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Extended Hückel Method: Calculation of the Ethylene Force Field

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All quadratic force constants of the ethylene molecule have been calculated using extended Hückel method with Hofmann's parameterization. Good agreement with the experimental values obtained for force constants of the deformation modes and a poor one for stretching modes is discussed together with the potentialities of this method for molecular shape, bond length and force constant predictions.

Alle quadratischen Kraftkonstanten des Äthylenmoleküls wurden unter Benutzung der erweiterten Hückelmethode mittels der Parametrisierung nach Hoffmann berechnet. Die gute Übereinstimmung mit den experimentellen Werten, die für die Kraftkonstanten der Deformationschwingungen erhalten wurde sowie die schlechte für Streckschwingungen und die Möglichkeiten, mittels dieser Methode die Molekülform, die Bindungslängen und die Kraftkonstanten vorauszusagen, werden diskutiert.

Toutes les constantes de force quadratiques d'ethylène ont été calculées en utilisant la méthode de Hückel étendue avec la parameterisation d'aprés Hoffmann. Un bon accord avec l'expérience a été obtenu pour les constantes de force des modes de déformation tandis que pour les constantes des modes de valences l'accord fut mauvais. Les resultats sont discutés ainsi que l'applicabilité de la methode pour prediction de la geometrie moléculaire et de constantes de force.

Introduction

A very extensive use of the extended Hückel method (EHM) in recent years[1] has definitely proved its usefulness for different practical purposes ranging from stability and shape predictions to chemical reactivity.

Unfortunately, in spite of all this wide usage of the method we are still far from deeper physical understanding of why it works at all. Furthermore, we even do not know fully the scope of the problems for which this method gives an adequate description and, unfortunately, there are not many papers where the method is applied from this point of view.

Perhaps the most serious step in this respect has been made recently by Allen and Russel [1], Fukui and Fujimoto [2] and Blyholder and Coulson [3].

Allen and Russel [1] compared in detail the "*ab initio*" SCF-LCAO-MO calculations for different triatomics with EHM results. This comparison showed that just the sum of the EHM orbital energies may yield reasonable bond angle predictions at least for non-ionic species.

More recent is the attempt by Fukui and Fujimoto [2] who showed that using some heuristic assumptions one can express the total HF energy as a sum of orbital energies and of a term independent of nuclear configuration.

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[1] Cf. list of papers cited in reference [1].

Finally, the assumption of the proportionality of the off-diagonal matrix elements of the Hamiltonian to the corresponding overlap integrals has been investigated very recently by Blyholder and Coulson [3]. They found that this assumption is fairly well satisfied except for the matrix elements corresponding to the nearest neighbors in which the kinetic energy terms play an important rôle.

In our opinion, it should be admitted that in spite of all these attempts there are many facets of this method which are presently not fully understood, be it the approximation of the total energy by just the sum of orbital energies; the actual values of the parameter k or the non-invariance of the method toward the energy zero to name but few.

The aim of this paper is to give additional supporting evidence to the fact that the method might be very useful in predicting molecular shapes while reliable bond length predictions cannot be expected. The actual calculations presented in this paper further supplement the above statement in the sense that the method seems to be capable of giving useful predictions even for such sensitive quantities as force constants which are associated with bond angle deformations while yielding very poor results for bond stretching force constants.

As far as the ethylene force constants calculation concerns we are not aware of any former work except that of Parr and Crawford [4], who calculated the torsional mode force constant in various electronic states using a π-electron approximation. Yet ethylene seems to be an excellent testing example for such calculations since it already represents a real polyatomic molecule with its 12 vibrational modes while being still accessible to a fairly accurate spectroscopic study so that the existing experimental data, last time updated by Cyvin and Cyvin [5], are both complete and very reliable.

Method and Results

In all the calculations reported below the standard version of the EHM as given by Hoffmann [6] was used: A simple arithmetic mean value formula was used for the off-diagonal matrix elements H_{ij} of the Hamiltonian matrix

$$H_{ij} = (1/2)k(H_{ii} + H_{jj})S_{ij}, \tag{1}$$

and the value $k = 1.75$ was used unless otherwise stated. The overlap integrals S_{ij} were calculated for Slater atomic orbitals with the effective nuclear charge $\xi = 1.0$ for 1s-orbitals of H-atoms and $\xi = 1.625$ for 2s- and 2p-orbitals of C-atoms.

First, the absolute minimum of the potential energy hypersurface was found. Since any out-of-plane distortion of the molecule leads to an energy increase, the molecule was kept planar and symmetric in the minimization procedure. Therefore, the following three parameters were chosen to describe the molecular structure: CC bond length, CH bond length and HCH angle.

The total EHM energy of ethylene molecule was calculated in about 400 points and least squares fits for different "cuts" of the energy surface (with two parameters fixed) were carried out. Next, the least squares fits of these energy minima as a function of the second parameter were carried out and, ultimately, these energy minima were fitted as a function of the last parameter and the structural parameters corresponding to these absolute minimum determined. In order to double check this procedure, we have carried it out for all six possible permutations of the sequence of the structural parameters used in the least squares procedure indicated above. In all cases, the same energy minimum and, consequently, the same structural parameters were obtained, irrespective of the 2nd or 3rd order least squares fits being used. The resulting molecular structure is given in Table 1 together with the corresponding experimental values and the values calculated by Hoffmann [6]. Our resulting parameters differ from those given by Hoffmann in spite of the fact that the same method and parameterization was used, since he carried out only an approximate minimization with one cycle for each parameter. Nevertheless, the difference between Hoffmann's [6] approximate and our accurate values are within the accuracy claimed in Hoffman's paper (i.e. 0.05 Å).

Table 1. *Structural parameters of ethylene (bond lengths in Å, angle in degrees)*

Parameter	Experimental [7]	Hoffmann [6]	This work
CC	1.337	1.47	1.51_6
CH	1.086	0.95	0.91_7
HCH	117°22′	125°	$126°3_8'$

Let us mention here that if the bond lengths are assigned the experimental values and only the HCH angle is varied we get a much better agreement with the experimental value for the latter, viz. 117° [8].

In vibrational studies of the planar X_2Y_4 molecules a number of different sets of symmetry coordinates has been used. For our purpose it is irrelevant which set is used, but sets without redundancies are preferred. Therefore, in our force constant calculation we have used systematically the same set of symmetry coordinates as Cyvin and Cyvin [5] for the sake of a direct comparison with their experimentally determined force constants. Using the numbering convention as shown in Fig. 1 these symmetry coordinates for the individual symmetry species of the point group D_{2h} are as follows:

$$\begin{array}{ll}
A_{1g} & S_1 = (r_1 + r_2 + r_3 + r_4)/2 \\
 & S_2 = d \\
 & S_3 = (RD)^{1/2}(\beta_1 + \beta_2 + \beta_3 + \beta_4)/2 \\
B_{1g} & S_4 = (r_1 - r_2 + r_3 - r_4)/2 \\
 & S_5 = (RD)^{1/2}(\beta_1 - \beta_2 + \beta_3 - \beta_4)/2 \\
B_{2u} & S_6 = (r_1 - r_2 - r_3 + r_4)/2 \\
 & S_7 = (RD)^{1/2}(\beta_1 - \beta_2 - \beta_3 + \beta_4)/2 \\
B_{3u} & S_8 = (r_1 + r_2 - r_3 - r_4)/2 \\
 & S_9 = (RD)^{1/2}(\beta_1 + \beta_2 - \beta_3 - \beta_4)/2 \\
B_{2g} & S_{10} = (RD/2)^{1/2}(\gamma_1 - \gamma_2) \\
A_{1u} & S_{11} = R\varphi \\
B_{1u} & S_{12} = (RD/2)^{1/2}(\gamma_1 + \gamma_2)
\end{array} \tag{2}$$

where R and D are the equilibrium bond lengths of the CH and CC bonds, respectively. Further, r_i and d are the displacements of the CH_i and CC bond lengths, respectively, and β_i is the in-plane bending of the H_iCC angle. Finally $\gamma_1(\gamma_2)$ is the out-of-plane bending of the $H_1H_2C\,(H_3H_4C)$ plane and φ is one half of the

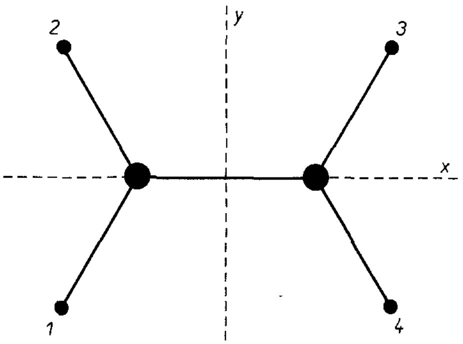

Fig. 1. The coordinate system and hydrogen atoms numbering used

torsional angle between the H_1CH_2 and H_3CH_4 planes. The angular coordinates are multiplied by $(RD)^{1/2}$ or by R so that all coordinates have the dimension of a length. This set of symmetry coordinates is complete and does not contain any redundancies.

In order to determine the diagonal quadratic force constant for each symmetry coordinate, we have calculated the energy in 8 points in which the molecule was distorted from its equilibrium position along the respective symmetry coordinate. The separation of these points was 0.01 Å for the stretching modes and 1 degree for the bending and torsional modes. The force constant was then obtained directly from the quadratic and cubic least squares fits of the pertinent 9 points "potential curve". The resulting force constants are given separately for bending (Table 2) and stretching (Table 3) modes for obvious reasons (see Discussion).

Table 2. *Calculated and experimental values of the deformation vibrational mode quadratic force constants. Calculated force constants obtained by quadratic as well as cubic least squares (lsqs) fits are given*

Type of the vibrational mode	Symmetry species	Symmetry coordinate	Quadratic force constants of the deformation vibrational modes (in mdyn/Å)				
			Experimental value [5]	Calculated in the equilibrium molecular configuration[a]		Calculated in the experimental molecular configuration[b]	
				2nd order lsqs	3rd order lsqs	2nd order lsqs	3rd order lsqs
in-plane	A_{1g}	S_3	0.96302	0.933	0.944	1.111	1.111
	B_{1g}	S_5	0.45585	0.495	0.500	0.530	0.530
	B_{2u}	S_7	0.31691	0.438	0.444	0.506	0.506
	B_{3u}	S_9	0.95955	0.919	0.933	1.079	1.079
out-of-plane	B_{2g}	S_{10}	0.15524	0.160	0.160	0.210	0.210
	A_{1u}	S_{11}	1.81997	1.802	1.802	1.595	1.595
	B_{1u}	S_{12}	0.20559	0.197	0.197	0.270	0.270

[a] These are the values of the force constants calculated for the EHM equilibrium molecular structure (see Table 1), i.e. calculated in the minimum of the EHM energy hypersurface.

[b] These are force constants calculated from the EHM energy hypersurface but in the point corresponding to the experimental molecular structure, which is clearly off the equilibrium of this hypersurface.

Table 3. *Calculated and experimental values of the stretching vibrational mode quadratic force constants. Calculated force constants obtained by quadratic as well as cubic least squares (lsqs) fits are given*

Symmetry species	Symmetry coordinate	Quadratic force constants of the stretching vibrational modes (in mdyn/Å)				
		Experimental value [5]	Calculated in the equilibrium molecular configuration[a]		Calculated in the experimental molecular configuration[b]	
			2nd order lsqs	3rd order lsqs	2nd order lsqs	3rd order lsqs
A_{1g}	S_1	6.78460	1.482	1.483	1.202	1.047
	S_2	10.75973	2.388	2.396	2.701	2.707
B_{1g}	S_4	5.14516	0.929	0.932	0.797	0.683
B_{2u}	S_6	5.68803	0.910	0.914	0.736	0.631
B_{3u}	S_8	5.82683	1.537	1.541	1.233	1.056

[a, b] See Table 2.

In these tables we have also included force constants, calculated not in the equilibrium position of the molecule but in the points of the energy hypersurface corresponding to the experimental molecular structure and, consequently, placed off the minimum of the EHM energy surface. In both cases we present the values calculated from both quadratic and cubic least squares fits. We observe that while in the equilibrium molecular configuration the 3rd order least squares values are systematically slightly higher than the 2nd order ones, the force constants calculated off the equilibrium position of the EHM hypersurface are identical in the case of the deformation modes and shifted to either side in the case of the stretching modes.

Further, we have calculated the interaction force constants. Unfortunately, due to the symmetry of the molecule there is not a single interaction constant in ethylene coupling two deformation modes. Consequently, quantitative agreement cannot be expected and we have made the calculation in order to see whether we can reproduce at least the sign of these constants. The results are shown in Table 4. In this table we present for obvious reasons only the force constants calculated in the equilibrium molecular configuration using second order least squares fits.

Table 4. *Calculated and experimental values of the quadratic interaction force constants*

Symmetry species	Symmetry coordinates involved	Quadratic interaction force constants (mdyn/Å)	
		Experimental [5]	Calculated
A_{1g}	S_1S_2	1.00232	0.504
	S_1S_3	−0.11082	−0.232
	S_2S_3	1.51281	0.630
B_{1g}	S_4S_5	0.19481	0.199
B_{2u}	S_6S_7	0.03269	0.107
B_{3u}	S_8S_9	−0.11082	−0.202

Discussion

Hoffmann [6] in his well known paper concerning the EHM parameterization which is now widely used has already pointed out that the EHM method will not give chemical binding for simple molecules like H_2.

Indeed, investigating the EHM scheme in greater detail one can see that at least in simple cases, which allow a closed formula to be used, the chemical binding obtained by the method is more or less an artifact. A realistic potential energy curve is obtained in this method only due to the proper character of the atomic overlaps and has nothing to do with the intimate interplay of the nuclear attraction, coulomb and exchange terms.

A most frapant and clear demonstration of this fact is obtained from the following simple two-electron diatomic model calculation. Suppose we have a two-electron homonuclear diatomic system, for example H_2 (the assumption of the model being homonuclear is not at all essential and the same conclusions may be drawn for the heteronuclear case as well, only the formulae being slightly more complicated) and we calculate the potential energy curves in a general electronic state of our model. Writing H for the VSIP and $S(r)$ for the overlap (as a function of the internuclear separation r) of the atomic orbitals used to represent our state, we get the following simple formula for the molecular orbital energies as a function of the internuclear separation

$$E^{\pm}(r) = H(1 \pm kS(r))/(1 \pm S(r)) . \tag{3}$$

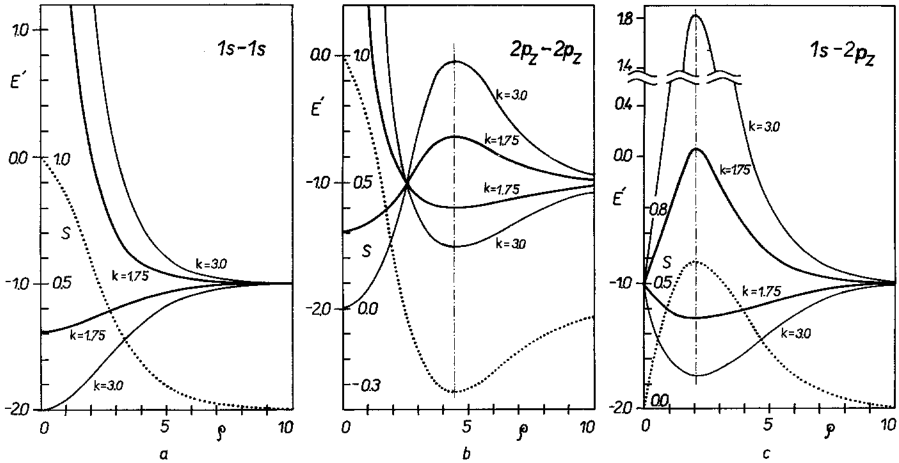

Fig. 2 a–c. The illustration of the interrelation between the shape of the potential energy curve and the character of the overlap as a function of the internuclear distance for simple two-electron homonuclear diatomic model. Three typical cases are shown corresponding to the following electronic configurations: a $(1s)^2$, b $(2p_z)^2$, c $(1s, 2p_z)$. Each figure shows the dependence of the overlap integral S (dotted line and right hand scales) and of the orbital energies E' (solid lines and left hand scales) as a function of the effective internuclear separation ϱ ($\varrho = \xi r$ where ξ is the effective nuclear charge and r is the internuclear distance in atomic units). The orbital energies E' are given by the relation (1) with $H = -1$ and are shown for two different values of the semiempirical parameter k (i.e. 1.75 and 3.0)

Accomodating two electrons of our model in either molecular orbital obtained (the ground state potential curve corresponds to E^+ for $S>0$ and $H<0$) one can see immediately that the resulting potential energy curve will be a monotonous function of the internuclear separation as far as $S(r)$ is a monotonous function. Indeed, our potential energy curve will have a minimum at some point $r=r_0$, ($r_0 \neq 0$ or ∞), only if $S(r)$ has an extremum as a function of r for some $r=r_e$, ($r_e \neq 0$ or ∞). Moreover, in this trivial case, if $S(r)$ has an extremum at $r=r_e$, then the minimum of the potential curve will appear for the same value of r, e.g. $r_0=r_e$, since

$$\frac{d(2E^\pm)}{dr} = \pm[2H(k-1)/(1\pm S)^2]\frac{dS}{dr}. \tag{4}$$

In other words, the equilibrium internuclear distance is predetermined in this simple case by the extremum of the overlap as a function of the internuclear distance. This is illustrated graphically for three typical cases in Fig. 2.

Without going into further details one can see that a similar mechanism will be at work even in more complicated systems. Therefore, one cannot expect to get reliable bond lengths from this method since the latter are by no means simply related to the internuclear separation corresponding to the overlap extremum.

On the other hand it is well known that a very simple principle of the maximum overlap is extremely useful not only for a qualitative prediction of the hybridization type which will occur but, in most cases, gives a reasonably good quantitative description of the molecular shapes (cf. [9]).

The intimate relationship of the EHM and the maximum overlap methods [10, 11] is quite obvious from their general structure; even though it is difficult to demonstrate this using simple algebra except in simple cases. The main difference is perhaps that in EHM the maximum overlap condition is replaced by a minimum condition for a certain "energy-type quantity" given by the sum of all occupied EHM orbital energies. Nevertheless, the resulting molecular orbitals are very similar in the maximum overlap method,EHM as well as in the SCF LCAO MO method [1]. Consequently, it is not very surprising that EHM gives reasonable molecular shape predictions just as the simple maximum overlap method does. Nevertheless, it is very surprising in our opinion that the "energy-like quantity" of the EHM gives not only reasonably predictions for the relative isomer stability and the order of magnitude of rotational bariers but, as our calculations presented in this paper demonstrate, it gives such a good representation of the potential energy hypersurface around the equilibrium that one can obtain very meaningful estimates for the force constants of the deformation modes (cf. Table 2). Further, this type of calculation might be useful for the sign determination of the interaction force constants which are sometimes difficult to obtain from the analysis of the experimental data (cf. Table 4).

The considerations presented above suggest why similar results cannot be expected for bond lengths and, consequently, stretching force constant estimates (cf. Table 3). Therefore, even the interaction force constants, which in our case always couple at least one stretching mode with the deformation or another stretching mode, are bound to give poor quantitative results. Nevertheless, the signs of these constants are always correct.

Similar conclusions can be made on the basis of the comparison with the *ab initio* SCF data which has been carried out by Allen and Russel [1]. Furthermore, on the basis of their results, as well as on the basis of other considerations, it may be stated that the method is likely to fail for molecules with non-homogeneous charge distribution e.g. for molecules involving strongly polarized or nearly ionic chemical bonds.

We have further examined how the resulting force constants are influenced by the value given to the semiempirical parameter k. As is well known, the commonly used value 1.75, which we have also used in our calculations, was determined by fitting the calculated and experimental values of the rotational barrier of ethane. One might, therefore, expect that calculation of different molecular properties will require different values for this parameter.

Again, consideration of a trivial example of a hydrogen-like molecule presented above, gives the following relationship for the dependence of the force constant on the parameter k:

$$\left.\frac{d^2(2E^{\pm})}{dr^2}\right|_{r=r_0} = \pm\,[2H(k-1)/(1 \pm S(r_0))^2]\,\left.\frac{d^2S}{dr^2}\right|_{r=r_0}, \tag{5}$$

since

$$\left.\frac{dS}{dr}\right|_{r=r_0} = 0\,.$$

On the basis of this simple estimate one can expect an approximate linear relationship between the force constante and the parameter k.

Indeed, the actual calculations shown in Figs. 3a and b are in very good agreement with the above estimate. For the sake of completeness we have to add that the calculation of force constants using different k values (Figs. 3a and b) has been always carried out for a fixed molecular structure corresponding to an absolute minimum of the potential hypersurface calculated with $k = 1.75$. Therefore, the force constants for $k \neq 1.75$ were calculated off the equilibrium point of the potential hypersurface since the equilibrium clearly depends on k, especially for the stretching modes. Nevertheless, the use of the fixed geometry in calculating force constants for different values of the semiempirical parameter k is not at all essential and is well justified as shows a comparison of force constants calculated *in* and *off* the equilibrium position given in Tables 2 and 3. Indeed, the potential surfaces are fairly well harmonic as follows from a comparison of the force constants calculated by 2^{nd} and 3^{rd} order least squares fits shown in Tables 2 and 3 and, clearly, a harmonic potential curve has the same second derivative in each point. Actually, using 3^{rd} order least squares fits either off or in the minimum of the respective potential curve for a couple of cases we have obtained practically the same results as with a 2^{nd} order least squares fits off the equilibrium geometry.

With the help of Figs. 3a and b we could now easily find the values of k giving the best agreement of experimental and calculated force constants, since we can find for each force constant a value of k giving an exact agreement. This is graphically demonstrated in Figs. 3a and b where on each plot we have marked a point corresponding to the experimental value of the given force constant. We see immediately that for deformation modes the value of $k = 1.75$ is well suited since all points are scattered around this value. The stretching modes, for which one cannot expect very good agreement with the given scheme anyway, would require quite unrealistic values of k of the order of 4.5–5.0. Nevertheless, it is quite interesting that for such a high value of k we would get approximately right values for these constants even though the accuracy would be much worse than for the deformation force constants. This fact seems to suggest that it would be interesting to use different values of k for different pairs of atomic orbitals as suggested by Boer, Newton and Lipscomb [12] or, eventually, to use the approximation for non-diagonal matrix elements introduced by Cusachs [13].

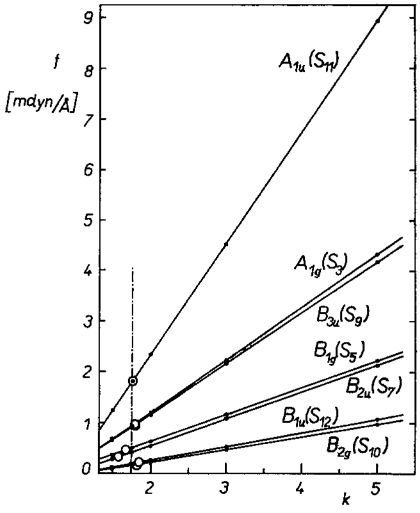

Fig. 3a

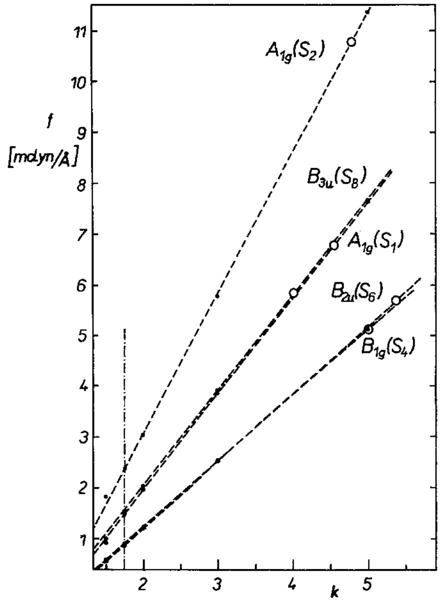

Fig. 3b

Fig. 3a. The dependence of the calculated force constants f_i of the deformation modes [designated by the pertinent symmetry species and symmetry coordinates (2)] on the semiempirical parameter k (for details see text). Large empty circles indicate the corresponding experimental values of the given force constants. The dotted vertical line corresponds to usually used value 1.75 of the semiempirical parameter k

Fig. 3b. The dependence of calculated stretching modes force constants on the semiempirical parameter k. (The same designations as in Fig. 3a used)

Force constant calculations are currently being undertaken for some other simple molecules in order to find out whether the results obtained for the ethylene molecule are typical.

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