H}$ and $\boldsymbol{M}$ commute, ($\boldsymbol{HM}-\boldsymbol{MH} = 0$), they also have the same set of eigenvectors.

Such a separation of topological problems from energetic effects is not restricted to $\pi$-electron systems but is also possible within the framework of a general LCAO treatment of symmetric molecules. This generalization enables the study of other organic and also inorganic molecules. For highly symmetric molecules with topologically equivalent atoms, topological effects are distinctly separable. A reduction of symmetry, however, leads to reduced separability of topological aspects, which for asymmetric molecules is only possible if large approximations are made. For instance a linear chain of three identical atoms is considered to be a highly symmetric molecule. However, only the two terminal atoms are topologically equivalent and different from that in the centre. The resolution of the orbital energy matrix as obtained in (2) for this case is only approximate, since the Coulomb integral of the terminal atoms is different from that of the central atom. For a tetrahedral molecule, where four identical atoms occupy the corners of a tetrahedron, all centres are topologically equivalent, so that the separation of a topological matrix from the energy matrix according to (2) is exact.

While the mathematical tool of treating symmetry is given by group theory, topological problems of a molecule can be handled by the fundamental theory of graphs[1,4]. Group theory furnishes the symmetry of the states and their degeneracy, graph theory in addition is able to supply information on the order of the orbital states. The symmetry and connectedness of a point grid corresponds to a special kind of graph. A graph $G(X; \Gamma)$ is defined by a set of points $X = P_1, P_2, \ldots P_\alpha$ and a function $\Gamma$ over this set which contains various edges $V_1, V_2, \ldots, V_\beta$. A close equivalence between general LCAO-MO theory and graph theory can be established[1,4]. This correspondence is given by the matrix representation of a graph, which corresponds either to the topological matrix or directly to the energy matrix $\boldsymbol{H}$, originated from the atomic orbital basis set. A matrix representation is obtained by assigning a number to each point and each edge of the graph (see Fig. 1). This marked and valued graph can then be represented by the matrix:

$$R = \begin{pmatrix} a & \alpha & \beta & 0 \\ \alpha & b & \gamma & \delta \\ \beta & \gamma & c & 0 \\ 0 & \delta & 0 & d \end{pmatrix} \tag{5}$$

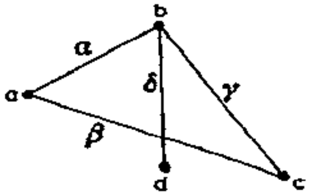

Fig. 1. A valued symmetric graph represented by equation (5).

Non-connected points correspond to zero elements in the matrix. Since the matrix is symmetric, the graph is also called symmetric. Only if the matrix describes the complete topology of the graph by a one to one correspondence do we call this matrix a topological matrix. One may think of several topological matrices representing the topology of a molecule. We then choose the simplest matrix in which identical edges (equal distances for identical types of connections) are represented by the same numbers.

In general such a one to one correspondence is given between a Hückel graph and its topological matrix, which by definition has only non-zero elements for bonded (neighbour) atoms. For three-dimensional molecules, however, a biunique relation is not obtained if we choose the topological matrix according to the Hückel method. For instance a square planar and tetrahedral complex $AB_4$ would have the same topological matrix if the topological matrix has non-zero elements only at positions corresponding to the A–B bond.

The above theory was outlined in detail elsewhere[4]. Here we shall apply it for some symmetry cases which are closely connected with coordination compounds. At first, we investigate the topological properties of four identical points having tetrahedral and square planar symmetry. In both cases a resolution of the energy and overlap matrix according to (2) is possible in a distinct way, since they both contain topologically equivalent points. The topological matrices are given for the tetrahedron by

$$M_t = \begin{pmatrix} 0 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{pmatrix} \tag{6}$$

and for the square by

$$M_s = \begin{pmatrix} 0 & 1 & \kappa & 1 \\ 1 & 0 & 1 & \kappa \\ \kappa & 1 & 0 & 1 \\ 1 & \kappa & 1 & 0 \end{pmatrix} \tag{7}$$

In the latter case $\kappa$ is a parameter which stands for the interaction between non-neighbours. It is, in general, different for a resolution of the energy and the overlap matrix. This parameter can be put equal to zero, if only topological problems are investigated since this matrix contains all topological properties. For energetic problems this parameter should be considered if it is desirable to resolve the matrices (2) in a completely exact way. In this case $\kappa$ is a parameter between 0 and 1. According to the value of $\kappa$ the matrix (7) describes all symmetry arrangements between square planar and tetrahedral symmetry. This situation is obtained if two points in trans-positions are lifted out of the square plane (squashed tetrahedron). The matrix (7) therefore describes topological arrangements in $D_{4h}$ and $S_4$ symmetry. The eigenvalues of the matrices (6) and (7) together with their group theoretical symbols in tetrahedral and square planar symmetry in Eisenstein's[5] notation are

$$\begin{array}{llll} & \rho_{2,3,4} = -1 \ (t_2) & D_{4h}: & \rho_{1,2} = \ -\kappa \ (e_u) \\ T_d: & \rho_1 \quad = \ \ 3 \ (a_1) & & \rho_3 \ \ = 2 + \kappa \ (a_{1g}) \\ & & & \rho_4 \ \ = -2 + \kappa \ b_{2g}) \end{array} \tag{8}$$

This result also represents a proof for the node rule, according to which the orbital energy is raised if the number of nodes is large. Since positive $\rho$'s represent bonding states and negative ones antibonding states, *cf.* (4), the orbital series in the tetrahedron is given by $a_1 < t_2$ and for the square $a_{1g} < e_u < b_{2g}$.

The topological matrix for an octahedron is correspondingly given by

$$M_0 = \begin{bmatrix} 0 & 0 & 1 & 1 & 1 & 1 \\ 0 & 0 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 & 0 & 0 \\ 1 & 1 & 1 & 1 & 0 & 0 \end{bmatrix} .$$

The eigenvalue spectrum is

$$\begin{array}{lcrl} \rho_1 & = & 4 & (a_{1g}) \\ \rho_{2,3} & = & -2 & (e_g) \\ \rho_{4,5,6} & = & 0 & (t_{1u}) \end{array} \tag{9}$$

which corresponds to the $\sigma$-orbital scheme of the ligands in an octahedral complex.

If the present topological method is extended to describe also $\pi$-bonded systems, different types of connections between the points in the graph have to be considered. This situation is anticipated in graph theory by the concept of multigraphs $G(X; \Gamma, \Delta, \ldots)$. Over a set of points X, different functions $\Gamma$, $\Delta$, ... are defined, which describe different types of interactions. The corresponding topological matrix is a supermatrix of degree $n \cdot m$, where $n$ is the number of points in X (power of X) and $m$ is the number of functions $\Gamma$, $\Delta$, ... For an octahedron this matrix is $6 \times 3 = 18$ dimensional. Because of the two-fold degeneracy of $\pi$ bonds two more functions are necessary for a graph representation. The elements of this matrix are either one or are equal to a parameter $\lambda$, which describes the $\pi$–$\pi$ orbital interaction between two different ligands. The topological matrix is easily split into smaller parts if one makes use of the symmetry properties. The orbital series of the octahedral framework, determined by the roots of the topological matrix, is given by

$$a_{1g} < t_{1u} < t_{2g} < t_{2u} < t_{1g} = e_g < t_{1u} \qquad (10)$$

This sequence which is valid only for ligand–ligand interactions, gives also some information on the order of bonded and non-bonded orbitals in the metal complex. In transition metal ions, $d$ orbitals interact in octahedral symmetry by $e_g$ and $t_{2g}$ states. For bonding states the corresponding ligand orbitals in (10) are stabilized by mixing into metal d orbitals. The interaction with metal $p$ orbital states occurring through $t_{1u}$ is expected to be relatively weaker. For large ligand–ligand interactions the series of the "ungerade" states is therefore predicted from topological reasons to be $t_{1u} < t_{2u} < t_{1u}$. These states are of particular importance for the assignment of the charge transfer bands in the spectra of complexes. An electron transfer from the "ungerade" ligand orbital states to the "gerade" metal $d$ orbital states is parity allowed and gives rise to very intense absorption.

An experimental assignment of the three charge transfer bands of $[Fe(CN)_6]^{3-}$ was recently made by Stephens[6], Schatz and others[7] on the basis of measurements of magneto-optical rotatory dispersion (Faraday effect). According to these authors the bands are due to the following orbital transitions:

| | band | molecular | orbital states |
|---|---|---|---|
| $d^5$: $[Fe(CN)_6]^{3-}$ | 24 kK | $^2T_{2u} \rightarrow {}^2T_{1g}$ | $t_{1u} \rightarrow t_{2g}$ |
| | 33 | $^2T_{2u} \rightarrow {}^2T_{2g}$ | $t_{2u} \rightarrow t_{2g}$ |
| | 38.5 | $^2T_{2u} \rightarrow {}^2T_{1g}$ | $t_{1u} \rightarrow t_{2g}$ |

An objection may be made that the cyanide ligand contains a $\pi$ orbital system itself and may disturb the topologically predicted series by interaction with the $\pi^*$ ligand system. However, the Faraday spectrum of $[IrCl_6]^{2-}$ is, according to Schatz[8], remarkably similar to that of the cyanide complex of iron, a fact which leads to the same orbital scheme also for the chloro complex.

The experimental results together with the topological effects undoubtedly prove that ligand–ligand interactions are, in general, extremely important in complex compounds. Any calculation for which a certain degree of rigour is claimed should consider these effects. In earlier calculations ligand–ligand interactions were considered to be small and have therefore been neglected. A theory which aims to explain charge transfer transitions certainly must be more rigorous with respect to this point.

When applying the topological procedure to a square planar framework, the following orbital series is obtained (in the Eisenstein notation[5]):

$$D_{4h}: a_{1g} = b_{1g} < a_{2u} < e_u < e_g < e_u < b_{1u} < a_{2g} = b_{2g}$$

The interaction with the central metal *d* orbitals goes through $b_{2g}$, $e_g$, $b_{1g}$, and $a_{1g}$. The "ungerade" orbitals are ordered in the complex according to $a_{2u} < e_u < e_u < b_{1u}$, so that the first charge transfer band for square planar complexes is predicted to come from the $b_{1u}$ and the second one from the $e_u$ ligand orbital state. The same order has been already anticipated by Gray and Ballhausen[9] for the assignment of the first two charge transfer bands of square planar halogeno complexes.

For three atoms arranged in an equilateral triangle an orbital series as

$$D_{3h}: a_1' < e' < a_2'' < e'' < e' < a_2'$$

is obtained from topological considerations. Since central metal *d* orbitals in this symmetry interact through $a_1'$, $e'$ and $e''$ the first charge transfer transitions are predicted to have the order $a_2'$, $a_2''$ and $e''$.

Topological procedures applied in a more heuristic way have been recently proposed by Kettle[10], who used an equivalent orbital approach to explain electronic structures of polynuclear compounds.

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