

## A valency method for the prediction of geometry of molecular excited states

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**Abstract.** A simple method, based on the concept of molecular valency and making use of the virtual orbitals of the ground state, is proposed to predict the geometry of molecules in various excited and ionised states. The method is found to be accurate for bond angle predictions.

**Keywords.** Molecular valency; excited state geometry; bond angle predictions.

### 1. Introduction

Theoretical calculations of the geometry of excited states of molecules usually proceed by determining the minimum point on a molecular potential energy surface by a point-by-point mapping through successive calculations of the total energy. Since wavefunctions at the configuration interaction (CI) level are required to achieve a fair degree of accuracy, such calculations become very costly in terms of computer time. Moreover a mere energy calculation, however sophisticated, does not by itself lead to an understanding of the chemical factors determining molecular shape. Further analysis of the wavefunction is required for this purpose, which is difficult at the CI level. In this paper, we propose a simple method for the determination of excited state geometries of molecules, using the ground state wavefunctions alone, based on the concept of valency.

### 2. The method

Valency of an atom  $A$  in a molecule has been defined previously (Armstrong *et al* 1973; Gopinathan and Jug 1983; Gopinathan 1986) as:

$$V_A = \sum_{B \neq A} \sum_a^A \sum_b^B P_{ab}^2, \quad (1)$$

where  $P_{ab}$  is the density matrix element between the orbitals  $a$  on atom  $A$  and  $b$  on atom  $B$  in an orthogonal basis. From (1), expressions for molecular orbital valency  $v_i$  and molecular valency  $V_M$  have been obtained (Gopinathan *et al* 1986):

$$v_i = \frac{1}{2} \sum_A \sum_a^A \sum_{B \neq A} \sum_b^B \sum_j n_i n_j C_{ia} C_{ib} C_{ja} C_{jb}, \quad (2)$$

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$$V_M = \sum_i V_i = \frac{1}{2} \sum_A V_A, \quad (3)$$

where  $n_i$  is the occupancy of the  $i$ th molecular orbital (*mo*). (1) and (2) apply to closed shell molecules. For open shell systems, since in general  $C_{ia}^\alpha \neq C_{ia}^\beta$ , one should use the following generalisations of (1) and (2).

$$V_A = \sum_{B \neq A} \sum_a^A \sum_b^B (P_{ab}^\alpha + P_{ab}^\beta)^2,$$

$$V_i = \frac{1}{2} \sum_A \sum_a^A \sum_{B \neq A} \sum_b^B \sum_j^B [n_i^\alpha n_j^\alpha C_{ia}^\alpha C_{ib}^\alpha C_{ja}^\alpha C_{jb}^\alpha$$

$$+ n_i^\beta n_j^\beta C_{ia}^\beta C_{ib}^\beta C_{ja}^\beta C_{jb}^\beta + n_i^\alpha n_j^\beta C_{ia}^\alpha C_{ib}^\beta C_{ja}^\beta C_{jb}^\alpha$$

$$+ n_i^\beta n_j^\alpha C_{ia}^\beta C_{ib}^\alpha C_{ja}^\alpha C_{jb}^\beta ], \quad (4)$$

where  $P_{ab}^\sigma$  ( $\sigma = \alpha$  or  $\beta$ ) is the spin polarised density matrix element. These valency quantities have been well studied and correlated with determination of structure (Gopinathan *et al* 1986), strain (Siddarth and Gopinathan 1986), and reaction pathways (Jug and Gopinathan 1985). In particular, we have shown earlier (Gopinathan *et al* 1986) that for the ground state, molecular valency reaches a maximum at the equilibrium bond angle and that molecular orbital valency serves as a quantitative ordinate for the well-known Walsh diagrams (Walsh 1953). Thus the equilibrium bond angle of molecules in their ground states can be determined quite accurately by means of either the molecular valency  $V_M$  or the molecular orbital valency  $V_i$ .

We now investigate whether the excited state bond angles also can be similarly predicted from valency. The procedure we adopt is as follows:

- A ground state calculation of the molecule at various bond angles is performed.
- Excited or ionised electronic configurations of the molecule are obtained simply by making use of the occupied and virtual orbitals from (a) as required.
- Molecular orbital valency and molecular valency at a particular bond angle are now calculated by using (2), (4) and (3), with the MO occupancies and coefficients determined as in (b).
- The equilibrium bond angle is then given by that angle for which molecular valency  $V_M$  is a maximum.

### 3. Results

We have presently calculated the bond angles for several excited as well as ionised states of some triatomic molecules as described above. Calculations were done using *ab initio* STO-3G Löwdin-orthogonalised wavefunctions. Table 1 presents the bond angles obtained by the present valency method as well as the results of previous *ab initio* calculations and available experimental data for the sake of comparison. We have also plotted  $\Delta V(\theta)$ , the difference of the molecular valency

**Table 1.** Valency calculation of bond angles of excited and ionised states of molecules.

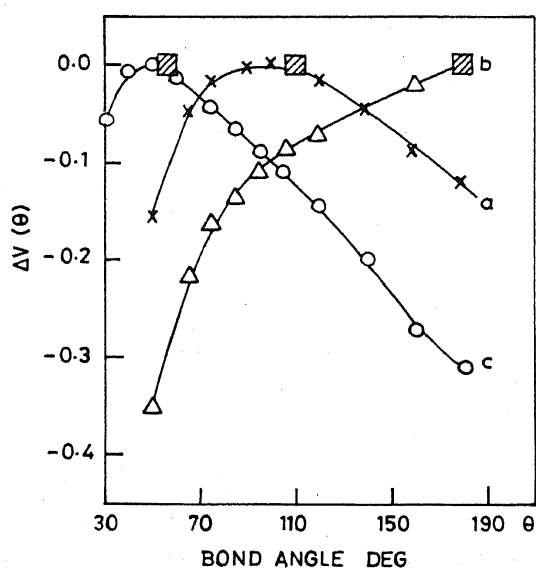
Molecule	Electronic configuration <sup>a</sup>	State	Bond angle	
			Present method	ab initio <sup>b</sup>
CH <sub>2</sub> <sup>+</sup>	(3a <sub>1</sub> ) <sup>1</sup>	<sup>2</sup> A <sub>1</sub>	140	141
CH <sub>2</sub>	(3a <sub>1</sub> ) <sup>1</sup> (1b <sub>1</sub> ) <sup>1</sup>	<sup>3</sup> B <sub>1</sub>	140	132 (134)
	(3a <sub>1</sub> ) <sup>2</sup>	<sup>1</sup> A <sub>1</sub>	100	101 (102)
CH <sub>2</sub> <sup>-</sup>	(3a <sub>1</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>1</sup>	<sup>2</sup> B <sub>1</sub>	100	104
	(3a <sub>1</sub> ) <sup>1</sup> (1b <sub>1</sub> ) <sup>2</sup>	<sup>2</sup> A <sub>1</sub>	140	131
NH <sub>2</sub> <sup>+</sup>	(3a <sub>1</sub> ) <sup>2</sup>	<sup>1</sup> A <sub>1</sub>	130	120
	(3a <sub>1</sub> ) <sup>1</sup> (1b <sub>1</sub> ) <sup>1</sup>	<sup>1</sup> B <sub>1</sub>	180	180
	(3a <sub>1</sub> ) <sup>1</sup> (1b <sub>1</sub> ) <sup>1</sup>	<sup>3</sup> B <sub>1</sub>	140	140
NH <sub>2</sub>	(3a <sub>1</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>1</sup>	<sup>2</sup> B <sub>1</sub>	100	103 (103)
	(3a <sub>1</sub> ) <sup>1</sup> (1b <sub>1</sub> ) <sup>2</sup>	<sup>2</sup> A <sub>1</sub>	140	143 (144)
	(3a <sub>1</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>2</sup>	<sup>2</sup> B <sub>2</sub> <sup>c</sup>	60	48
H <sub>2</sub> O <sup>+</sup>	(3a <sub>1</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>1</sup>	<sup>2</sup> B <sub>1</sub>	100	111 (112)
	(3a <sub>1</sub> ) <sup>1</sup> (1b <sub>1</sub> ) <sup>2</sup>	<sup>2</sup> A <sub>1</sub>	180	180
	(3a <sub>1</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>2</sup>	<sup>2</sup> B <sub>2</sub> <sup>c</sup>	50	55
HCN	(1a'') <sup>1</sup> (7a') <sup>1</sup>	1 <sup>3</sup> A''	130	123 (125)
	(1a'') <sup>1</sup> (7a') <sup>0</sup> (2a'') <sup>1</sup>	1 <sup>3</sup> A'	160	160 <sup>d</sup>
HCN <sup>-</sup>	(1a'') <sup>2</sup> (7a') <sup>1</sup>	<sup>2</sup> A'	140	130

<sup>a</sup>The inner electronic configurations (1a<sub>1</sub>)<sup>2</sup> (2a<sub>1</sub>)<sup>2</sup> (1b<sub>2</sub>)<sup>2</sup> for AH<sub>2</sub> type molecules and (1a')<sup>2</sup> (2a')<sup>2</sup> (3a')<sup>2</sup> (4a')<sup>2</sup> (5a')<sup>2</sup> (6a')<sup>2</sup> for HCN are omitted;

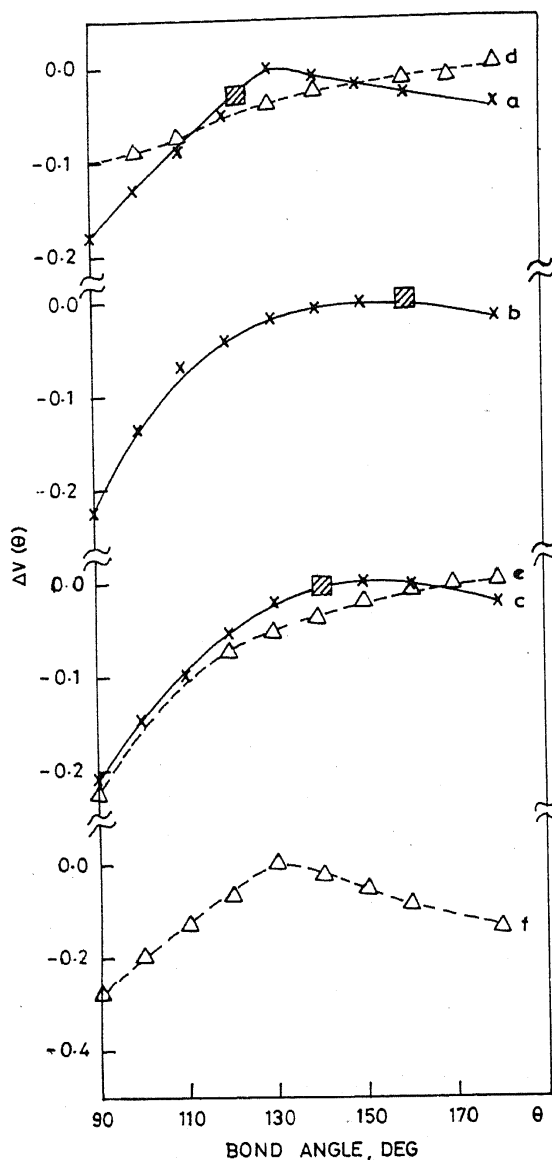
<sup>b</sup>Mulliken and Ermler (1981); values in parenthesis are experimental;

<sup>c</sup>one electron missing from 1b<sub>2</sub>;

<sup>d</sup>Schwenzer *et al* (1974).



**Figure 1.** Plots of  $\Delta V(\theta)$  versus  $(\theta)$  for (a) <sup>2</sup>B<sub>1</sub> (b) <sup>2</sup>A<sub>1</sub> (c) <sup>2</sup>B<sub>2</sub> states of H<sub>2</sub>O<sup>+</sup>. See table 1 for the electronic configurations of these states. ▨ denotes the equilibrium bond angles found by *ab initio* methods.



**Figure 2.** Plots of  $\Delta V(\theta)$  versus  $(\theta)$  for (a)  $1^3A''$  (b)  $1^3A'$  (c)  $2^2A'$  (d)  $2^3A'$  (e)  $2^3A''$  (f)  $3^3A'$  states of HCN. Full lines indicate present valency results for states already studied while broken lines are for as yet unknown states. See tables 1 and 2 respectively for the electronic configuration of these states.  $\blacksquare$  denotes the equilibrium bond angle calculated by *ab initio* methods.

at a particular bond angle from the maximum value, i.e.  $V_M(\theta) - V_M^{\max}$  versus  $\theta$ , to give an idea of the change in molecular valency with bond angle. These are given in figures 1 and 2 for various excited and ionised states of  $H_2O$  and HCN as two typical cases.

It is clear from table 1 and figures 1 and 2 that for all the molecules presently studied, valency predictions compare reasonably well with the reported values. In fact, the agreement may be said to be very good when we take into account the simplicity of our method, in contrast to the other more sophisticated but time-consuming methods involving extensive CI. What is remarkable is that even very acute angles such as  $55^\circ$  for the  $^2B_2$  state of  $H_2O^+$  and  $47.5^\circ$  for the  $^2B_2$  state of

**Table 2.** Valency prediction of bond angles of unknown excited and ionised states of molecules.

Molecule	Electronic configuration <sup>a</sup>	State	Bond angle
CH <sub>2</sub>	(2a <sub>1</sub> ) <sup>2</sup> (1b <sub>2</sub> ) <sup>1</sup> (3a <sub>1</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>1</sup>	<sup>3</sup> A <sub>2</sub>	50
	(2a <sub>1</sub> ) <sup>2</sup> (1b <sub>2</sub> ) <sup>1</sup> (3a <sub>1</sub> ) <sup>1</sup> (1b <sub>1</sub> ) <sup>2</sup>	<sup>3</sup> B <sub>2</sub>	45
	(2a <sub>1</sub> ) <sup>1</sup> (1b <sub>2</sub> ) <sup>2</sup> (3a <sub>1</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>1</sup>	<sup>3</sup> B <sub>1</sub>	90
	(2a <sub>1</sub> ) <sup>1</sup> (1b <sub>2</sub> ) <sup>2</sup> (3a <sub>1</sub> ) <sup>1</sup> (1b <sub>1</sub> ) <sup>2</sup>	<sup>3</sup> A <sub>1</sub>	180
H <sub>2</sub> O <sup>+</sup>	(2a <sub>1</sub> ) <sup>1</sup> (1b <sub>2</sub> ) <sup>2</sup> (3a <sub>1</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>2</sup>	<sup>2</sup> A <sub>1</sub>	85
HCN	(5a') <sup>2</sup> (6a') <sup>1</sup> (1a'') <sup>2</sup> (8a') <sup>1</sup>	<sup>2</sup> <sup>3</sup> A'	180
	(5a') <sup>2</sup> (6a') <sup>2</sup> (1a'') <sup>1</sup> (8a') <sup>1</sup>	<sup>2</sup> <sup>3</sup> A''	180
	(5a') <sup>1</sup> (6a') <sup>2</sup> (1a'') <sup>2</sup> (7a') <sup>1</sup>	<sup>3</sup> <sup>3</sup> A'	130

<sup>a</sup>Inner electronic configurations (1a<sub>1</sub>)<sup>2</sup> for CH<sub>2</sub> and H<sub>2</sub>O<sup>+</sup> and (1a')<sup>2</sup> (2a')<sup>2</sup> (3a')<sup>2</sup> (4a')<sup>2</sup> for HCN are omitted.

NH<sub>2</sub> are reproduced fairly well by the present method, which gives values of 50° and 60°, respectively. Our method also distinguishes correctly between the singlet and triplet states of the same electronic configurations (for example the <sup>1</sup>B<sub>1</sub> and <sup>3</sup>B<sub>1</sub> states of NH<sub>2</sub><sup>+</sup> – see table 1).

We have also predicted bond angles of some as yet unknown excited states. These are given in table 2 and plots of  $\Delta V(\theta)$  versus  $\theta$  for the unknown states of HCN have been included in figure 2. It may be remarked that the linearity or bent nature of these states are what one would predict qualitatively from Walsh's type of arguments (Walsh 1953). However, it should be noted that such arguments cannot quantitatively predict bond angle values.

Theoretical reasons for the surprising success of this simple model are not fully understood. Efforts are under way to establish this method on a firmer footing by examining the basis of Walsh diagrams and the general applicability of MO valency as a quantitative ordinate of Walsh diagrams for excited and ionised states of molecules. Details will be published elsewhere (Siddarth and Gopinathan 1987).

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