

## Relationes

# Integral Hellmann-Feynman Investigations of *trans* Bent Acetylene

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The integral Hellmann-Feynman (IHF) theorem has been applied to various wavefunctions representing the  ${}^1A_u$  state of acetylene with a view to testing traditional explanations of the excited state geometry. When LCAOSCF wavefunctions are used, the electronic energy changes associated with the individual corresponding orbitals (CMO's) are in sympathy with the trend in orbital (*i.e.* MO) energies suggested by Walsh. However, when LMO wavefunctions based on hybrid AO's are employed, the IHF results are against all experience; and imply that a change in hybridisation, from  $sp$  to  $sp^2$ , is not a viable model for the change in geometry.

### Introduction

The experimental fact [1] that acetylene is *trans* bent in its first electronically excited state has long been of theoretical interest. The original qualitative explanation of Walsh [2] argues that, in so far as the change in molecular energy parallels the change in orbital energies, bending is favoured by the introduction of  $s$  character into the excited MO ( $\pi_g$  when CCH angle =  $180^\circ$ ) which reduces the orbital energy until (when CCH angle =  $90^\circ$ ) the  $a_g$  MO becomes almost non-bonding. This tendency is opposed by the  $b_u$  MO (corresponding to bonding  $\pi$  in the linear case) which becomes destabilised by increasing  $s$  character. The experimental bond angle [1] is almost exactly  $120^\circ$ , and it is tempting to suggest [3], in terms of localised molecular orbitals (LMO's), that these changes might equivalently be described by a change in hybridisation from  $sp$  to  $sp^2$ .

The first SCF calculation on acetylene to consider all the electrons was due to Burnelle [4] and confirmed the trend in  $\pi_g - a_g$  orbital energy suggested by Walsh; but it failed to predict the correct geometry for the excited  ${}^1A_u$  state from the total energy calculation, probably because of excessive integral approximations. Most of the theoretical studies of acetylene have since been concerned with the linear molecule, but recently Kammer [5] has reported SCF and CI calculations of linear and bent acetylene which agree extensively with the spectroscopic facts. Accurate *ab-initio* wavefunctions must provide the ultimate explanation for the shapes of molecules: but it may be difficult in some cases to relate the concepts of exact MO theory to the older, qualitative orbital theories. Peyerimhoff, Buenker and Allen [6] have shown that the success of the Walsh rules in predicting the geometries of  $AH_2$  and  $AH_3$  molecules with 6–9 valence electrons can be attributed to the fact that for these molecules changes in the sum of the SCF one electron

energies are approximately parallel to changes in the total energy. On the other hand, Pan and Allen [7] have shown that in HCN, with ten valence electrons, the total energy and total orbital energy curves diverge as the bond angle is decreased from 180°. However, it must be pointed out that in the work cited above [6, 7] it has been assumed that the MO energies in Walsh diagrams are the one-electron eigenvalues of closed-shell SCF Hamiltonians. The geometries of open-shell molecules and of excited states are discussed using the lowest virtual orbitals – which do not have the same physical meaning as the MO's used in formulating the SCF Hamiltonians. Another difficulty in the interpretation of *ab-initio* wavefunctions arises in the localised orbital approach: that wavefunctions expressed in terms of extended atomic basis sets or, as in the calculations [5–7] cited above, in terms of gaussian lobe functions [8] may not be easy to visualise in terms of hybridisation.

In principle at least, the integral Hellmann-Feynman theorem (IHF), revived by Parr [9], offers a direct way of analysing the change in geometry from a one electron point of view. With a fixed CC bond length for each geometry, the change in electronic energy may be expressed as the difference of proton attraction operators integrated over the transition density between two configurations. The electronic energy change may then be analysed into contributions from the corresponding orbitals (CMO's) – the orbitals which diagonalise the 1-particle transition density matrix. Unfortunately, since the successful application of the IHF method to internal rotation in ethane [10], there has accrued considerable evidence [11–13] to suggest that simple LCAO wavefunctions do not give reliable IHF total energy differences. This, however, does not prevent the IHF theorem from giving insight into isoelectronic changes, particularly when the transition density is described in a way which is qualitatively correct [14]. Moreover, the error in an IHF calculation is entirely inherent in the wavefunctions used and, therefore, such calculations may be regarded as tests of the molecular models which the wavefunctions represent. One of the objects of the present study of *trans* bent acetylene was to see if the assumption of  $sp^2$  hybridised carbon might account for the geometry of excited acetylene.

### IHF Formula and the Configurations Considered

Within the framework of the Born-Oppenheimer approximation the IHF energy difference between linear and bent acetylene is given by

$$\Delta W_I = \frac{\langle \Phi_L | \Delta V_{ne} | \Phi_B \rangle}{\langle \Phi_L | \Phi_B \rangle} + \Delta V_{nn} \quad (1)$$

where  $\Phi_L$  and  $\Phi_B$  are electronic states associated with the linear and bent nuclear frames respectively. The normal and excited states of acetylene may be represented approximately by the following configurations:

$${}^1\Sigma_g^+ (1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (\pi_u)^2 (\pi_u)^2, \\ {}^1A_u (1a_g)^2 (1b_u)^2 (2a_g)^2 (2b_u)^2 (3a_g)^2 (3b_u)^2 (4a_g) (a_u).$$

Now a direct substitution of the above wavefunctions for  $\Phi_L$  and for  $\Phi_B$  in (1) leads to a  $\frac{0}{0}$  indeterminacy; and it was therefore decided to calculate instead the energy variation of the  ${}^1A_u$  state ( ${}^1A_u$  in the linear case) as a function of CCH angle. No complication in applying (1) arises from the fact that the  ${}^1A_u$  state formally requires two determinants. Since the singly occupied MO's are of different symmetry, there are no matrix elements of  $\Delta V_{ne}$  between determinants which differ by an interchange of the spin factors of the  $4a_g$  and  $a_u$  orbitals. Thus a single determinant is adequate for the IHF calculation. CMO's for state of the linear and bent nuclear frames were constructed by unitary transformations [10] of the MSO's with identical spin factors. In terms of single occupied CMO's Eq. (1) becomes

$$\Delta W_l = \sum_{i=1}^{i=14} \frac{\langle \hat{\psi}_i^L | \Delta V_{ne} | \hat{\psi}_i^B \rangle}{\langle \hat{\psi}_i^L | \hat{\psi}_i^B \rangle} + \Delta V_{nn}. \quad (2)$$

### Geometry and Orbitals

Fig. 1 shows the nuclear frame and cartesian coordinates to which all wavefunctions are referred.

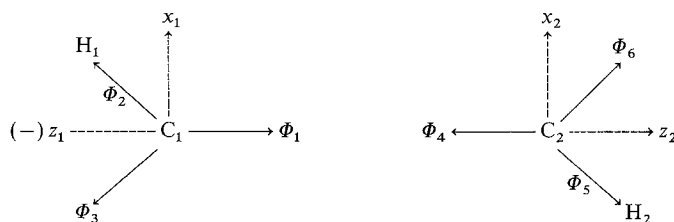


Fig 1. Coordinate system and hybrid orbitals

The decision to fix the bond lengths was taken for an important reason. With bond lengths at their normal values ( $CH = 1.0568 \text{ \AA}$ ;  $CC = 1.208 \text{ \AA}$ ) a change in CCH angle of  $60^\circ$  produces a  $\Delta V_{nn}$  value of 0.45358 a.u., which is *opposed* to bending. Thus in order to predict bending one is looking for a change in electronic energy,  $\Delta E_l$  whose magnitude is about seven times as great as the  $\Delta E_l$  magnitudes for the *rotation* of a bond in a comparable molecule [11]. The percentage error in the calculation of  $\Delta E_l$  for the bending problem will thus be considerably smaller than for the rotation. (Of course, the algebraic sum  $\Delta E_l + \Delta V_{nn}$ , may be no more reliable than before.) If, however, the CC bond is allowed to relax (to the excited state value of  $1.383 \text{ \AA}$ ) simultaneously with the change in CCH angle, then at  $120^\circ$  the value of  $\Delta V_{nn}$  is very small and actually in favour of the bent state. The value of  $\Delta E_l$  might then also be very small – and too subtle for the wavefunctions envisaged here.

Three kinds of LCAO wavefunction were considered: –

*a) The SCF MO's of Burnelle*

Although these wavefunctions were calculated with integral approximations now regarded as too severe, the LCAO coefficients give reasonable populations [15] and are probably not very different from the coefficients of an exact minimal basis calculation. They were employed here because they appear to be the only MO's for bent acetylene which have been reported using a Slater-type AO basis. The orbital exponents were: C 1s, 5.7; C 2s, 1.59; C 2p, 1.59; and H 1s, 1.0.

*b) Two Centre MO's Constructed from Orthogonal Hybrids*

Employing precisely the same AO basis and bond lengths as in a), hybrid AO's were formed on each carbon atom according to

$$\Phi_i = (s + \lambda_i p_i) N_i \quad (3)$$

where  $\Phi_i$  represents an  $sp^{\lambda_i}$  hybrid pointing in the direction (see Fig. 1) of a  $2p_i$  orbital. Apart from normalising factors, Eqs. (3) contain six unknowns ( $i = 1, 2, 3$ ) of which three may be eliminated by orthogonality criteria,

$$\langle \Phi_i | \Phi_j \rangle = \delta_{ij} \quad (4)$$

and the remaining three on the assumptions that  $\Phi_1$  and  $\Phi_2$  point along the CC and CH bonds respectively and that  $\lambda_1 = \lambda_2$ . With these assumptions the  $\Phi_i$  take the usual forms of  $sp$  hybrids at  $180^\circ$  and  $sp^2$  at  $120^\circ$ . Taking the inner shell MO's to be the C 1s orbitals themselves, two centre LMO's were constructed (ignoring normalising factors) as follows:

$$\begin{aligned} (\sigma_1)_{\text{CH}} &= k\Phi_2 + h_1, \\ (\sigma_2)_{\text{CH}} &= k\Phi_5 + h_2, \\ (\sigma)_{\text{CC}} &= \Phi_1 + \Phi_4 (3a_g), \\ (\pi)_{\text{CC}} &= \Phi_3 - \Phi_6 (3b_u), \\ (\pi^*)_{\text{CC}} &= \Phi_3 + \Phi_6 (4a_g). \end{aligned}$$

The symbol  $h$  represents a hydrogenic 1s orbital. The MO designations refer to the linear molecule, while corresponding non-linear species are indicated in parentheses. The out-of-plane  $a_u$  orbital is identical with the  $\pi_y$  orbital throughout.

Only the factor  $k$  – the polarity of the CH bond – remains to be specified, and this was taken to be 1.09 [16]. It is interesting to note that in calculations by Woznicki [16] the expectation value of the  ${}^1A_u$  state, calculated from the above MO's, gave a minimum in the energy curve when angle CCH =  $120^\circ$ . (The CC bond length in Woznicki's calculation was 1.383 Å, and the Mulliken approximation for polycentric integrals was used).

*c) Two Centre LMO's Constructed from Non-Orthogonal Hybrids*

As an alternative to the conventional  $sp^2$  hybrids, it was decided to construct two centre MO's for the  ${}^1A_u$  state at CCH =  $120^\circ$  from the hybrids theoretically determined in LMO studies [17] of ethylene from *ab-initio* LCAOSCF wave-

functions [18]. These hybrids may be represented approximately as  $sp^{1.74}$ ,  $sp^{1.85}$  and  $sp^{1.85}$ . These hybrids are not orthogonal, and the two which are equivalent lie at  $1.2^\circ$  to the line of the CH bonds. Referred to Fig. 1, they are

$$\begin{aligned}\Phi_1 &= N_1 (s + \sqrt{1.74} p_z) \\ \Phi_2 &= N_2 [s + \sqrt{1.85} (p_x \cos 31.2^\circ - p_z \cos 58.8^\circ)] \\ \Phi_3 &= N_3 [s + \sqrt{1.85} (-p_x \cos 31.2^\circ - p_z \cos 58.8^\circ)].\end{aligned}$$

With these hybrids instead of (3), two centre MO's for the bent state were constructed exactly as in b), except that  $k$  took the ethylenic value 1.13. For the linear molecule the recommended [17] hybrids were:

$$\Phi_1 = N_1 (s + \sqrt{1.01} p_z); \quad \Phi_2 = N_2 (s - \sqrt{1.01} p_z); \quad \Phi_3 = p_x;$$

and the value of  $k$  was 1.37.

Both procedures – b) and c) – give LMO's which are not orthogonal (the largest overlap is  $\sim 0.2$ ), and prior to forming CMO's, the LMO's were Schmidt orthogonalised. These processes did not prevent the form of the hybrids from being approximately recognised in the final CMO's.

Overlap and nuclear attraction integrals over basis AO's – necessary for implementing (2) – were calculated by methods discussed previously [11].

## Results and Discussion

Table 1 gives the various contributions to  $\Delta E_i$  for the change in CCH angle  $180^\circ \rightarrow 120^\circ$  (*trans*), using the three different wavefunctions. (The symmetry designations are appropriate throughout because, in the LMO wavefunctions, inner shell and CH orbitals were symmetry adapted). Tables 2 and 3 show the LCAO coefficients for the CMO's derived from Burnelle's wavefunctions.

Table 1. Contributions to  $\Delta E_i$  (a.u.) for  $180^\circ$  (linear)  $\rightarrow 120^\circ$  (*trans*)

CMO pair	LCAOSCF wavefunctions a)		LMO wavefunctions b)		LMO wavefunctions c)	
	Contribution to $\Delta E_i$		Contribution to $\Delta E_i$		Contribution to $\Delta E_i$	
	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$
$1a_g$	-0.0360	-0.0440	-0.0365	-0.0356	-0.0339	-0.0330
$1b_u$	-0.0360	-0.0360	-0.0360	-0.0360	-0.0322	-0.0322
$2a_g$	0.0760	0.0069	-0.0432	-0.0963	-0.0553	-0.1268
$2b_u$	-0.0867	-0.0867	-0.0017	-0.0017	-0.0473	-0.0473
$3a_g$	-0.0876	-0.0561	-0.0705	-0.0818	-0.0691	-0.0788
$3b_u$	0.0230	0.0230	-0.0389	-0.0389	-0.0017	-0.0017
$a_u$	-0.0396		-0.0396		-0.0369	
$4a_g$		-0.0454		0.0639		0.0848
Total	-0.1869	-0.2483	-0.2664	-0.2264	-0.2774	-0.2360
$\Delta V_{nn}$		0.4536		0.4536		0.4212
$\Delta W_i$		0.0176		-0.0392		-0.0922

Table 2. Corresponding orbitals ( $\alpha$  spin factors) from Burnelle's MO's,  $180^\circ$  (linear)  $\rightarrow 120^\circ$  (*trans*)

CMO pair	Overlap integral	Coefficients <sup>a</sup>					
		C <sub>1</sub> 1s	C <sub>1</sub> 2s	C <sub>1</sub> 2pz	C <sub>1</sub> 2px	C <sub>1</sub> 2py	H <sub>1</sub> 1s
1a <sub>g</sub>	0.99996	0.70572	0.00425	-0.00048	0.00000	0.0	0.00160
		0.70557	0.00652	-0.00199	0.00098	0.0	-0.00151
1b <sub>u</sub>	0.99993	0.70497	0.01816	0.00541	0.00038	0.0	0.00036
		0.70466	0.02272	0.00754	0.00091	0.0	-0.00137
2a <sub>g</sub>	0.85993	-0.07576	0.27100	-0.32145	0.00000	0.0	0.35193
		-0.06278	0.23379	-0.36578	0.13674	0.0	0.36132
2b <sub>u</sub>	0.92334	-0.10007	0.33241	-0.20515	0.26721	0.0	0.30779
		-0.11440	0.48657	-0.11937	0.11384	0.0	0.34372
3a <sub>g</sub>	0.99883	0.14504	-0.36587	-0.38596	0.00000	0.0	0.03904
		0.14135	-0.32068	-0.41790	0.00355	0.0	-0.02095
3b <sub>u</sub>	0.98468	-0.04835	0.16225	-0.10012	-0.54750	0.0	0.15022
		-0.05433	0.11427	-0.34478	-0.51949	0.0	-0.05075
a <sub>g</sub>	1.00000	0.0	0.0	0.0	0.0	0.60923	0.0
		0.0	0.0	0.0	0.0	0.60923	0.0

<sup>a</sup> Coefficients of the other AO's may be found by symmetry.

Table 3. Corresponding orbitals ( $\beta$  spin factors) from Burnelle's MO's,  $180^\circ$  (linear)  $\rightarrow 120^\circ$  (*trans*)

CMO pair	Overlap integral	Coefficients <sup>a</sup>					
		C <sub>1</sub> 1s	C <sub>1</sub> 2s	C <sub>1</sub> 2pz	C <sub>1</sub> 2px	C <sub>1</sub> 2py	H <sub>1</sub> 1s
1a <sub>g</sub>	1.00000	0.64702	-0.23051	-0.20551	0.14463	0.0	0.00018
		0.64701	-0.23004	-0.20578	0.14484	0.0	-0.00043
1b <sub>u</sub>	0.99993	0.70497	0.01816	0.00541	0.00038	0.0	0.00036
		0.70466	0.02272	0.00754	0.00091	0.0	-0.00137
2a <sub>g</sub>	0.92956	-0.06895	0.24960	-0.31474	0.27165	0.0	0.33538
		-0.06263	0.24347	-0.38997	0.82680	0.0	0.35467
2b <sub>u</sub>	0.92334	-0.10007	0.33241	-0.20515	0.26721	0.0	0.30779
		-0.11440	0.48657	-0.11937	0.11384	0.0	0.34372
3a <sub>g</sub>	0.99990	-0.31734	-0.30326	-0.26692	0.16737	0.0	-0.00018
		-0.31739	-0.30289	-0.26703	0.16767	0.0	-0.00065
3b <sub>u</sub>	0.98468	-0.04835	0.16225	-0.10012	-0.54750	0.0	0.15022
		-0.05433	0.11427	-0.34478	-0.51949	0.0	-0.05075
4a <sub>g</sub>	0.98689	0.02710	-0.02032	-0.19938	-0.80196	0.0	0.11360
		0.01444	0.13524	-0.30218	-0.74331	0.0	-0.10059

<sup>a</sup> Coefficients of the other AO's may be found by symmetry.

For the LCAOSCF wavefunctions a) the total  $\Delta E_l$  is not quite large enough to cover  $\Delta V_{nn}$  and so favour bending. However, it is believed that the contributions from the CMO's are qualitatively correct. The fact that there is some internal consistency in Burnelle's wavefunctions may be indicated by the fact that when

$\Delta E_i$  for  $180^\circ \rightarrow 120^\circ$  is compared to the value of  $\Delta E_i$  for  $180^\circ \rightarrow 150^\circ$  plus  $\Delta E_i$  for  $150^\circ \rightarrow 120^\circ$ , the result is conservative to within 1%. The contributions of the CMO pairs show a considerable agreement with the ideas of Walsh, who, it should be stressed, was thinking in terms of the change in orbital (*i.e.* self) energies rather than one-electron transition energies. Thus, the  $4a_g$  CMO pair is in favour of bending, and the  $3b_u$  opposes bending. From the coefficients in Table 2 it would appear that this is due to the introduction of  $p_z$  rather than  $s$  character into the  $\pi$  orbitals. Walsh's ideas are also supported by the behaviour of the  $3a_g$  orbital (CC  $\sigma$  bond) which becomes less favourable to bending through the acquisition of  $p_x$  character (in the  $\beta$  set) than it is when dominated by  $s$  and  $p_z$  (in the  $\alpha$  set). However, CMO's being unitary mixtures of MO's of the same symmetry, it is possibly unwise to look too closely at the form of individual CMO's; but rather one should compare the total contribution of the  $a_g$  orbitals when mixed with  $4a_g$  (*i.e.* in the  $\beta$  set) with the total contribution of the  $a_g$  orbitals in the  $\alpha$  set. The difference is nearly 0.1 a.u.

For the wavefunctions b) based on hybrid AO's, the results are quite different – and unacceptable. Firstly, the  $4a_g$  CMO pair is opposed to bending, and the set of orbitals which contains the excited orbital (the  $\beta$  set) gives a smaller  $\Delta E_i$  than the set which does not. Worse still, the orbitals of the  $\alpha$  set actually represent, on this model, the orbitals of the closed shell ground state,  $^1A_g$ . Twice the value of  $\Delta E_i$  for the  $\alpha$  CMO's thus represents the change in electronic energy of the  $^1A_g$  state,  $180^\circ \rightarrow 120^\circ$ . Since this quantity exceeds  $\Delta V_{nn}$  in magnitude, the hybrid wavefunctions indicate a non-linear ground state for acetylene.

To show that these conclusions were not merely dependent on the arbitrary factors in the LMO wavefunctions b), the IHF calculations were repeated with various CH bond polarities. First the value of  $k$  was increased by 10%; then the hydrogenic exponent was changed to 1.2. Finally, the calculations were repeated using the excited CC bond length, 1.383 Å. Although the increase in bond length reduced the magnitudes of both  $\Delta V_{nn}$  and  $\Delta E_i$ , none of the changes mentioned materially affected the conclusions drawn from the second column of Table 2: the distribution of  $\Delta E_i$  among the CMO's remained much the same; and the ground state orbitals were still more favourable to bending than the excited state orbitals.

The calculations using LMO wavefunctions c) were undertaken to counter possible objections to arbitrariness in the actual construction of the LMO's in b) – the two centre approximation; the hybridisation determined on CCH angle; and the Schmidt orthogonalisation which ignores orthogonality with the unoccupied LMO's. The hybrids and  $k$  values in wavefunctions c) were specially determined for two centre MO's on theoretical criteria [14], from *ab-initio* wavefunctions with carefully optimised exponents [15]. These exponents were used in the IHF calculation, together with bond lengths appropriate to ethylene [15]. The third column of Table 3 shows that the conclusions are the same as for wavefunctions b).

The calculations described in this work have employed very simple wavefunctions. It will be interesting to see if the conclusions are confirmed by LMO and IHF studies of more sophisticated wavefunctions, such as those reported by Kammer [4].

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