

NUCLEAR CHARGE CHANGES: INFLUENCE ON THE ENERGY OF HIGHLY SYMMETRICAL MOLECULES

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The stability of molecules in orbitally degenerate electronic states with respect to nuclear charge variations is investigated. The results are compared with the Jahn–Teller effect.

1. Introduction

As stated by the Jahn–Teller theorem [1] a polyatomic molecule in an orbitally degenerate electronic state cannot possess a potential surface minimum at a symmetric configuration of nuclei. There always exists a nonsymmetric distortion such that the energy is a linear function of this distortion. Here we consider the influence of nuclear charge changes on the energy of degenerate electronic states at a fixed geometrical configuration. We are interested in the nuclear charge changes which result in breaking the molecular symmetry, i.e. in splitting degenerate electronic states. The continuous change of nuclear charge is appropriate for example in a valence electron approximation to the electronic equation when the effective nuclear charges are model parameters.

2. General theorem

The solution of this problem is analogous to the Jahn–Teller proof. Let ζ_k be small nuclear charge variations classified according to irreducible representations Γ_k of the point group of the nuclear configuration. The Hellmann–Feynman theorem enables one to express $(\partial E/\partial \zeta_k)_0$ as

$$(\partial E/\partial \zeta_k)_0 = \langle \Phi_\alpha | \partial H_e / \partial \zeta_k | \Phi_\alpha \rangle, \quad (1)$$

where H_e is an electronic hamiltonian which may be

represented as a power series in ζ_k . Φ_α is an eigenfunction of H_e at $\zeta_k = 0$. Φ_α belongs to an irreducible representation Γ_α . Thus the matrix element (1) is equal to zero if the product $\Gamma_\alpha^* \times \Gamma_k \times \Gamma_\alpha$ does not include the identity representation. Testing of all symmetry groups and all types of molecules has shown that nonsymmetrical charge changes leading to nonzero values of matrix elements (1) exist for almost all molecules except the following ones:

1. Linear molecules. (A similar exclusion takes place in the Jahn–Teller theorem.)
2. The molecules of T_d symmetry which are in E states and consist of sets of 4 equivalent atoms (and maybe one atom in the centre of symmetry). Examples are: CH_4 and P_4 .
3. The molecules of O_h symmetry which are in E_g or E_u degenerate states and consist of sets of 8 equivalent atoms (and maybe one atom in the centre of symmetry). Examples are: cuban – C_8H_8 and OsX_8 .

In other words all the molecules in orbitally degenerate electronic states are unstable to nonsymmetrical nuclear charge changes except for the above mentioned three types of molecules.

3. Comparison with Jahn–Teller effect

Let us compare $(\partial E/\partial \zeta_k)_0$ and $(\partial E/\partial Q)_0$ which are correspondingly proportional to the energy shifts due to the nuclear charge changes and the geometrical con-

figuration distortion

$$\langle \partial E / \partial Q \rangle_0 \propto \langle \partial \langle z / |r - R| \rangle / \partial Q \rangle_0 \propto \langle z / |r - R|^2 \rangle_0,$$

$$\langle \partial E / \partial \xi \rangle_0 \propto \langle \partial V / \partial \xi \rangle_0 \propto \langle 1 / |r - R| \rangle_0.$$

These crude estimations show that contributions to the energy shifts from the geometry distortions and charge variations depend on the expectation values of $(r - R)^{-2}$ and $(r - R)^{-1}$ respectively. Thus the redistribution of nuclear charges should become more important than the geometrical distortions for molecules composed of heavy many-electron atoms. One should expect that the new interpretation may be done for some experimental evidences of the Jahn-Teller effect in heavy element compounds. In this connection the model semi-empirical calculations of symmetrical systems with an unsymmetrical distribution of the nuclear charge and inclusion of the non-symmetrical electronic configurations in ab initio calculations of degenerate states are of great importance.

4. Crossing problem

Eigenvalues of an electronic equation for highly symmetric molecular systems surely possess the degeneracy points corresponding to symmetric nuclear configurations if the point group admits degenerate representations. For a long time the discussion on the existence of degeneracy points which are not due to the point symmetry takes place [2-8]. Longuet-Higgins has shown with the aid of topological arguments that such points sometimes may exist [5]. For example the symmetry may be broken simultaneously by the geometrical distortion and nuclear charge changes in such a way that degeneracy is maintained. One can compare the influence of the nuclear charge redistribution and the geometrical distortion on a degeneracy point. If both of these effects result in a linear splitting of energy levels, they can simultaneously lead to the cancellation of the linear terms. When charge changes yield no linear splitting the geometry distortion splitting cannot be compensated for by any charge redistribution. In such a case simultaneous geometry distortions and charge changes cannot conserve the degeneracy point even through the linear terms.

Table 1 shows the discrepancy in charge change and geometry distortion effects. The first and second cases from table 1 correspond to the absence of linear splitting due to the charge changes. Besides there are many molecules for which the number of charge changes active to symmetry breaking is less than the number of the proper active vibrational dis-

Table 1 a)

1	2	3	4	5	6	
O _h	e	C ₃ , σ _d	E _g , E _u	E _g	-	
	g	all				
T _d	d	C ₃ , σ	E	E	-	
	e	all				
I _h	e	C ₅ , σ	$\left\{ \begin{array}{l} G_g, G_u \\ H_g, H_u \end{array} \right\}$	G _g , H _g	H _g	
	f	all				
O _h	e	C ₃ , σ _d	$\left\{ \begin{array}{l} F_{1g}, F_{2g} \\ F_{1u}, F_{2u} \end{array} \right\}$	E _g , F _{2g}	F _{2g}	
	g	all				
O _h	f	C _{2v} , C ₄ , σ _h , σ _d	$\left\{ \begin{array}{l} F_{1g}, F_{2g} \\ F_{1u}, F_{2u} \end{array} \right\}$	E _g , F _{2g}	E _g	
	g	all				
T _d	d	C ₂ , σ	F ₁ , F ₂	E, F ₂	F ₂	
	e	all				
S _{4p} ^v	b	σ _v				
	c	C ₂	E _p	B ₁ , B ₂	B ₂	
	d	C _{2p}				
	e	all				
C _{2p} ^v	b	σ	E _p	B ₁ , B ₂	B ₁	
	d	all				
C _{2p} ^v	c	σ'	E _p	B ₁ , B ₂	B ₂	
	d	all				
D _{2p} ⁱ	b	σ	$\left\{ \begin{array}{l} E_{p/2,g} \\ E_{p/2,u} \end{array} \right\}$	B _{1g} , B _{2g}	B _{2g}	
	f	σ _h , C ₂ , σ'				
	g	C _{2p} , σ, σ'				
	h	all				
D _{2p} ⁱ	c	σ'	$\left\{ \begin{array}{l} E_{p/2,g} \\ E_{p/2,u} \end{array} \right\}$	B _{1g} , B _{2g}	B _{1g}	
	e	σ _h , C ₂ , σ				
	g	C _{2p} , σ, σ'				
	h	all				

a) The columns denote correspondingly: 1 - molecular symmetry group. 2 - types of atoms in a molecule. 3 - symmetry elements which the atoms are situated on. 4 - electronic states which the discrepancy takes place for. 5 - symmetry types of the vibrations resulting in linear splitting of a degenerate electronic state. 6 - symmetry types of the nuclear charge changes resulting in the linear splitting of a degenerate electronic state. Abbreviations used here coincide with those of Jahn-Teller [1].

tortions. It seems probable that for real molecular systems geometrical distortion should result in redistribution of effective nuclear charge in such way that symmetry types for both kinds of distortion will be the same. In order to have the degeneracy point which is not due to the nuclear configuration symmetry, geometrical distortions and charge changes in a molecule should be the same symmetry type. Further developments require calculations of molecular systems to clarify the connection between charge changes and geometry distortions. Do these two effects cancel or enhance each other in concrete molecular systems?

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