

Use of semiempirical molecular orbital calculations for the evaluation of force fields

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Abstract. Various methods, employing molecular orbital calculations of varying approximations, for evaluation of force fields of polyatomic molecules have been reviewed. Applications of CNDO/force method for the force field calculations are specially dealt with in detail because of its ease of operation and being economically more viable in terms of computer time. The calculated C=O stretching force constants for a series of organic molecules are shown to have linear relationship with substituent constants.

Keywords. Force fields; vibrational analysis; molecular orbital calculations; CNDO/force.

1. Introduction

In the past two decades considerable interest has been shown in the calculation of force fields of polyatomic molecules using molecular orbital calculations. The force constant F_{ij} is defined as

$$F_{ij} = (\partial^2 E / \partial q_i \partial q_j)_e \quad (1)$$

where E is the total energy of the molecule and q_i, q_j are symmetry or internal coordinates. The methods for the evaluation of force constants include (Kanakavel 1976) double numerical differentiation (Baron *et al* 1962; Leies 1963; McLean 1964; Goodisman 1963; Paldus and Hrabe 1968), double analytical differentiation (Bratoz 1958; Gerratt and Mills 1968; Bishop and Randic 1966; Bishop and Mancias 1969, 1970; Swanstrom *et al* 1971; Bloemer and Brunner 1972) and analytical differentiation followed by numerical differentiation (Pulay 1969, 1970a, b; Pulay and Meyer 1971, 1972; Pulay 1974). The double numerical differentiation method uses systematic variation of nuclear configuration accompanied by SCF-MO calculations for each configuration. The energy hypersurface built in this fashion is used to evaluate the force constants by numerical differentiation to second order. In double analytical differentiation method, the expression for the SCF energy is differentiated twice to obtain an analytical expression for the force constants in terms of the parameters of the electronic SCF-MO wavefunctions. In the third method developed by Pulay and coworkers (Pulay 1969, 1970a, b; Pulay and Meyer 1971, 1972; Pulay 1974) the energy is differentiated analytically (thus building force hypersurfaces) followed by numerical differentiation to first order. In the series of papers, Pulay and coworkers have shown that their method (also called force method and more recently gradient method) has certain advantages over the other two methods discussed above. The double numerical

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differentiation is not economical because the wavefunctions must be computed for a number of nuclear configurations and might be inaccurate because of the two numerical differentiations. The number of necessary points on the energy surface varies with the strategy used to find the equilibrium configuration but becomes excessive if there are three or more coordinates. In the case of the force method all the force constants F_{ij} ($i = 1$ to N and j is fixed) can be obtained by varying only the coordinates q_j . This advantage is pronounced for molecules with several degrees of freedom. The method makes possible a quick iterative procedure to determine the equilibrium configuration. Semiempirical methods like CNDO/2 have also been used (Pople and Beveridge 1970; Klopman and O'Leary 1970; Ribegard 1974; Colthup and Orloff 1974) to determine force fields using the energy hypersurface (double numerical differentiation) method. Pulay and Torok (1973) have shown that the semiempirical quantum chemical calculations on molecular geometry and force constants by energy hypersurface method become impractical as the size of the molecule increases and that the application of the force method to semiempirical wavefunctions makes it possible to carry out an economical and simple calculation of molecular geometry and force constants.

2. CNDO/force calculations

Kanakavel *et al* (1976) performed CNDO/force calculations on a series of molecules, H_2CO , F_2CO , CF_4 , CHF_3 , CH_2F_2 and CH_3F . As discussed by Pulay and Torok (1973) the first derivatives of the total energy with respect to the nuclear coordinates are calculated analytically from the CNDO wavefunctions. The forces acting on each atom in the molecule are computed for an arbitrary geometry. Since the forces are directed towards the equilibrium geometry of the molecule, all atoms are moved in the direction of force over a small distance, say 0.01 Å. The forces are calculated again for the new geometry and the nuclei are allowed to relax towards the equilibrium geometry. The process is repeated until the norm of the forces becomes smaller than the preset threshold value. This method is known as the steepest descent method. When the energy is minimized, the norm of the forces keeps decreasing. It was concluded that when the norm of the forces is less than 0.001 further iterations do not change the energy and geometry to any considerable extent. The experimental and optimized geometries for H_2CO and F_2CO are given in table 1.

The Cartesian forces are calculated for the equilibrium geometry of the molecule.

Table 1. Calculated and experimental molecular geometry parameters (distances in Å and angles in degrees).

	H_2CO		F_2CO		
	Calc.	Exp.*	Calc.	Exp.†	
r_{CO}	1.247	1.208	r_{CO}	1.251	1.170
r_{CH}	1.114	1.116	r_{CF}	1.324	1.316
$\angle \text{HCH}$	116.2	116.5	$\angle \text{FCF}$	109.8	107.6

* Tokagi and Oka (1963); † Carpenter (1974).

The molecule is then deformed by an amount $\pm \frac{1}{2}\Delta R_i$ where ΔR_i is the displacement of the i th internal coordinate. The Cartesian forces (f_i) are found for possible configurations representing different modes of vibration. The displacements given for stretching and bending internal coordinates were $\pm 0.01 \text{ \AA}$ and $\pm 1^\circ$ respectively. For each deformed configuration the symmetry forces (ϕ_i) are calculated by using suitable transformations. The symmetry force constants F_{ij} are obtained as the ratios of $\Delta\phi_i$ and ΔS_j . The GMAT program of Schachtschneider (1964) was used to compute the B matrices. In table 2 the symmetry force constants for H_2CO and F_2CO obtained by CNDO/force method are compared with experimental force fields.

In several cases considered it is found that the stretching force constants obtained by CNDO/force are more than twice the experimental values and the stretch-stretch interaction force constants are slightly different in magnitude in comparison with experimental values. The bending force constants and stretch-bend interaction force constants are found to be comparable with the experimental values. The signs of the interaction constants are in agreement with those predicted by Mills (1963) and Heath and Linnett (1945) based on orbital following arguments. The value of F_{13} in H_2CO is in accordance with HOFF constraint. The stretching force constants, though found to have higher values than the experimental values, have some interesting trends. As can be noticed from table 3, in a series of molecules the CH and CF stretching force constants, in general, are found to have the same trend as the experimental force constants. For example, with increasing number of hydrogens in the series CHF_3 , CH_2F_2 , CH_3F , CH_4 , the calculated force constants for symmetric C-H stretching vibration are found to increase. A roughly similar trend is found in the experimental force constants also. Similarly for ν_{CF} (symmetric stretching) with increasing number of fluorine atoms in the series, CH_3F , CH_2F_2 , CHF_3 , CF_4 the experimental force constants and those obtained by the CNDO/force method are found to increase. Though the trends in experimental and calculated force constants are found to be similar for corresponding asymmetric stretching vibrations, a similar trend in calculated force constants with increasing

Table 2. Comparison of experimental and calculated symmetry force fields of X_2CO ($\text{X}=\text{H}, \text{F}$) (mdyn/ \AA , mdyn and mdyn \AA for the stretching, stretching/bending and bending force constants, respectively)^a.

Force constants	Assignments	H_2CO			F_2CO		
		CNDO/Force		<i>Ab initio</i> ^c	CNDO/Force		Exp. ^d
		Calc.	Exp. ^b		Calc.	Exp. ^d	
F_{11}	$\text{CX}_2\text{s. str.}$	11.99	4.963	4.990	25.78	7.601	7.695
F_{12}	CX/CO str.	0.980	0.739	0.676	2.5	1.549	1.491
F_{13}	$\text{CX/CX}_2 \text{ def.}$	0.101	0.077	0.106	0.330	0.540	0.568
F_{22}	CO str.	30.41	12.903	13.905	31.4	14.818	14.996
F_{23}	$\text{CO/CX}_2 \text{ def.}$	-0.48	-0.408	-0.414	-0.443	-0.331	-0.488
F_{33}	$\text{CX}_2 \text{ def.}$	0.614	0.57	0.645	1.134	1.404	1.370
F_{44}	CO wag.	0.469	0.403	0.514	0.65	0.735	0.735
F_{55}	$\text{CX}_2 \text{ a. str.}$	11.60	4.852	4.909	23.52	5.867	5.718
F_{56}	$\text{CX/CX}_2 \text{ rock.}$	0.212	0.171	0.157	0.619	0.688	0.635
F_{66}	$\text{CX}_2 \text{ rock.}$	0.82	0.833	0.946	0.902	1.117	1.146

^a Kanakavel (1976); ^b Duncan (1973); ^c Pulay (1974); ^d Mallinson *et al* (1975).

Table 3. Comparison of calculated and experimental force constants for stretching vibrations in a series of molecules (in mdyn/A).

Stretching mode	Molecule	Force constant	
		Calc.	Exp.*
ν_{CH} (sym) (A_1)	CH_4	12·700	5·842
	CH_3F	12·205	5·368
	CH_2F_2	11·755	4·873
	CHF_3	11·49	5·340
ν_{CF} (sym) (A_1)	CF_4	27·000	9·250
	CHF_3	25·946	8·669
	CH_2F_2	25·130	7·075
	CH_3F	24·060	5·764
ν_{CH} (asym)	$\text{CH}_4(\text{F}_2)$	12·08	5·383
	$\text{CH}_2\text{F}_2(\text{B}_2)$	11·421	4·904
	$\text{CH}_3\text{F}(\text{E})$	11·126	5·433
ν_{CF} (asym)	$\text{CF}_4(\text{F}_2)$	23·08	6·220
	$\text{CH}_2\text{F}_2(\text{B}_2)$	22·85	5·111
	$\text{CHF}_3(\text{E})$	21·265	5·303

* See Kanakavel *et al* (1976).

number of fluorine and hydrogen atoms cannot be found for the series of molecules considered. This is attributed to the fact that ν_{CF} (asymmetric) as well as $\nu_{\text{C-H}}$ (asymmetric) belong to three different symmetry species. Plots (figure 1) of experimental and calculated force constants of the CH and CF symmetric stretching modes in a series of molecules show different slopes and intercepts. This indicates that there is a definite relationship between experimental and calculated stretching force constants though the indices of the relations may differ for different modes of vibration.

3. Applications

In the conventional least squares method of force fields refinement using vibrational frequencies, the initial force field is set up (Annamalai and Singh 1982a, b, c) by transferring the force constants from structurally related molecules. The final force fields resulting from these calculations are found to depend on the initial force fields. The diagonal force constants may reasonably be transferred among structurally related molecules but such a transfer is rather difficult in the case of off-diagonal force constants since they greatly depend on the nature of molecules and their geometries. The interaction force constants also play an important role in determining the potential energy distributions (PED) of a molecule. It is therefore essential to consider reliable values for these force constants while constructing the initial force field.

As mentioned above simple CNDO/MO calculations predict in general the signs of interaction force constants correctly. The magnitudes of bending, stretch-bend, and bend-bend force constants obtained from these calculations are close to the experimental values whereas those of stretch-stretch interaction constants are about 50% higher than the experimental values. The stretching force constants are exaggerated by a factor

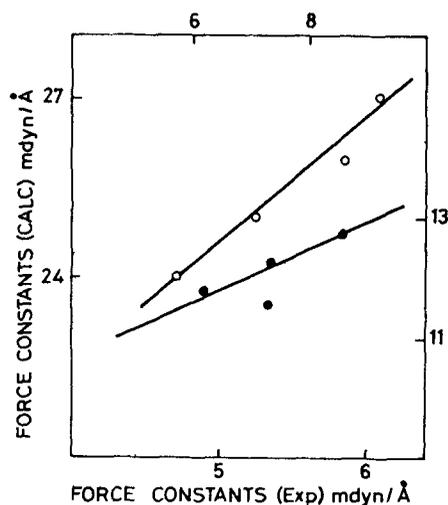
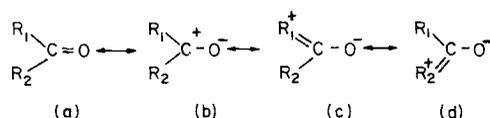


Figure 1. Plots of calculated force constants vs experimental force constants for a series of molecules CF_4 , CHF_3 , CH_2F_2 , CH_3F , CH_4 . For $\nu_{\text{C-H}}$ (sym), the X and Y coordinates respectively correspond to lower and RHS values and for $\nu_{\text{C-F}}$ (sym) O, the upper and LHS values.

of 2-3.5. *Ab initio* calculations prove to yield good results but require a lot of computation time. It is proposed that for large molecules reasonable force fields can be obtained using the following procedure: CNDO/force calculations are performed for the molecule under consideration and the CNDO force field is obtained. The stretch-stretch interaction force constants of the CNDO force field are scaled down using a scale factor. The initial force field is constructed by considering the scaled values of stretch-stretch interaction constants whereas the other interaction and bending force constants are taken from the CNDO force field. The stretching force constants are transferred from structurally related molecules. The initial force field thus constructed is refined further using the vibrational frequencies of normal and isotopic species. Reasonable constraints on the force fields are imposed when the number of force constants to be evaluated is greater than the number of frequencies used. Earlier workers (Kozumutza and Pulay 1975; Torok *et al* 1976) expressed the scale factor for the interaction force constants F_{ij} empirically as the geometric mean of the scale factors for the diagonal force constants F_{ii} and F_{jj} . This requires one to calculate separate scale factors for all F_{ij} force constants. Annamali and Singh (1982) suggested that if the force field has to be further refined using vibrational frequencies, one-common scale factor may be enough to reduce all stretch-stretch interaction constants whereas stretch-bend and bend-bend interaction constants can be transferred from CNDO force field.

We have (Kanakavel 1976; Kanakavel *et al* 1976; Annamalai *et al* 1978; Annamalai 1981; Annamalai and Singh 1982a, b, c 1983a, b; Jothi *et al* 1982; Jothi 1983; Brakaspathy *et al* 1984; Annamali, unpublished results) recently applied the above method for calculation of redundancy-free generalised valence force fields for a series of organic molecules. Studies on carbonyls (Annamalai *et al* 1978; Annamalai 1981; Annamalai and Singh 1982a, b, c, 1983a, b, unpublished) revealed some very interesting results on the effects of substituents on diagonal and off-diagonal force constants.



In the carbonyl compounds, represented by R_1R_2CO , the inductive and resonance effects of the substituents R_1 and R_2 provide a satisfactory basis to understand the influence of the substituents on the electronic structure in and around the carbonyl group. For R_1R_2CO Hartwell *et al* (1948) considered the following contributing structures. The contribution of the structure (b) is controlled by the inductive effects whereas those of (c) and (d) are controlled by the resonance effects of the substituents. The electron attracting groups will decrease the contribution of the structure (b) thus strengthening the carbonyl bond whereas the electron repelling groups will cause the reverse effect. The resonance effects increase the contribution of the structures (c) and (d) leading to a weakening of the carbonyl bond. Accordingly the bond order of CO will change with varying nature of R_1 and R_2 . This will lead to a change in the carbonyl stretching force constant $F_{C=O}$. The electron withdrawing or donating character of the substituents has been related to the free energy contributions of the substituents to the free energy of the total molecule (Hine 1962). This has been related to the substituent constants called σ constants as defined by Hammett (1940) and Taft (1956). The σ constants find applications in chemical kinetics (Hine 1962; Hammett 1940; Taft 1956; Taft *et al* 1958) and molecular spectroscopy (Katritzky and Topson 1972) for studying the substituent effects.

Stretching frequencies have often been correlated with σ values and other electrical parameters (Katritzky and Topson 1972). The carbonyl stretching frequencies were correlated with ionization potentials of carbonyl oxygen atoms (Cook 1958, 1961), effective electronegativities of the substituents (Kagarise 1955; Seth-Paul and Duyse 1972), sigma values (Thompson *et al* 1957; Jones *et al* 1957; Nyquist 1967; Liler 1967; Rao *et al* 1958) and carbonyl bond orders resulting from Huckel type calculations (Berthierr *et al* 1952; Forsen 1962). The above calculations showed, however, limited success. It is well known (Mills 1963; Overend and Scherer 1960; Overend *et al* 1961; Evans and Overend 1963) that the frequency of a vibrational mode in a polyatomic molecule is influenced by various factors like: (a) diagonal force constant corresponding to the vibrational mode under consideration, (b) other diagonal force constant as dictated by potential energy distributions, (c) field effects as represented by the interaction force constants, (d) mass effects, (e) Fermi resonance interactions in some cases and (f) molecular geometry. Bratoz and Besnainou (1959) have demonstrated that the coupling of carbonyl stretching vibration with other modes is significant. As mentioned earlier, the effects of substituents are directly reflected in the force constants and hence they should be related to σ values and not to the vibrational frequencies.

The inductive and resonance effects of a number of substituents have opposite influences in affecting the carbonyl bond strength and consequently the carbonyl stretching force constant is altered. But it is difficult to guess *a priori* which effect plays the predominant role. However, useful information in this regard can be obtained from any possible relation between force constants and sigma values (σ_1 and σ_R of the substituents). Regarding the frequency correlations, some doubt was expressed by Thompson *et al* (1957) whether logically ν was the quantity to be correlated with σ . It

was suggested alternatively to correlate ν^2 with σ , since it is related to the force constant. The σ values are linearly related to free energies (Hine 1962; Hammett 1940) and hence Katritzky and Topson (1972) suggested that σ might reasonably be related to ν rather than ν^2 . Based on these arguments it can be understood that the square root of the force constants are the appropriate quantities and not the force constants which should be correlated with σ values.

In table 4 the values of force constants reported are listed along with the $\Sigma_{R_1, R_2} \sigma_I$ and $\Sigma_{R_1, R_2} \sigma_R$ values. Multiple regression using the relationship

$$F_{C=O}^{1/2} = a_0 + a_1 \Sigma_{R_1, R_2} \sigma_I + a_2 \Sigma_{R_1, R_2} \sigma_R \quad (1)$$

was carried out for the force constants obtained. The relationship obtained is satisfactory with a correlation coefficient of 0.98. The coefficients a_0 , a_1 and a_2 are found to be 3.578, 0.427 and 0.158 respectively. A constant C is defined as the ratio between a_2 and a_1 . The plot of $F_{C=O}^{1/2}$ vs $\Sigma(\sigma_I + C \sigma_R)$ is shown in figure 2. The value obtained for the ratio C (0.37) suggests that the inductive term is about three times more significant than the resonance term in determining $F_{C=O}^{1/2}$. The values of $C \Sigma \sigma_R$ are also included in table 4 for reference.

The σ_I and σ_R values for all the substituents considered, except for CH_3 group, are opposite in sign. The coefficients a_1 and a_2 are found to be positive in the correlation obtained above. From these observations, it is concluded that the inductive and resonance contributions have opposite effects on $F_{C=O}$ values for all the substituents except in the case of CH_3 group. The inductive effect enhances the value of $F_{C=O}$ whereas the resonance effect diminishes. Comparison of σ_I with $C \sigma_R$ (cf table 4) reveals that, for the substituents F, OH and OCH_3 , the actual inductive contribution to the force constant $F_{C=O}$ outweighs the resonance contribution whereas for the substituent NH_2 , the reverse is true. This explains why the values of $F_{C=O}$ are higher in acid fluorides and lower in amides than those in corresponding aldehydes. In the case of CH_3 group both the inductive and resonance effects act together in bringing down the

Table 4. Carbonyl stretching force constants (in mdyn/A) obtained, carbonyl stretching frequencies (in cm^{-1}), and substituent constants*.

No.	R_1, R_2	$F_{C=O}$	$F_{C=O}^{1/2}$	$\nu_{C=O}$	$\Sigma_{R_1, R_2} \sigma_I$	$\Sigma_{R_1, R_2} \sigma_R$	$C \Sigma_{R_1, R_2} \sigma_R$
1	H, H	12.812	3.579	1746	0	0	0
2	H, CH_3	12.368	3.517	1743	-0.06	-0.87	-0.03
3	CH_3, CH_3	12.060	3.473	1731	-0.12	-0.14	-0.05
4	H, OH	13.120	3.622	1774	0.28	-0.68	-0.25
5	CH_3, OH	12.692	3.563	1779	0.22	-0.75	-0.28
6	H, OCH_3	13.063	3.615	1754	0.31	-0.63	-0.23
7	$\text{CH}_3, \text{OCH}_3$	12.717	3.566	1771	0.25	-0.70	-0.26
8	H, F	14.260	3.776	1837	0.56	-0.59	-0.22
9	CH_3, F	13.545	3.680	1870	0.50	-0.66	-0.24
10	F, F	14.677	3.831	1942	1.12	-1.18	-0.44
11	H, NH_2	12.301	3.507	1710	0.11	-0.78	-0.29
12	CH_3, NH_2	12.023	3.467	1704	0.05	-0.85	-0.31
13	NH_2, NH_2	11.667	3.416	1695	0.22	-1.56	-0.58

* Exner (1972).

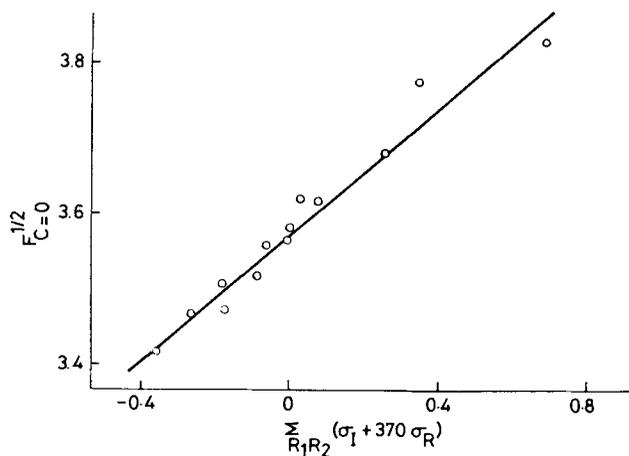


Figure 2. Plots of $F_{C=O}^{1/2}$ against $\sum_{R_1, R_2} (\sigma_I + C\sigma_R)$, where σ_I and σ_R are inductive and resonance contributions of the substituent constants.

value of $F_{C=O}$, since both $a_1\sigma_I$ and $a_2\sigma_R$ are negative quantities for CH_3 group. Similar relations were also tried for C-H, C-O, C-N and C-F stretching, C=O bending, R_1CR_2 bending and several interaction force constants.

Other molecules considered in this series included ethylene (Jothi *et al* 1982), amide (Annamalai and Singh 1982b), glyoxol, oxalyl fluoride, biacetyl, acetic anhydride (Kanakavel 1976), fluoroethylenes (Jothi 1983; Kanakavel 1976), allene and fluoroallenes, vinylacetylenes, vinylcyanamide and propene (Jothi 1983), diacetamide (Annamalai and Singh 1983a; Kanakavel 1976), nitromethane (Brakaspathy 1984). Murthy and Ranganathan (1982a, 1983) have applied this method to evaluate force fields of carbon suboxide and carbonyl and formyl fluoride. This method has also been applied for the effect of molecular interactions on force fields of donors and acceptors exhibiting alcohol + ketone interactions (Kanakavel 1976) and carbonyl + lithium interactions (Murthy and Ranganathan 1982b).

Torok and Pulay (1978) in their recent calculations compared the results from different semiempirical methods and concluded that CNDO and INDO produce almost identical results. Nelander and Ribbegard (1974) point out that MINDO stretching force constants for linear molecules are close to the experimental values. Kozumutza and Pulay (1975), Kozumutza (1976), Gleghorn and McConkey (1975) and Marmer *et al* (1979) have also used semiempirical MO methods to evaluate force fields with varying degrees of success.

Another method for the evaluation of force fields using MO calculations has been developed by Swanson and coworkers (1978a, b; Rafalko *et al* 1979). It is based on MNDO MO calculations and limited vibrational data. This approach involves molecular orbital constraint of interaction constants and is called MOCIC. Expressed in the language of compliance constants the method has been applied to a series of molecules.

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