A link between the second-order Jahn-Teller effect and the highest occupied molecular orbital postulate for molecular shapes

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Abstract. For a closed-shell molecule, a connection is drawn between two recent models for molecular shapes, namely, those based on the second-order Jahn-Teller (SOJT) effect and the highest occupied molecuar orbital (HOMO) postulate respectively. Two necessary and sufficient conditions are derived within the molecular orbital framework for the approximation inherent in the SOJT model to be valid. One of these conditions is akin to the HOMO postulate.

Keywords. Jahn-Teller effect; HOMO postulate; molecular geometry.

1. Introduction

The frontier molecular orbital theory of Fukui (1971) as well as Woodward and Hoffmann's (1969) rationalisations on the basis of symmetry considerations have enjoyed great success in predicting the course of chemical reactions. In their wake arrived qualitative models, such as the one based on the second-order Jahn-Teller (SOJT) effect (Bader 1962; Pearson 1969, 1970, 1971; Bartell 1968) and the Hellmann-Feynman (HF) model based on the HOMO postulate (Deb 1974, 1975; Deb *et al* 1974, 1976) which tried to obtain similar broad rationalisations in the field of molecular geometry. In the SOJT model the focus is on the interaction between the HOMO and the lowest unoccupied molecular orbital (LUMO), and this interaction can be used not only for explaining molecular shapes but also for predicting the courses of chemical reactions. The HF model, on the other hand, postulates that molecular shapes are determined primarily by the behaviour of the HOMO (for the complete HOMO postulate as well as possible complicating situations, see Deb 1974), and this simple assumption is capable of providing consistent qualitative answers to all problems dealing with static aspects of molecular geometry.

In this paper we show that the approximation inherent in the SOJT model, concerning the contributions from excited states to an infinite sum, can be reduced to two conditions involving overlaps between certain functions within the orbital approximation. One of these conditions is akin to the HOMO postulate.

2. The two conditions

Let $\{u_i\}$ denote the set of occupied orbitals of a closed-shell ($2n$-electron) molecule. The normalised ground-state wavefunction, of energy E_0, is written as

$$\psi_o = (1/\sqrt{2n!}) \, \mathscr{A} \left\{ u_1 \, \bar{u}_1 \, \ldots \, u_n \, \bar{u}_n \right\} \tag{1}$$

where $\mathscr{A}$ is the antisymmetriser, unbarred u_i denotes α-spin and barred u_i denotes β-spin. Let us form a complete orthonormal set of orbitals by adding to $\{u_i\}$ a further set of virtual orbitals, $\{v_j\}$, $j = n + 1, n + 2, \ldots \infty$. The orbitals in $\{u_i\}$ and $\{v_j\}$ are so numbered that a higher subscript indicates a higher energy.

A singly-excited state, of energy $E_{k(i)}$, where the electron in u_i has been transferred to v_k may be represented by

$$\psi_{k(i)} = \left(1/\sqrt{2n!}\right) \mathscr{A} \{u_1\bar{u}_1 \ldots \bar{u}_{i-1} v_k\bar{u}_i \ldots u_n\bar{u}_n\}. \tag{2}$$

Now, assuming first order distortions to have already occurred, the SOJT effect examines the change in energy from an initial nuclear configuration with respect to a normal coordinate Q. We have

$$\Delta E_{\text{SOJT}} = \tfrac{1}{2} f_{oo} Q^2 + \tfrac{1}{2} f_{ok} Q^2 \tag{3}$$

where $$f_{oo} = \langle \psi_o | \partial^2 H/\partial Q^2 | \psi_o \rangle \tag{4a}$$

$$f_{ok} = 2 \sum_{k \neq 0} |\langle \psi_o | \partial H/\partial Q | \psi_k \rangle|^2/(E_o - E_k). \tag{4b}$$

In (4b) ψ_k represents an excited state and the summation extends over *all* excited states of the system including the continuum states. f_{ok} is always negative and f_{oo} is positive for any reasonable nuclear configuration (Pearson 1969, 1970, 1971).
In qualitative applications of (3) one makes the assumption that only one or two lowest-lying excited states in the above sum need to be considered.
Let us view this assumption in the light of the orbital approximation. One can readily show that

$$\langle \psi_o | \partial H/\partial Q | \psi_k \rangle = (E_o - E_k) \langle \partial\psi_o/\partial Q | \psi_k \rangle. \tag{5}$$

Since $\partial\psi_o/\partial Q$ contains only singly-excited wave functions (Coulson 1971), (4b) reduces to

$$f_{ok} = 2 \sum_{k(i)} |\langle \partial\psi_o/\partial Q | \psi_{k(i)} \rangle|^2 (E_o - E_{k(i)}). \tag{6}$$

Further, from (1)

$$(\partial\psi_o/\partial Q) = \left(1/\sqrt{(2n)!}\right) [\mathscr{A} \{(\partial u_1/\partial Q) \bar{u}_1 \ldots u_n\bar{u}_n\}$$

$$+ \mathscr{A} \{u_1 (\partial\bar{u}_1/\partial Q) \ldots u_n \bar{u}_n\} + \ldots + \mathscr{A} \{u_i \bar{u}_1 \ldots u_n (\partial\bar{u}_n/\partial Q)\}]. \tag{7}$$

Since the u's and the v's form a complete orthonormal set,

$$(\partial u_i/\partial Q) = \sum_j c_{j(i)} v_j + \sum_{i \neq j} d_{j(i)} u_j. \tag{8}$$

Substituting (8) into (7), we find

$$(\partial\psi_o/\partial Q) = \sum_j [c_{j(1)}\,\psi_{j(1)} + c_{j(I)}\,\psi_{j(I)} + \dots c_{j(n)}\,\psi_{j(n)}]. \tag{9}$$

In (9) terms with $d_{j(t)}$ vanish because every determinantal function involving these coefficients has two identical columns (or rows).

Using (8), (9) and the orthogonality of the ψ's, we obtain

$$\langle \partial\psi_o/\partial Q \mid \psi_{k(t)} \rangle = c_{k(t)} = \langle \partial u_i/\partial Q \mid v_k \rangle. \tag{10}$$

Thus, (6) becomes

$$f_{ok} = 2 \sum_{k\,(i)} \mid c_{k(t)} \mid^2 (E_o - E_{k(t)}). \tag{11}$$

Therefore, the approximation that only one or two lowest excited states contribute significantly to the infinite sum in (4b) leads to the following necessary and sufficient conditions:

$$\mid c_{k(t)} \mid^2 (E_o - E_{k(t)}) \gg \mid (c_{k+1(t)} \mid^2 (E_o - E_{k+1(t)}) \tag{12a}$$

$$\mid c_{k(t)} \mid^2 (E_o - E_{k(t)}) \gg \mid (c_{k(t-1)} \mid^2 (E_o - E_{k(t-1)}). \tag{12b}$$

Condition (12a) highlights the role of the lowest virtual orbital, i.e. LUMO, by implying that excitation from a given occupied orbital to higher and higher unoccupied orbitals would result in progressively much smaller contributions. Condition (12b) emphasises the role of the HOMO by implying that excitation to a given unoccupied orbital from lower and lower occupied orbitals would bring in progressively much diminished contributions. However, although (12b) bears some resemblance to the HOMO postulate, it should be noted that in the SOJT model both (12a) and (12b) have to be employed together; none of them can be used by itself. Taken together, they imply that the most dominant term in (4b) arises from the HOMO to LUMO transition.

In order to test for the very rapid convergence indicated in (12a) and (12b) for many-electron polyatomic molecules, one has to calculate a number of $c_{k(t)}$'s and $E_{k(t)}$'s and, therefore, one must have a sufficiently large number of virtual orbitals which are (i) orthogonal amongst themselves and to the occupied orbitals, as well as (ii) accurate enough to provide a reasonably good description of the excited states. It may be worthwhile to generate such virtual orbitals according to the prescription of Huzinaga *et al* (1973). However, this dependence on virtual orbitals does make the link between the SOJT model and the HOMO postulate somewhat tenuous. Further, the role (Brown and Steiner 1962) of the continuum wavefunctions in (4b) remians unclear.

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