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Note on the Significance of Walsh's Rules

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The success of Walsh's method is due to the fact that several large errors cancel out approximately. The ordinate of the correlation diagrams corresponds to the eigenvalues of the self-consistant hamiltonian.

Introduction

The remarkable success of the predictions based on Walsh's correlation diagrams [*9*] has been the subject of much speculation [*1, 3, 8*]. The first question which arises is the significance of the "binding energy" associated with each orbital in Walsh's diagrams. Is it equivalent to the ionization potential ? Does it, or not, contain the internuclear Coulomb repulsion ?

SCHMIDTKE and PREUSS [*8*] consider the eigenvalues of a pseudo-hamiltonian, containing no interelectronic and internuclear operators, and where the effective nuclear charge of the central atom is given an arbitrary value. The diagrams they get reproduce those of WALSH rather satisfactorily.

COULSON and NEILSON [*3*] have attempted to justify Walsh's rules in the framework of the self-consistent field theory. They criticize the identification of Walsh's binding energies to the one-electron energies defined in the SCF theory as

$$\varepsilon_i \equiv E_i + \sum_j (2\, J_{ij} - K_{ij}) \,. \tag{1}$$

They indicate two reasons against this. First, the electronic energy is not given by the sum of these quantities. Secondly, the nuclear repulsion energy V_N is not taken into account. COULSON and NEILSON then define "partitioned energies"

$$e_i \equiv \tfrac{1}{2}\,(E_i + \varepsilon_i)\,, \tag{2}$$

which have the property that

$$E_{\text{ground state}} = 2 \sum e_i + V_N \,. \tag{3}$$

A plot of these partitioned energies as a function of the geometrical configuration of the molecule still does not take the nuclear repulsion into account. Besides, these diagrams are different from those of WALSH [*3, 6*].

Recent work by BOER, NEWTON and LIPSCOMB [*2*] throws, however, some light on the matter. These authors have shown that, in the framework of the SCF theory, the atomization energy A of a molecule is approximately given by

$$A \simeq \sum_i \varepsilon_i^m - \sum_{i,a} \varepsilon_i^a , \tag{4}$$

where ε_i^m and ε_i^a refer to the molecule and its dissociated atoms, respectively. The total energy (electronic and nuclear) thus varies as a function of the geometry of the molecule in the same way as does the quantity $\sum_i \varepsilon_i^m$. In other words, the two errors pointed out by Coulson and Neilson approximately cancel each other.

It therefore appears that the use of a rough approximation to a SCF calculation such as the extended Hückel method [*5*, *7*] which assimilates the total energy to the sum of the one-electron energies, can yield useful results in the prediction of molecular geometries. This is precisely what Schmidtke and Preuss found. We arrived at the same conclusion using a more conventional method.

Calculations-Discussion

We investigated these ideas in the course of other calculations, to be described more fully elsewhere. Briefly, we use a basis of valence atomic orbitals, and neglect the overlap everywhere as suggested by Pople and Santry [*7*]. The Coulomb integrals α are chosen as valence state ionization potentials ($\alpha_{2sC} = -21.4$ eV; $\alpha_{2pC} = -11.4$ eV; $\alpha_{2sN} = -26.0$ eV; $\alpha_{2pN} = -13.4$ eV; $\alpha_{2sO} = -35.2$ eV; $\alpha_{2pO} = -18.2$ eV; $\alpha_{1sH} = -13.6$ eV). The most satisfactory relation for the off-diagonal elements β_{pq} was found to be:

Table 1. *Equilibrium* HXH *angles. The accuracy of the determination of the angle which minimizes the calculated energy is about* 2° *everywhere*

Molecule	calc.	exp.	Molecule	calc.	exp.
CH_2	84°	103°	CH_3	110°	≃120°
CH_2^+	125°	–	CH_3^+	120°	–
NH_2	93°	103°	NH_3	96°	107°
NH_2^+	93°	–	NH_3^+	120°	120°
OH_2	110°	105°	OH_3^+	114°	116°
OH_2^+	110°	–			

$$\beta_{pq} = \tfrac{1}{2} K (\alpha_p + \alpha_q) S_{pq} (1 - |S_{pq}|) . \tag{5}$$

K is taken equal to 0.58 for CH and NH bonds, and to 0.37 for an OH bond. This choice reproduces dissociation energies fairly well; equilibrium geometries are given in Tab. 1.

When the one electron energies are plotted as a function of the valence angle, diagrams completely similar to those of Walsh are obtained (Figs. 1 and 2). The order of occupancy does depend on the nature of the central atom (compare, e.g., CH_2 and NH_2), but the rise or fall of the curves corresponding to the first occupied orbitals remarkably agrees with Walsh's predictions.

On the other hand, the expression of the molecular orbitals does not correspond to Walsh's predictions, at least as far as the relative weight of the 2*s* and 2*p* orbitals is concerned. Their ratio does not vary very much as the valence angle changes from 90° to 180°, in contradiction with Walsh's first "principle". This has been known for a long time [*4*, *6*].

The situation thus appears to be the following. Walsh's method is a simulation of a Hückel calculation, which is itself a simulation of a SCF calculation [*2*], which is itself an approximation to the exact solution of the Schrödinger equation. The errors inherent to all stages cancel out in an intricate way. The relationship between the Hückel and the SCF methods is about to be understood. The relationship between Walsh's and Hückel's procedures is even more complex, since the former relies on an assumption concerning the weight of the 2*s* orbital as a function of the geometry which is known to be invalid.

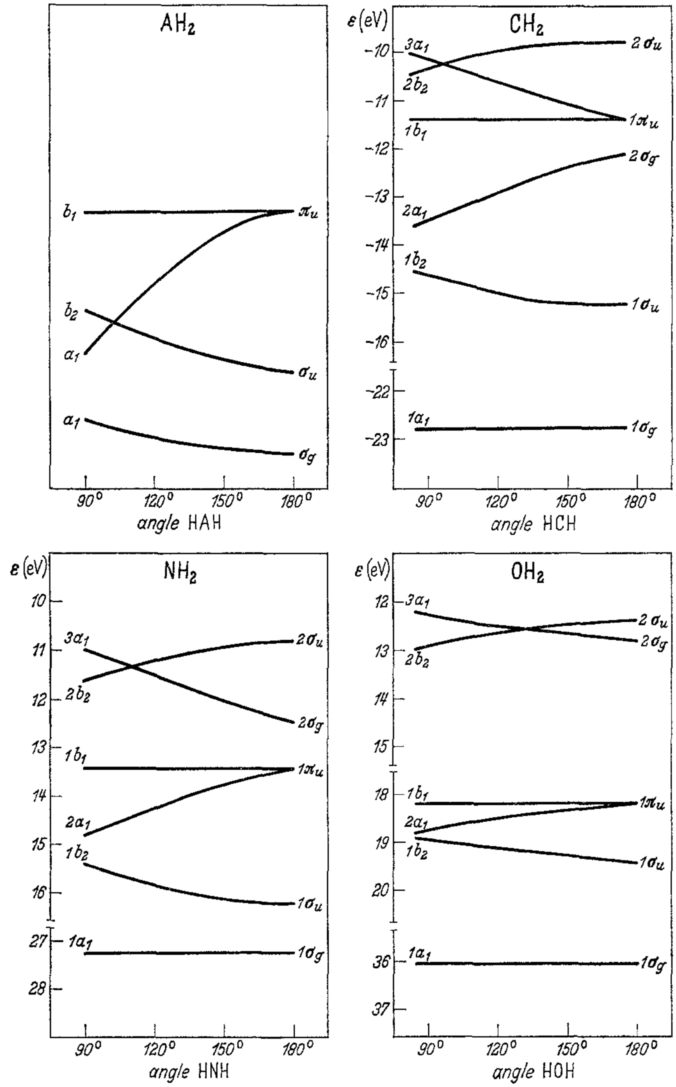

Fig. 1

Comparison between Walsh's diagram for AH_2 molecules, and the one-electron energies of CH_2, NH_2, and OH_2

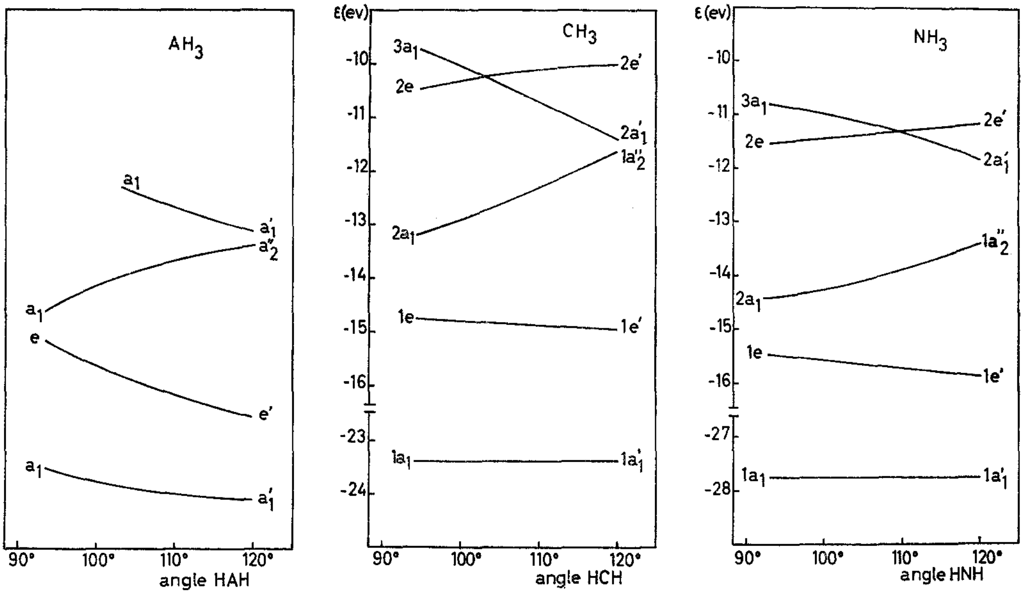

Fig. 2. Comparison between Walsh's diagram for AH_3 molecules, and the one-electron energies of CH_3 and NH_3

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