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Relationes

Walsh's Rules for AH_4 Systems Derived from United Atom Molecular Orbitals

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Recently BINGEL [1] has calculated, using a united atom approximation, the united atom molecular orbital energies of AH_2 and AH_3 systems as a function of nuclear position. The results agree qualitatively with the predictions of WALSH [2] concerning these systems.

The purpose of this paper is the extension of the analysis of BINGEL to AH_4 type systems. Specifically we will assess the changes in orbital energy as the nuclear geometry undergoes the transformation from a tetrahedral (T_d) configuration to the square planar (D_{4h}) configuration.

We shall first briefly outline the derivation of the pertinent formulas, their detailed derivation having been given by BINGEL. It is assumed that an effective one-electron Hamiltonian of the form $h = h_u + V$ can be written where the perturbation term V is given by

$$V = \sum_{\alpha} Z_{\alpha} \left(\frac{1}{|\boldsymbol{r}|} - \frac{1}{|\boldsymbol{r} - \boldsymbol{R}_{\alpha}|} \right) . \tag{1}$$

Fig. 1 displays the various distances and the coordinate system used.

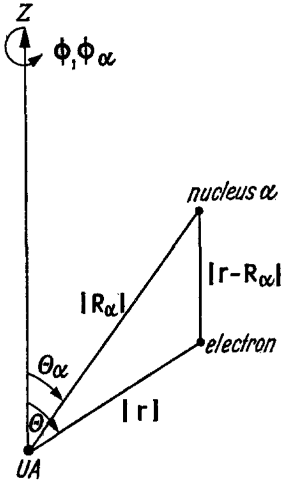

Fig. 1. Coordinate system and distances in the UA expansion (after BINGEL)

It is further assumed that a set of zero-order united atom functions ψ exist which are eigenfunctions of h_u, i e., $h_u \psi_i = \varepsilon_i \psi_i$. Furthermore, we shall restrict ourselves to considerations of s and p type orbitals only. The evaluation of the elements of the perturbation matrix V proceeds as follows: we write

$$V_{ij} = \int \psi_i^* V \psi_j dv = \int \varrho^{ij} (\boldsymbol{r}) \; V(\boldsymbol{r}) \; dv \tag{2a}$$

$$V_{ij} = \sum_{\alpha} Z_{\alpha} \int \varrho^{ij}(\boldsymbol{r}) \left(\frac{1}{|\boldsymbol{r}|} - \frac{1}{|\boldsymbol{r} - \boldsymbol{R}_{\alpha}|} \right) dv \, . \tag{2b}$$

The transition density ϱ^{ij} and $(|\,\boldsymbol{r} - \boldsymbol{R}_a\,|)^{-1}$ are expanded about the origin of the united atom (defined by $\sum\limits_{\alpha} Z_\alpha \boldsymbol{R}_\alpha = 0$) as follows:

$$\varrho^{\,j}(\boldsymbol{r}) = \sum_{L=0}^{\infty} \sum_{M=-L}^{+L} \frac{2L+1}{4\pi} \frac{(L-|\,M\,|)!}{(L+|\,M\,|)!} P_L^{|M|}(\cos\theta)\, e^{-iM\varphi}\, r^L\, \varrho_{LM}^{ij}(r) \tag{3a}$$

$$|\,\boldsymbol{r} - \boldsymbol{R}_\alpha\,|^{-1} = \sum_{K=0}^{\infty} \sum_{N=-K}^{+K} \frac{r_<^K}{r_>^{K+1}} \frac{(K-|\,N\,|)!}{(K+|\,N\,|)!} P_K^{|N|}(\cos\theta)\, P_K^{|N|}(\cos\theta_\alpha)\, e^{iN(\varphi-\varphi_\alpha)}\,. \tag{3b}$$

Where $r_<(r_>)$ is the lesser (greater) or r and R_α. Integration using (3a), (3b) gives the result

$$\int \varrho^{ij}(\boldsymbol{r}) \frac{1}{|\boldsymbol{r} - \boldsymbol{R}_\alpha|}\, dv = \sum_L \sum_M \frac{(L-|\,M\,|)!}{(L+|\,M\,|)!} P_L^{|M|}(\cos\theta_\alpha)\, e^{-iM\varphi_\alpha} \times$$
$$\times \{R_\alpha^L \int_0^\infty r\varrho_{LM}^{ij}\, dr - \int_0^{R_\alpha} \varrho_{LM}^{ij}\, [rR_\alpha^L - r^{2L+2}\, R_\alpha{}^{-(L+1)}]\, dr\}\,. \tag{4a}$$

Substitution of $\varrho_{LM}^{ij}(r) \approx \varrho_{LM}^{ij}(0)$ and $tR_\alpha = r$ into the second integral on the right hand side and subsequent integration over t gives

$$\int \varrho^{ij}(\boldsymbol{r}) \frac{1}{|\,\boldsymbol{r} - \boldsymbol{R}\,|}\, dt = \sum_L \sum_M \frac{(L-|\,M\,|)!}{(L+|\,M\,|)!} P_L^{|M|}(\cos\theta_\alpha)\, e^{-iM\varphi_\alpha} \times$$
$$\times \left\{ R_\alpha^L\, Q_{LM}^{ij} - R_\alpha^{L+2}\, \varrho_{LM}^{ij}(0)\, \frac{2L+1}{2(2L+3)} \right\} \tag{4b}$$

where Q_{LM}^{ij} is the multipole coefficient $\int\limits_0^\infty r\varrho_{LM}^{ij}(r)\, dr$.

Furthermore the requirement of inversion symmetry restricts L to even integers only. Retaining terms up to and including $L = 2$ we have

$$V_{ij} = \tfrac{1}{6}\, \varrho_{00}^{ij}(0) \cdot T - \sum_{M=-2}^{+2} \frac{(2-|\,M\,|)!}{(2+|\,M\,|)!} Q_{2M}^{ij} \cdot T_M \tag{5}$$

where

$$T = \sum_\alpha Z_\alpha R_\alpha^2;\ T_M = \sum_\alpha Z_\alpha\, R_\alpha^2\, P_2^{|M|}(\cos\theta_a)\, e^{-iM\varphi_\alpha}\ .$$

For the case where

$$\varrho^{ij} = R_{n_i l_i}\, R_{n_j l_j}\, Y_{l_i m_i}^{*}\, Y_{l_j m_j} = \sum_L \sum_M \frac{2L+1}{4\pi} \frac{(L-|\,M\,|)!}{(L+|\,M\,|)!} P_L^{|M|}(\cos\theta)\, e^{-iM\varphi}\, r^L\, \varrho_{LM}^{ij}(r) \tag{6}$$

the multipole coefficient Q_{LM}^{ij} becomes

$$Q_{LM}^{ij} = \left[\frac{(L-|\,M\,|)!}{(L+|\,M\,|)!}\right]^{-1/2} \delta\,(M, m_i - m_j)\,(-1)^{m_i}\, C^L(l_i m_i; l_j m_j) \cdot S \cdot \int_0^\infty r^{-(L+1)}\, R_{n_i l_i} R_{n_j l_j} dr \tag{7}$$

where the sign factor $S = (-1)^{1/2(|m_i| + |m_j| + |m_j - m_i|)}$ and the C^L are the Condon-Shortley angular coefficients.

Having restricted ourselves to s and p orbitals only there are no off-diagonal elements of V between the s orbital and three p orbitals and thus

$$E(2S) = \varepsilon_{2s} + \tfrac{1}{6}\, \varrho_{2s}(0) \cdot T\,. \tag{8}$$

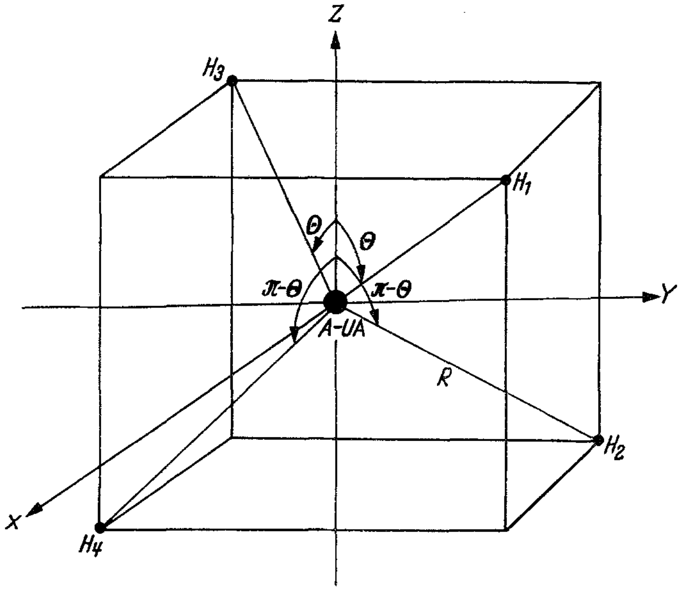

Fig. 2. Coordinate system, choices of axes, and UA position for AH$_4$ molecules ($\phi_1 = \pi/4$; $\phi_2 = 3\pi/4$; $\phi_3 = 5\pi/4$; $\phi_4 = 7\pi/4$)

For the p orbitals the perturbation matrix becomes, using Eqs. (5, 7)

$$\begin{array}{cccc} m_i/m_j & 1 & -1 & 0 \\ 1 & T_0 & -\frac{1}{2}T_2 & -1/\sqrt{2}T_1 \\ -1 & -\frac{1}{2}T_2^* & T_0 & -1/\sqrt{2}T_1^* \\ 0 & -1/\sqrt{2}T_1^* & -1/\sqrt{2}T_1 & -2T_0 \end{array} \times \tfrac{1}{5}\langle r^{-3}\rangle \tag{9a}$$

where

$$\langle r^{-3}\rangle = \int_0^\infty \frac{R_{np}^2}{r^3} r^2\,dr\,. \tag{9b}$$

The geometrical arrangement of the five atoms in AH$_4$ and the UA position are indicated in Fig. 2. (All A-H bond lengths are assumed equal.)

Here

$$\begin{aligned} &T = 4R^2 \\ &T_0 = 4R^2 P_2(\cos\theta) = T\cdot P_2^0(\cos\theta) = \frac{T}{2}(3\cos^2\theta - 1) \\ &T_1 = T_2 = 0 \end{aligned} \tag{10}$$

and the V matrix is completely diagonal giving the energies

$$E(2p_1) = E(2p_{-1}) = \varepsilon_{2p} + T_0\cdot\tfrac{1}{5}\langle r^{-3}\rangle \tag{11a}$$

$$E(2p_0) = \varepsilon_{2p} - 2T_0\cdot\tfrac{1}{5}\langle r^{-3}\rangle\,. \tag{11b}$$

For the tetrahedral arrangement $\theta = \frac{1}{2}$ (109°28′) and $\cos\theta = 1/\sqrt{3}$ and $T_0 = 0$. Hence $E(2p_0) = E(2p_1) = E(2p_{-1}) = \varepsilon_{2p}$. For the square planar arrangement

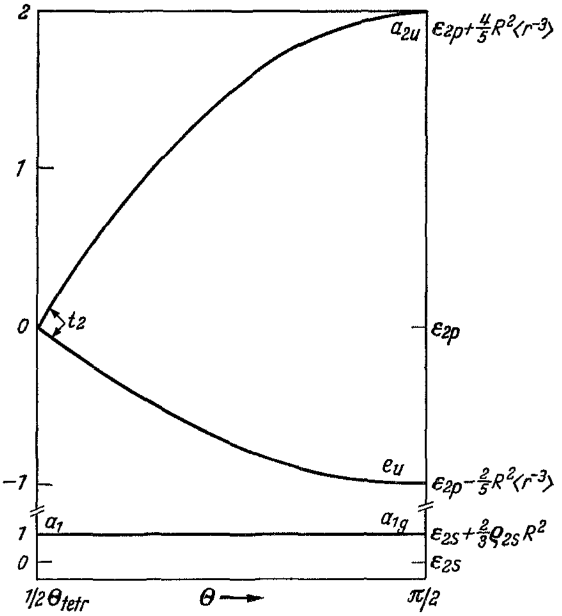

Fig. 3. Correlation diagram for AH_4 molecules. The right ordinate has an absolute scale, the left one a relative scale. Note that there is a break in the ordinates between the *s* and *p* orbitals

$\theta = \pi/2$ and $\cos\theta = 0$ and $T_0 = -\frac{1}{2}T$. Hence

$$E(2p_0) = \varepsilon_{2p} + \tfrac{4}{5}\,R^2\,\langle r^{-3}\rangle \tag{12a}$$

$$E(2p_1) = E(2p_{-1}) = \varepsilon_{2p} - \tfrac{2}{5}\,R^2\,\langle r^{-3}\rangle\,. \tag{12b}$$

Thus with Eqs. (10, 11a, 11b) we can draw a correlation diagram for AH_4 molecules, which is shown in Fig. 3. From the diagram we conclude that AH_4 systems with between 3 and 7 valence electrons should be planar, for example CH_4^+ (7 valence electrons). Furthermore, the first excited state of such systems should be non planar (except for the case of 6 valence electrons).

References

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