THE INSTABILITY OF H_3

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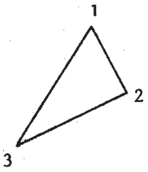
An explicit solution for the orbital stabilization energy of H_3 can be given within a semi-empirical molecular-orbital approach. Correct predictions of the instability of H_3 are made independent from a screening factor. Some generalizations for X_3 systems are possible.

We know the potential surface of H_3 because very accurate calculations have been carried out [1]. We alo know that the simple HMO model leads to the wrong prediction that H_3 is stable [2]. But we would like to know why this approach is not satisfactory in the present case and what kind of result is obtained by applying a more sophisticated semi-empirical model. Such a study may lead to a better qualitative understanding of the difference between H_3 and the alkali trimers. From experimental [3] as well as – for Li_3 [4] – from accurate theoretical investigations, we know that alkali trimers are stable.

Since the energy difference between the 1s and the 2s orbitals in the hydrogen atom is very large, it is obvious that for a description of the ground state within a simple LCAO MO approach we have but to include 1s orbitals. This leads in all geometric situations to the following problem:

$$\begin{vmatrix} \alpha-\epsilon & h_{12}-\epsilon S_{12} & h_{13}-\epsilon S_{13} \\ h_{12}-\epsilon S_{12} & \alpha-\epsilon & h_{23}-\epsilon S_{23} \\ h_{13}-\epsilon S_{13} & h_{23}-\epsilon S_{23} & \alpha-\epsilon \end{vmatrix} = 0\,, \qquad (1)$$



α is called the Coulomb integral, h_{ij} the resonance integral and S_{ij} the overlap integral; ij = 12, 23, 13. Without loss of information, we fix the numbering in a way that $|h_{12}|$ is larger than or equal to $|h_{23}|$ and that $|h_{23}|$ is larger than or equal to $|h_{13}|$. By applying the definitions

$$q_{23} = (h_{23} - \epsilon S_{23})/(h_{12} - \epsilon S_{12})\,,$$

$$q_{13} = (h_{13} - \epsilon S_{13})/(h_{12} - \epsilon S_{12}),$$

$$X = (\alpha - \epsilon)/(h_{12} - \epsilon S_{12})\,,$$

we can write

$$\begin{vmatrix} X & 1 & q_{13} \\ 1 & X & q_{23} \\ q_{13} & q_{23} & X \end{vmatrix} = 0\,, \qquad (2)$$

or

$$X^3 + aX + b = 0\,,$$

$$a = -(q_{13}^2 + q_{23}^2 + 1)\,, \quad b = 2q_{13}q_{23}\,.$$

By definition q_{13} and q_{23} may only take values between 0 and 1 as long as h_{ij} and S_{ij} have similar dependence on the distance between the nuclei i and j; eq. (6). Therefore, a and b fulfil the condition

$$a^3/27 + b^2/4 < 0$$

and the solutions of eq. (2) are

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$$X(n) = A_0 \cos(\tfrac{1}{3}\phi + \tfrac{2}{3}n\pi)\,, \quad n = 0, 1, 2\,, \tag{3}$$

with

$$\cos\phi = -q_{13}q_{23}\,[3/(1 + q_{13}^2 + q_{23}^2)]^{3/2}\,,$$

$$A_0 = 2\,[\tfrac{1}{3}(1 + q_{13}^2 + q_{23}^2)]^{1/2}\,.$$

Because of the restrictions on q_{13} and q_{23} we know

$$\pi/2 \leqslant \phi \leqslant \pi \quad \text{and} \quad (\tfrac{4}{3})^{1/2} \leqslant A_0 \leqslant 2\,.$$

The eigenvalues $\epsilon(X_n)$ are given by

$$\epsilon(X_n) = [\alpha - X(n)h_{12}]/[1 - X(n)S_{12}]\,. \tag{4}$$

Inspection of (3) leads to the results given in table 1.

It is interesting that the HMO condition for D_{3h} corresponds to $q_{13} = q_{23} = 1$ and that in the case of a linear arrangement we have to set $q_{23} = 1$ and $q_{13} = 0$ which leads to the solutions $X_{-1}' = 2^{1/2}, X_0 = 0$, $X_1 = -2^{1/2}$. The last solutions never appear within the present approach, since $q_{23} = 0$ corresponds to $h_{23} = S_{23} = 0$ and this means necessarily $h_{13} = S_{13} = 0$ because the largest difference in distance d between 23 and 13 is $d_{12} + d_{13} \leqslant 2d_{13}$ and the decrease of S_{ij} is approximately exponential.

In a next step we introduce the assumption that the distance dependence of h_{ij} is approximately proportional to the overlap integral:

$$h_{ij} \approx S_{ij}f(H_{ii}, H_{jj})\,. \tag{5}$$

The best known example of this type of approximation is the Wolfsberg–Helmholz approach [5] which is successfully used in extended Hückel calculations [6]. Other treatments of this type have been discussed by Longuet-Higgins [7], Ballhausen and Gray [8] and Yeranos [9]. Inserting (5) into the definition equations for q_{23} and q_{13} leads to the interesting result

$$q_{23} = S_{23}/S_{12} \quad \text{and} \quad q_{13} = S_{13}/S_{12}\,, \tag{6}$$

which shows clearly that q_{23} and q_{13} cannot be varied independently:

$$q_{13} = (S_{13}/S_{23})q_{23}\,.$$

All the mentioned approximations lead to the same formula for homonuclear systems

$$h_{ij} = K\alpha S_{ij}\,, \tag{5a}$$

where K is an empirical constant.

For the orbital energy we get

$$\epsilon_i = \alpha(1 - X_iS_{12}K)/(1 - X_iS_{12})\,. \tag{7}$$

By setting $\alpha = \alpha_H$, the orbital stabilization energy ΔE_{orb} of H_3 is

$$\Delta E_{orb}(H_3) = \alpha_H\left[2\,\frac{1 - X_1S_{12}K}{1 - X_1S_{12}} + \frac{1 - X_0S_{12}K}{1 - X_0S_{12}}\right] - 3\alpha_H\,.$$

The orbital stabilization energy of H_2 + H is equal to

$$E_{orb}(H_2) + E_{orb}(H) = \left[2\alpha_H\,\frac{1 + KS_{H_2}}{1 + S_{H_2}} + \alpha_H\right] - 3\alpha_H\,.$$

In order to discuss the stability of H_3 relative to H_2 + H, we have to compare these two orbital stabilization energies:

$$\Delta = \Delta E_{orb}(H_3) - [\Delta E_{orb}(H_2) + \Delta E_{orb}(H)]\,,$$

$$\Delta = \alpha_H\left\{2\left[\frac{1 - X_1S_{12}K}{1 - X_1S_{12}} - \frac{1 + KS_{H_2}}{1 + S_{H_2}}\right] + \left[\frac{1 - X_0S_{12}K}{1 - X_0S_{12}} - 1\right]\right\}\,. \tag{8}$$

After some algebraic manipulation we find the following interesting result:

$$\Delta = (1 - K)\,\frac{\alpha_H S_{12}}{(1 + S_{H_2})(1 - X_1S_{12})(1 - X_0S_{12})} \times [2S_{H_2}/S_{12} - X_1X_0S_{12}(3 + S_{H_2}) + X_0(1 - S_{H_2}) + 2X_1]\,. \tag{9}$$

This result shows that the sign of Δ is independent of K, as long as K is larger than 1. Smaller values of K never make sense. This means that K appears just as a scaling factor and does not influence the qualitative predictions. Since the expression

Table 1
Values of X_i for the two extreme situations

	X_i	
	$q_{13}=q_{23}=0$	$q_{13}=q_{23}=1$
$n = 0 \rightarrow X_{-1} = A_0\cos(\frac{1}{3}\phi)$	1	1
$n = 2 \rightarrow X_0 = A_0\cos(\frac{1}{3}\phi + \frac{4}{3}\pi)$	0	1
$n = 1 \rightarrow X_1 = A_0\cos(\frac{1}{3}\phi + \frac{2}{3}\pi)$	−1	−2

$$(1-K)\frac{\alpha_H S_{12}}{(1+S_{H_2})(1-X_1S_{12})(1-X_0S_{12})}$$

can only be positive or zero, the sign of Δ is determined by the relative magnitude of

$$2S_{H_2}/S_{12}+X_0(1-S_{H_2})-X_1X_0S_{12}(3+S_{H_2})$$

and $2X_1$. The first of these expressions can only be positive, since X_1 is negative and $2X_1$ always lies between –2 and –4. By inserting the expressions for X_1 and X_0 into the second part of eq. (9) and by applying the substitution $\phi_1=\frac{1}{3}\phi+\frac{2}{3}\pi$ and $\phi_0=\frac{1}{3}\phi+\frac{4}{3}\pi$ we get

$$\Delta=(1-K)\frac{\alpha_H S_{12}2A_0}{(1+S_{H_2})(1-X_1S_{12})(1-X_0S_{12})}\Delta_0\,,$$

$$\Delta_0=S_{H_2}/S_{12}A_0+\cos\phi_1 \qquad (10)$$
$$+[1-S_{H_2}-A_0S_{12}(3+S_{H_2})\cos\phi_1]\tfrac{1}{2}\cos\phi_0\,.$$

Since Δ_0 alone can influence the sign of Δ we can restrict the discussion to Δ_0. ϕ can only take values between $\frac{1}{2}\pi$ and π. Therefore it is easy to see that

$$\tfrac{5}{6}\pi\leqslant\phi_1\leqslant\pi\,,\quad -(\tfrac{3}{4})^{1/2}\leqslant\cos\phi_1\leqslant-1$$

and

$$\tfrac{3}{2}\pi\leqslant\phi_0\leqslant\tfrac{5}{3}\pi\,,\quad 0\leqslant\cos\phi_0\leqslant\tfrac{1}{2}\,.$$

It is important to notice that the interdependence of q_{23} and q_{13} leads to $\phi_1=\frac{1}{3}\phi+\frac{2}{3}\pi$ and $\phi_0=\frac{1}{3}\phi+\frac{4}{3}\pi$ which means that for discussing eq. (10) we can e.g. start at $\phi_0=\frac{9}{6}\pi$ and $\phi_1=\frac{5}{6}\pi$ and advance in equal increments to $\phi_0=\frac{10}{6}\pi$ and $\phi_1=\frac{6}{6}\pi$. This leads to the conclusion that for any reasonable value of S_{12} and S_{H_2} the single situation in which ϕ_0 might become negative is $\cos\phi_0=0$, which corresponds to $q_{13}=q_{23}=0$ and therefore $A_0=(\frac{4}{3})^{1/2}$. But $q_{13}=q_{23}=0$ corresponds to infinite distance between H_2 and H. In this situation the value of S_{12} is equal to that of S_{H_2} and therefore

$$\Delta_0=1/A_0+\cos\phi_1=(\tfrac{3}{4})^{1/2}-\cos(\tfrac{5}{6}\pi)=0\,.$$

The value of Δ at infinite distance between H_2 and H is predicted to be equal to zero as it should be.

Within the model there is in any case no net orbital stabilization for H_3 relative to H_2 + H. This means that H_3 is predicted to be unstable in any geometric arrangement. It is now obvious why the HMO model does not lead to correct predictions regarding the stability of H_3. One of the failures is the unreasonable condition $q_{23}=1, q_{13}=0$. The other one is that the HMO eigenvalues are equal to

$$\epsilon(X_n)=\alpha-X(n)h_{12}\,,$$

instead of $[\alpha-X(n)h_{12}]/[1-X(n)S_{12}]$.

But $1-X(n)S_{12}$ cannot be set equal to one since otherwise the splitting between bonding and antibonding orbitals is largely underestimated. This can easily be shown by looking at the splitting of the bonding and antibonding orbitals in H_2. The orbital stabilization energy ΔE^+ of H_2 is within the approach (1) equal to

$$\Delta E^+=(h_{12}-S\alpha)/(1+S) \qquad (11a)$$

and the destabilization energy is equal to

$$\Delta E^-=(h_{12}-S\alpha)/(1-S)\,. \qquad (11b)$$

Since S_{H_2} is calculated to be 0.618 [10], this means that $|\Delta E^-|$ is more than four times larger than $|\Delta E^+|$. If this result is reasonable, it should be possible to set $|\Delta E^-|+|\Delta E^+|$ approximately equal to the energy $E_g^u=11.37$ eV [11] needed for the $B\,^1\Sigma_u^+\leftarrow X\,^1\Sigma_g^+$ transition:

$$E_g^u\approx|\Delta E^+|+|\Delta E^-|=2(h_{12}-\alpha S)/(1+S)(1-S). \qquad (12)$$

The orbital stabilization energy is for H_2 equal to $\frac{1}{2}$ of the dissociation energy D_0 [12]. Therefore we get

$$E_g^u\approx D_0/(1-S)\,, \qquad (13)$$

which leads to E_g^u(calc) = 4.477 eV/(1 – 0.618) = 11.7 eV.

It is interesting that eq. (13) gives in addition a reasonable explanation for the comparatively small $B\,^1\Sigma_u^+\leftarrow X\,^1\Sigma_g^+$ transition energy observed in the alkali dimers. They have much smaller dissociation energies [11] but only slightly lower values for the $\langle ns|ns\rangle$ overlap integral, e.g. $S_{Na_2}\approx0.6$.

We can now make another conclusion. Eq. (1) and therefore eq. (6) does not only apply to H_3. They describe linear combinations of three equivalent ns orbitals in any X_3 system. This means that within the approach applied it is not possible to describe a stable homonuclear X_3 molecule such as Li_3, Na_3 or K_3. The main dissimilarity between these systems and H_3 lies in our initial condition that the energy difference between the 1s orbitals and the 2s, 2p orbitals in the hydrogen atom is very large. There is no equivalent condition for the alkali trimers. It is also clear that a minimal basis set is not sufficient to describe any stable excited state of H_3. Such states have been discovered recently by Herzberg [13]. Within a LCAO MO approach atomic orbitals with $n \geqslant 2$ have to be included.

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