

Calculation of Optimum Geometries and Force Fields by the CNDO/Force Method

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CNDO/Force calculations have been performed on a series of molecules, H_2CO , F_2CO , CF_4 , CHF_3 , CH_2F_2 and CH_3F . The optimum geometries and force fields are reported. It is found that the method can successfully predict the geometries of polyatomic molecules. The bending force constants and interaction force constants are, in general, comparable with experimental values both with respect to sign and magnitude. The stretching force constants have higher values than the experimental force constants. However, the trend in stretching force constants of a series of molecules is comparable with that of the corresponding experimental values.

Key words: CNDO force method - Optimum geometry and force fields

1. Introduction

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

$$F_{ij} = \left(\frac{\partial^2 E}{\partial q_i \partial q_j} \right)_e$$

where E is the total energy of the molecule and q_i, q_j are the various internal coordinates. The different methods for the evaluation of these force constants include double numerical differentiation [1-5], double analytical differentiation [6-12] and analytical differentiation followed by numerical differentiation [13-17]. In the method of double numerical differentiation a systematic variation of nuclear configuration is accompanied by SCF-MO calculations for each configuration. The energy hypersurface built in this way is used for the evaluation of the force constants by numerical differentiation to second order. In the method of double analytical differentiation, 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 wave functions. In the third method developed by Pulay *et al.* [13-17] the energy is first differentiated analytically and the corresponding force hypersurfaces are built.

The force constants are then evaluated by numerical differentiation to first order. In this series of papers, Pulay *et al.* have shown that their method (also called force method) has certain advantages over the other two methods discussed above. The double numerical differentiation is not economical because the wavefunctions must be computed for a number of nuclear configurations and may 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 in a symmetry species. The method makes possible quick iterative procedure to determine the equilibrium configuration. Semiempirical methods like CNDO/2 have also been used [18–21] for the determination of force fields using the energy hypersurface (double numerical differentiation) method. In a recent paper by Pulay *et al.* [22], it was shown that the semiempirical quantum chemical calculations on molecular geometry and force constants by the energy hypersurface method becomes 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. Recent CNDO/Force calculations by Pulay *et al.* show that the signs and magnitude of stretch-bend interaction constants agree with the experimental values and that the stretching force constants are twice as high as the experimental force constants. We have now calculated force fields for a series of molecules employing the CNDO/Force method with a view to understanding these force fields in comparison with the experimental force fields and to study the trends or relationship between the experimental and calculated values. The various molecules considered include H_2CO , F_2CO , CF_4 , CHF_3 , CH_2F_2 and CH_3F . The optimized geometries and the force fields are being reported.

2. Results and Discussion

As discussed by Pulay [22] the exact 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 (usually the experimental geometry if known). Since these 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 computed 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. The CNDO/Force calculations were performed by slightly modifying¹ the procedure reported by Pulay *et al.* [13] and using a modified form of the computer program of Pople *et al.* [18]. Calculations were carried out on an IBM 370/155 Computer. When the energy is minimized, the norm of the force keeps decreasing. From our experience we find that when the norm of the force is less than 0.001 further iterations do not change the energy and

¹ See Appendix.

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

H ₂ CO			F ₂ CO		
	Calc.	Exp. [23]		Calc.	Exp. [24]
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	FCF	109.8	107.6

geometry to any considerable extent. The experimental and optimized geometries are given in Tables 1 and 2.

The optimum geometries for H₂CO and F₂CO have been compared with the microwave data obtained by Tokagi and Oka [23] and Carpenter [24] respectively. The experimental geometries for CH₃F given in Table 2 have been taken from microwave studies by Anderson *et al.* [25]; for CF₄, the electron diffraction studies of Livingston *et al.* [26]; and for CHF₃ the experimental geometry of Ghosh *et al.* [27] have been given. For CH₂F₂, Lide [28] and Hirota *et al.* [29] have reported the geometry from the microwave data. The agreement between the calculated and experimental values is found to be uniformly good. The increasing trend in CF bond distances from CF₄ to CH₃F observed in experimental values is found to have been maintained in the calculated values also.

In our calculations the Cartesian forces were calculated for the equilibrium geometry of the molecule. The molecule was 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) were thus found for possible configurations representing different modes of vibration. The displacements given for stretching and bending internal coordinates were ± 0.01 Å and $\pm 1^\circ$ respectively. For each deformed configuration the symmetry forces (ϕ_i) were calculated by using suitable transformations. The symmetry force constants F_{ij} were obtained as the ratios of $\Delta\phi_i$ and ΔS_j . The GMAT program of Schachtschneider [30] was used to compute the B matrices. The symmetry coordinates used were similar to those given in the literature [31-34].

In Tables 3 and 4 the symmetry force constants for H₂CO, F₂CO, CF₄, CHF₃, CH₂F₂ and CH₃F obtained by the CNDO/Force method are compared with the experimental force fields. In a recent publication of Pulay *et al.* [17] the symmetry force field for H₂CO was obtained by an *ab initio* force method. Recently Duncan *et al.* [31] determined the force field of H₂CO by using the newly available isotopic frequency shift, centrifugal distortion and Coriolis coupling data. For F₂CO the UBFF force field of Overend *et al.* [42] is based on the vibrational frequencies and force field of Mirri *et al.* [43] is based on centrifugal distortion data. In a recent publication of McKean *et al.* [44] the force field was determined from vibrational frequencies, isotopic frequency shifts obtained in the argon matrix, Coriolis coupling and centrifugal distortion coefficients. Also the inertia defects were used to check the force field. In the case of CF₄ the experimental force field obtained by Mills *et al.* [45] is based on vibrational frequencies and Coriolis constants. Another force field for F₂ species calculated by Chalmers *et al.* [46]

Table 2. Comparison of CNDO optimized structural parameters with experimental structural parameters (distances in Å and angles in degrees)

Bond Distance and Bond Angles	CF ₄		CHF ₃		CH ₂ F ₂		CH ₃ F	
	Calc.	Exp. [26]	Calc.	Exp. [27]	Calc.	Exp. [29]	Calc.	Exp. [25]
r _{C-F}	1.3378	1.32	1.342	1.332	1.3431	1.3574	1.3457	1.386
r _{C-H}	—	—	1.1234	1.098	1.1225	1.0934	1.1184	1.095
∠FCF	109.5	109.8	107.58	108.8	106.77	108.31	—	—
∠HCH	—	—	—	—	110.67	113.66	109.6	111.32
∠HCF	—	—	111.28	110.13	—	—	109.3	108.6

Table 3. Comparison of experimental and calculated symmetry force fields of X₂CO (X = H, F) (mdyn/Å, mdyn and mdyn · Å for the stretching, stretching/bending and bending force constants, respectively)

Force Constants	Assignments	H ₂ CO		F ₂ CO			
		CNDO/Force Calc.	Exp. [31]	Ab initio [17]	CNDO/Force Calc.	Exp. [44]	Exp. [44]
F ₁₁	CX ₂ 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	CX/CX ₂ 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	CO/CX ₂ def.	-0.48	-0.408	-0.414	-0.443	-0.331	-0.488
F ₃₃	CX ₂ 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	CX ₂ a. str.	11.60	4.852	4.909	23.52	5.867	5.718
F ₅₆	CX/CX ₂ rock.	0.212	0.171	0.157	0.619	0.688	0.635
F ₆₆	CX ₂ rock.	0.82	0.833	0.946	0.902	1.117	1.146

The experimental force fields given are comparatively more recent and complete. Other force fields are available in Refs. [35-43]. s., str., def., wag, a. and rock designate symmetric, stretching, deformation, wagging, asymmetric and rocking respectively.

Table 4. Comparison of experimental and calculated symmetry force fields of CF₄, CHF₃, CH₂F₂ and CH₃F (in mdyn/Å, mdyn and mdyn · Å for the stretching, stretching/bending and bending force constants, respectively)

Molecule	Force Constant	Assignment	Calc. CNDO/Force	Exp.		
CF ₄	F_{11}	CF s. str.	27.0	9.25 ^a		
	F_{22}	CF ₄ tw.	0.9372	1.08		
	F_{33}	CF a. str.	23.08	6.22		
	F_{34}	CF/CF ₄ def.	-0.93	-1.108		
	F_{44}	CF ₄ a. def.	1.501	1.78		
CHF ₃	F_{11}	CF s. str.	25.946	8.669 ^b		
	F_{12}	CH/CF ₃ def.	0.53	0.490		
	F_{13}	CF/CH str.	0.766	1.134		
	F_{22}	CF ₃ def.	1.49	1.53		
	F_{23}	CH/CF ₃ def.	-0.400	-0.526		
	F_{33}	CH str.	11.49	5.340		
	F_{44}	CF a. str.	21.268	5.303		
	F_{45}	CF/CF ₃ a. def.	-0.653	-0.592		
	F_{46}	CF/CF ₃ rock.	0.550	0.510		
	F_{55}	CF ₃ a. def.	1.47	1.41		
	F_{56}	CF ₃ def./CF ₃ rock.	0.261	-0.048		
	F_{66}	CF ₃ rock.	0.862	0.813		
CH ₂ F ₂	F_{11}	CH ₂ s. str.	11.755	4.873 ^c		
	F_{22}	CF ₂ s. str.	25.13	7.075		
	F_{33}	CH ₂ s. def.	0.943	0.590		
	F_{44}	CF ₂ s. def.	1.75	1.429		
	F_{55}	CH ₂ tw.	0.602	0.740		
	F_{66}	CH ₂ a. str.	11.421	4.904		
	F_{77}	CH ₂ rock.	0.939	1.137		
	F_{88}	CF ₂ a. str.	22.85	4.904		
	F_{99}	CH ₂ wag.	0.904	0.882		
	F_{12}	CH ₂ str./CF ₂ str.	0.940	1.321		
	F_{13}	CH ₂ str./CH ₂ def.	0.113	-0.267		
	F_{14}	CH ₂ str./CF ₂ def.	-0.201	-0.352		
	F_{23}	CF ₂ str./CH ₂ def.	-0.442	-0.308		
	F_{24}	CF ₂ str./CF ₂ def.	0.477	0.584		
	F_{34}	CH ₂ def./CF ₂ def.	0.129	0.087		
	F_{67}	CH ₂ a. str./CH ₂ rock.	0.350	0.298		
	F_{89}	CF ₂ a. str./CH ₂ wag.	0.792	0.769		
	CH ₃ F	F_{11}	CH s. str.	12.205	5.368 ^d	5.38 ^e
F_{12}		CH/CH ₃ def.	0.132	-0.109	-0.065	0.197
F_{13}		CH/CF str.	0.854	0.382	0.320	0.200
F_{22}		CH ₃ s. def.	0.902	0.752	0.747	0.735
F_{23}		CH ₃ def./CF str.	-0.688	-0.687	-0.657	-0.676
F_{33}		CF str.	24.06	5.764	5.740	5.774
CH ₃ F		F_{44}	CH a. str.	11.126	5.433	5.420
	F_{45}	CH/CH ₃ def.	-0.123	-0.131	-0.113	-0.118
	F_{46}	CH/CH ₃ rock.	0.294	0.359	0.240	0.2628
	F_{55}	CH ₃ a. def.	0.688	0.602	0.592	0.595
	F_{56}	CH ₃ def./CH ₃ rock.	0.247	-0.078	-0.063	-0.088
	F_{66}	CH ₃ rock.	1.026	0.902	0.906	0.908

s., str., def., a., rock., tw., wag. designate symmetric, stretching, deformation, asymmetric, rocking, twisting and wagging respectively.

^aRef. [45]. ^bRef. [50]. ^cRef. [34]. ^dRef. [55]. ^eRef. [54]. ^fRef. [56].

from isotopic vibrational frequency shift ($^{12}\text{CF}_4$ and $^{13}\text{CF}_4$), vibrational frequencies, and Coriolis constants is comparable with the experimental force field given in Table 4. The modified force field for CHF_3 of Galasso *et al.* [47] was determined from vibrational frequencies. The force field of E species was calculated by Hoskins [48] using vibrational frequencies and Coriolis constants data. More recently Ruoff *et al.* [49] have determined the force field from the vibrational frequencies, Coriolis coupling constants, and centrifugal distortion data. They concluded that the E species force field was more accurate. Romola D'Cunha [50] obtained two sets of force field for CHF_3 . The set I force field is compared with CNDO/Force values. The experimental force field for CH_2F_2 calculated from vibrational frequencies and Coriolis coupling constants obtained by Shimanouchi *et al.* [34] is given for comparison. A similar force field for asymmetric vibration has been reported by Dennen [51] and is not included in the table for the sake of brevity. The modified valence force fields for CH_3F of Pace [52] and Edgell *et al.* [53] do not agree with the general force field [54] since these calculations are based on vibrational frequencies only. Overend *et al.* [57] obtained the Urey-Bradley force field from vibrational frequencies. The Coriolis coupling constants and centrifugal distortion constants calculated from their force constants are in large error with the experimental values [54]. The force field obtained by Mills *et al.* [54], Russel *et al.* [55], and Barnett [56] were based on vibrational frequencies, Coriolis coupling and centrifugal distortion data. The force fields of Mills *et al.* [54], Russel *et al.* [55] and Barnett [56] are more reliable and compared with our values.

In all the cases considered it is found that the stretching force constants obtained by CNDO/Force are more than twice the experimental values, and the bending force constants are found to be comparable with experimental force constants. The stretch-stretch interaction force constants are slightly different in magnitude in comparison with experimental values. The 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 [58] and Linnett [59] based on orbital following arguments. The value of F_{13} in H_2CO is in accordance with HOFF constraint, $F_{13} = 1/(\sqrt{3})F_{56}$. The larger value obtained for F_{12} for H_2CO in comparison with other interaction and bending force constants by CNDO/Force is in agreement with the observation made by Duncan *et al.* [31]. This was explained on the basis of isotopic shift and centrifugal distortion. The bend-bend interactions are either constrained to have zero values in the force field calculation available in the literature or are found to have very small values. The bend-bend interaction force constants for CHF_3 and CH_3F obtained with the aid of a CNDO/Force calculation are found to be of the order 0.2 to 0.3.

The stretching force constants, though found to have higher values than the experimental values, seem to have some interesting trends. As can be noticed from Table 5, 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 constant for symmetric C-H stretching vibration are found to increase. A roughly similar trend is found in the experimental force constants. 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

Table 5. Comparison of calculated and experimental force constants for stretching vibrations in a series of molecules (in mdyne/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)	CH_4 (F_2)	12.08	5.383
	CH_2F_2 (B_2)	11.421	4.904
	CH_3F (E)	11.126	5.433
ν_{CF} (asym)	CF_4 (F_2)	23.08	6.220
	CH_2F_2 (B_2)	22.85	5.111
	CHF_3 (E)	21.265	5.303

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 number of fluorine and hydrogen atoms cannot be found for the series of molecules considered. For example, the force constant for asymmetric stretching vibration, ν_{CF} , for CH_2F_2 is found to lie between those of CF_4 and CHF_3 . Similarly the CH asymmetric stretching force constant for CH_2F_2 is found to lie between the force constants of CH_3F and CH_4 . This can probably be attributed to the fact that ν_{CF} (asymmetric) as well as $\nu_{\text{C-H}}$ (asymmetric) belong to three different symmetry species (B_2 for CH_2F_2 , E for CHF_3 and F_2 for CF_4 and CH_4). Plots (Fig. 1) of experimental and calculated force constants for 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. Conclusions

From the above studies it can be seen that the force field obtained by the CNDO/Force method can be helpful in various calculations. The facts that the bending force constants are comparable with experimental values, and the signs and in some cases the magnitudes of interaction force constants obtained by the CNDO/Force method are comparable with experimental values and theoretical predictions of the hybrid orbital force field method of Mills [58] and the orbital valence force field of Linnett [59], show that these calculations can be helpful in the determination of the unique force field of a polyatomic molecule when combined with conventional force field calculations from vibrational frequencies, Coriolis couplings and centrifugal distortions. Though the stretching force constants calculated using the CNDO/Force method are high in comparison with experimental values, they are found to have trends similar to experimental

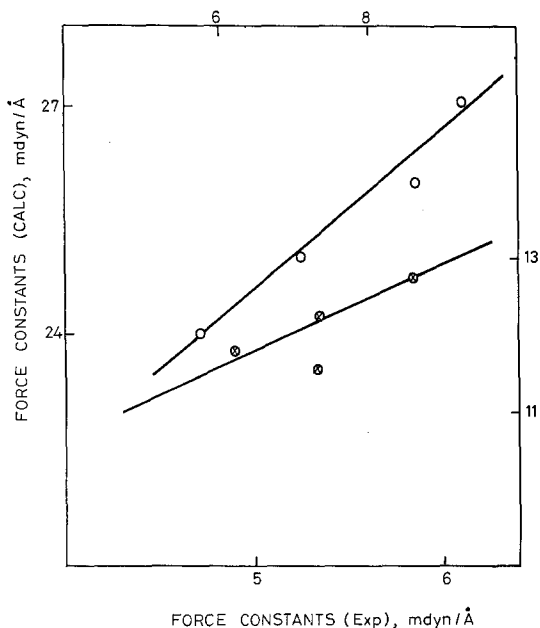


Fig. 1. Plot of calculated force constants *vs.* experimental force constants for a series of molecules (CF_4 , CHF_3 , CH_2F_2 , CH_3F , CH_4), $\nu_{\text{C-H}}(\text{sym})$ \circ , $\nu_{\text{C-F}}(\text{sym})$ \circ . For $\nu_{\text{C-F}}$ the *X* and *Y* coordinates correspond to upper and LHS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

force constants when compared for a particular mode of vibration in a series of molecules. The symmetric and asymmetric stretching force constants in the same molecule are also found to have trends similar to the experimental force constants. This can help in the prediction of positions of vibrational bands for symmetric and asymmetric modes of vibrations, conformational analysis and the study of molecular interactions. Further, similar trends found in the calculated and experimental stretching force constants in a homologous series of molecules indicate that some attempt to improve the parameterization in CNDO calculations may lead to the successful determination of force fields of polyatomic molecules. Further studies along these lines are in progress and results will be communicated shortly elsewhere.

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Appendix

The CNDO total energy is given by

$$E = \sum_A E_A + \sum_{A < B} E_{AB} \quad (1)$$

Because the one-atom contributions do not explicitly depend on the nuclear coordinates the force on atom A can be written as

$$\frac{\partial E}{\partial x_A} = \sum_{A < B} \frac{\partial E_{AB}}{\partial x_A} \quad (2)$$

The diatomic energy contribution E_{AB} is given as

$$E_{AB} = \sum_{\mu}^A \sum_{\nu}^B (2P_{\mu\nu}\beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}^2\gamma_{AB}) \\ + (P_{AA}P_{BB} - P_{AA}Z_B - P_{BB}Z_A)\gamma_{AB} + Z_A Z_B / R_{AB} \quad (3)$$

All the symbols have their usual meaning [18].

To compute the forces acting on the atoms, the derivatives of the energy function (Eq. (3)) with respect to Cartesian nuclear displacements have to be determined. The differentiation of Eq. (3) requires the evaluation of the derivative of the overlap integrals $S_{\mu\nu}$ and the Coulomb integrals γ_{AB} . Closed expressions for evaluating these derivatives for a basis set containing only $2s$ and $2p$ functions have been given by Panciř [60]. Since we were interested in studying molecules containing second row atoms also, we preferred to adopt a slightly different procedure which requires little programming effort but may take up a trifle more computer time.

In subroutine INTGRL [18], the derivative with respect to internuclear distance R_{AB} is simultaneously evaluated with the diatomic overlap integral. The function SS has been modified to a subroutine to yield the values of the reduced overlap integral and its derivative. The evaluation of the derivative of the Coulomb integral with respect to internuclear distance is also straightforward.

$$\frac{dS_{ab}}{dR_{AB}} = (n_a + n_b + 1) \frac{S_{ab}}{R} + N_a N_b \left(\frac{R}{2}\right)^{(n_a + n_b + 1)} \frac{ds(n_a, l_a, m, n_b, l_b, \alpha, \beta)}{dR}$$

$$\frac{ds}{dR} = D(l_a, l_b, m) \sum_{i,j} Y_{ij\lambda}(-\frac{1}{2}) \{ (\zeta_1 + \zeta_2) A_{i+1} [\frac{1}{2}(\alpha + \beta)] B_j [\frac{1}{2}(\alpha - \beta)] \\ + (\zeta_1 - \zeta_2) A_i [\frac{1}{2}(\alpha + \beta)] B_{j+1} [\frac{1}{2}(\alpha - \beta)] \}$$

$$\frac{d\gamma_{AB}}{dR_{AB}} = \frac{(2\zeta_b)^{2n_b+1}}{(2n_b)!} \left[\text{DTERM1} + \sum_{l=1}^{2n_a} \text{DTERM2} \right]$$

where

$$\text{DTERM1} = n_b \left(\frac{R}{2}\right)^{2n_b-1} s(0, 0, 0, 2n_b - 1, 0, 0, 2\zeta_b R) \\ + \left(\frac{R}{2}\right)^{2n_b} \frac{ds}{dR}(0, 0, 0, 2n_b - 1, 0, 0, 2\zeta_b R)$$

$$\begin{aligned}
 \text{DTERM2} &= \frac{(2n_a - l + 2n_b)l(2\xi_a)^{2n_a - l} \left(\frac{R}{2}\right)^{2n_a - l + 2n_b}}{R(2n_a - l)! (2n_a)} \\
 &\quad s(2n_a - 1, 0, 0, 2n_b - 1, 0, 2\xi_a R, 2\xi_b R) \\
 &\quad + \frac{l(2\xi_a)^{2n_a - l} \left(\frac{R}{2}\right)^{2n_a - l + 2n_b}}{(2n_a - l)! (2n_a)} \\
 \frac{ds}{dR} &(2n_a - l, 0, 0, 2n_b - 1, 0, 2\xi_a R, 2\xi_b R)
 \end{aligned}$$

After completing the SCF calculation the components of the forces on all the atoms are calculated. The evaluation of the derivative of the overlap integral over the molecular basis from that over the diatomic basis requires the transformation matrix T and its derivatives. The subroutine HARMTR has been suitably augmented to handle the calculation of the derivatives of the transformation matrix. The calculation of the forces involves negligible computer time and practically no additional storage requirements.

Further, the Cartesian forces² obtained for the optimized geometry are converted to symmetry or internal forces by making corresponding transformations. Pulay *et al.* [13] pointed out some difficulty in the calculation of internal forces from the Cartesian forces and recommended the use of a modified m matrix in the expression,

$$B^{+^{-1}} = (BmB^+)^{-1} Bm \quad (4)$$

where $B^{+^{-1}}$ is the matrix that transforms Cartesian to internal forces, m is a $3N$ by $3N$ matrix. In these calculations m was not taken as an inverse mass matrix, M^{-1} , but was replaced by a diagonal matrix with zeros in the diagonal for those Cartesians which have to be kept constant and with arbitrary non-zero diagonal elements, usually 1 elsewhere. This was suggested to avoid the appearance of a singular BmB^+ matrix obtained if m is taken as the inverse mass matrix due to which the inversion of a BmB^+ matrix becomes difficult. We found that such a problem does not arise if instead of a transformation from Cartesian to internal forces, the transformation of Cartesian to symmetry forces is preferred. Accordingly the symmetry force vector ϕ_s is obtained as given below:

$$\phi_s = (B^{+^{-1}})_s f \quad (5)$$

where $(B^{+^{-1}})_s = (B_s M^{-1} B_s^+)^{-1} B_s M^{-1}$ and f is the vector of Cartesian forces, B_s represents the symmetrized B matrix ($B_s = UB$).

The modified CNDO/2 program to suit the CNDO/Force calculations can be had from the authors on request.

² If X , R , S represent the Cartesian, internal and symmetry coordinates respectively, the familiar relations between these coordinates can be given as

$$R = BX; \quad S = UR$$

The inverse kinetic energy matrix G is represented by

$$G^{-1} = (BM^{-1} B^+)^{-1}$$

where M^{-1} represents the inverse mass matrix.

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