# Semiempirical Calculation of Harmonic Force Constants: CNDO/2 and MINDO/2 Study of $C_2H_6$, $C_2H_4$ and $C_2H_2$

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The complete quadratic force fields of ethane, ethylene and acetylene have been calculated from CNDO/2 and MINDO/2 wavefunctions by the force method. Agreement with experiment is satisfactory for both methods. In the CNDO method the stretching force constants must be scaled empirically to obtain realistic values. It is particularly significant that stretching-deformation and deformation-deformation coupling force constants are correctly reproduced by the CNDO method and with the exception of the rocking-rocking couplings, also by the MINDO method. It is concluded that such calculations may usefully contribute to the determination of force fields.

Key words: Ethane – Ethylene – Acetylene

## 1. Introduction

Recent *ab initio* calculations [1, 2] have shown that harmonic force constants can be obtained from near Hartree-Fock wavefunctions more accurately than thought so far. There is little hope, however, that *ab initio* calculations could be extended to large systems. In this paper we investigate whether semiempirical Hartree-Fock-type calculations can yield useful informations on the harmonic part of molecular force fields. We shall pay special attention to the coupling or interaction force constants. These constants are less well known experimentally than the diagonal ones, and even crude approximations to them (e.g. the knowledge of the sign and the order of magnitude) can contribute significantly to the solution of experimental problems like band assignments. In spite of this almost all previous semiempirical force constant calculations have been limited to diagonal force constants, probably because of the numerical problems associated with the calculation of coupling constants from energy hyper-surfaces.

We have calculated the quadratic force constants of seven molecules: $H_2O$, $CH_4$ [3], $NH_3$, $C_2H_6$, $C_2H_4$, $C_2H_2$, and $H_2CO$ by two widely used

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semiempirical methods, CNDO/2 [4, 5] and MINDO/2 [6, 7]. Recently Dewar and Metiu [8] have published a complete MINDO/2 force field for ethane. Our values do not agree with theirs; we shall return to a discussion of the results.

## 2. Calculations

We have determined the force constants by the force method [9]. This method saves much computer time and is also numerically accurate. Our force program is attached to the CNDO/2 and MINDO/2 programs (for CNDO see [3]; for MINDO the same procedure, parameters taken from Refs. [6, 7]) and calculated the forces (the exact derivatives of the total SCF energy with respect to the nuclear coordinates) automatically at the end of the SCF iteration. The Cartesian forces thus obtained are then transformed to a specified set of internal valence or symmetry coordinates. Force constants are calculated as the numerical derivatives of the internal forces with respect to internal coordinates: $F_{ij} = -\Delta\varphi_i/\Delta q_j$. The finite distortions of the molecule from the reference geometry, $\frac{1}{2}\Delta q_j$, usually amount $\pm 0.02$ Å for bond stretching coordinates and $\pm 2°$ for deformations. We have checked our procedure by comparing $F_{ij}$ with $F_{ji} = -\Delta\varphi_j/\Delta q_i$, the two values agree within 0.001 mdyn/Å. Force programs for geometry optimization have been reported for the CNDO/2 [10–13] and MINDO/2 methods [14].

Force constants may be evaluated either at the calculated or at the experimental molecular geometry. Although the former may seem to be the more consistent procedure, the latter has many advantages. The core-core repulsion makes dominant contribution to most force constants and this contribution is obtained more exactly if the experimental geometry is used as reference geometry [15]. We have determined complete sets of force constants both at the experimental and calculated geometries. For the MINDO calculations, a third geometry was also tried, the corrected experimental geometry (CH-bond lengths increased by 0.1 Å, for a reason see Ref. [6]). As the calculated force constants at the three geometries do not differ significantly, only the results obtained at the corrected experimental geometry are given in the tables.

It is well known that the CNDO/2 method greatly overestimates the diagonal stretching force constants. We have corrected empirically for this deficiency. In order to preserve invariance against transformations of the internal coordinates, the following correction was applied: all stretch-stretch force constants are multiplied by a factor $\alpha^2$, all stretch-bend ones by a factor $\alpha$. The value of $\alpha$ was determined to give the best agreement with the experimental diagonal stretching force constants in the above seven molecules, our final value is 0.617. Only the corrected CNDO/2 force constants at the experimental geometry are shown in the tables.

The experimental and calculated molecular geometries of the title compounds are given in Table 1. The calculated geometries have been determined by the force relaxation method [9]. This method converges quickly and the final geometry is sharply characterized by vanishing force on the atoms.

Table 1. Calculated and experimental molecular geometries (in $\text{Å} = 10^{-10}$ m and degree units)

| Molecule | | CNDO/2 | MINDO/2 | Exp.[a] |
|---|---|---|---|---|
| $C_2H_6$ | CC | 1.456 | 1.480 | 1.536 |
| | CH | 1.120 | 1.107 | 1.091 |
| | ⊀HCC | 111.85 | 113.38 | 109.62 |
| $C_2H_4$ | CC | 1.310 | 1.310 | 1.339 |
| | CH | 1.113 | 1.095 | 1.086 |
| | ⊀HCC | 124.12 | 123.63 | 121.35 |
| $C_2H_2$ | CC | 1.197 | 1.185 | 1.208 |
| | CH | 1.093 | 1.060 | 1.058 |

[a] G. Herzberg: Electronic spectra and electronic structure of polyatomic molecules. New York: Van Nostrand 1966.

## 3. Results

Our results are presented as force constants. This makes it possible to separate correctly the effects of physically different constants (e.g. diagonal or coupling and stretching or bending ones). The calculated force constants are compared to the best available experimental estimates, and also to *ab initio* results. This latter comparison is necessary because the smaller coupling constants are probably less exactly known from experiment than from *ab initio* calculations.

Force constants are presented in semi-symmetry coordinate representation defined in Table 2 [16]. These coordinates proved very advantageous as a compromise between full symmetry and valence coordinates. The semi-symmetry force constants of $C_2H_6$, $C_2H_4$, and $C_2H_2$ are given in Tables 3–5, respectively. Stretch-stretch force constants are given in mdyn/Å $(= 10^2\,\text{N/m})$, stretch-deformation ones in mdyn/rad $(= 10^{-8}\,\text{N/rad})$ and deformation-deformation ones in mdynÅ/rad$^2$ $(= 10^{-18}\,\text{J/rad}^2)$.

The physically different types of force constants are discussed separately below.

Table 2. Definition of the semi-symmetry coordinates[a]

| Coordinates<br>R | Ethane<br>R | Ethylene<br>R | Acetylene<br>R |
|---|---|---|---|
| symm.r | $3^{-\frac{1}{2}}(r_1 + r_2 + r_3)$ | $2^{-\frac{1}{2}}(r_1 + r_2)$ | $r_1$ |
| symm.bend | $6^{-\frac{1}{2}}(\beta_1 + \beta_2 + \beta_3 - \alpha_1 - \alpha_2 - \alpha_3)$ | $6^{-\frac{1}{2}}(\beta_1 + \beta_2 - 2\alpha_1)$ | |
| rock | $6^{-\frac{1}{2}}(2\beta_1 - \beta_2 - \beta_3)$ | $2^{-\frac{1}{2}}(\beta_1 - \beta_2)$ | |
| symm.r' | $3^{-\frac{1}{2}}(r_4 + r_5 + r_6)$ | $2^{-\frac{1}{2}}(r_3 + r_4)$ | |
| symm.bend' | $6^{-\frac{1}{2}}(\beta_4 + \beta_5 + \beta_6 - \alpha_4 - \alpha_5 - \alpha_6)$ | $6^{-\frac{1}{2}}(\beta_3 + \beta_4 - 2\alpha_2)$ | |
| rock' | $6^{-\frac{1}{2}}(2\beta_4 - \beta_5 - \beta_6)$ | $2^{-\frac{1}{2}}(\beta_4 - \beta_3)$ | |
| asymm.r | $6^{-\frac{1}{2}}(2r_1 - r_2 - r_3)$ | $2^{-\frac{1}{2}}(r_1 - r_2)$ | $r_2$ |
| asymm.bend | $6^{-\frac{1}{2}}(2\alpha_1 - \alpha_2 - \alpha_3)$ | | |
| asymm.r' | $6^{-\frac{1}{2}}(2r_4 - r_5 - r_6)$ | $2^{-\frac{1}{2}}(r_4 - r_3)$ | |
| asymm.bend' | $6^{-\frac{1}{2}}(2\alpha_4 - \alpha_5 - \alpha_6)$ | | |
| wagging | | $\delta_1$ | $\varphi_1$ |
| wagging' | | $\delta_2$ | $\varphi_2$ |
| torsion | | $\tau$ | |

[a] All notations see Ref. [17], Table 2 and Fig. 1.

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Table 3. Force constants of ethane in semi-symmetry coordinate representation[a]

| Force constants | CNDO/2 | MINDO/2 | Ab initio[b] | Exp.[c] |
|---|---|---|---|---|
| R | 4.67 | 5.10 | 5.073 | 4.450 |
| symm.r | 5.27 | 5.91 | 5.678 | 4.900 |
| asymm.r | 5.05 | 5.47 | 5.543 | 4.764 |
| R/symm.r | +0.212 | +0.444 | +0.140 | 0[d] |
| symm.r/symm.r' | +0.005 | +0.065 | +0.007 | −0.007 |
| asymm.r/asymm.r' | +0.002 | −0.005 | −0.035 | −0.050 |
| R/symm.bend | +0.283 | +0.357 | +0.390 | +0.346 |
| symm.r/symm.bend | −0.136 | −0.091 | −0.123 | −0.050 |
| symm.r/symm.bend' | +0.021 | +0.057 | +0.024 | 0[d] |
| asymm.r/asymm.bend | −0.172 | −0.157 | −0.220 | −0.076 |
| asymm.r/asymm.bend' | −0.004 | 0.000 | −0.009 | 0[d] |
| asymm.r/rock | +0.160 | +0.192 | +0.206 | +0.076 |
| asymm.r/rock' | +0.040 | +0.047 | +0.078 | 0[d] |
| symm.bend | 0.811 | 0.522 | 0.756 | 0.606 |
| asymm.bend | 0.769 | 0.368 | 0.688 | 0.560 |
| rock | 0.809 | 0.529 | 0.850 | 0.682 |
| symm.bend/symm.bend' | +0.043 | +0.039 | +0.033 | +0.033 |
| asymm.bend/asymm.bend' | −0.007 | −0.008 | −0.005 | −0.005 |
| rock/rock' | +0.142 | +0.022 | +0.193 | +0.139 |
| asymm.bend/rock | −0.058 | −0.057 | −0.008 | +0.007 |
| asymm.bend/rock' | +0.013 | +0.023 | +0.004 | +0.004 |

[a] The torsion force constant has not been calculated.
[b] Ref. [17].
[c] Ref. [16].
[d] Constrained value.

Table 4. Force constants of ethylene in semi-symmetry coordinate representation

| Force constants | CNDO/2 | MINDO/2 | Ab initio[a] | Exp.[b] |
|---|---|---|---|---|
| R | 8.75 | 9.62 | 9.939 | 9.395 |
| symm.r | 5.22 | 5.82 | 5.943 | 5.620 |
| asymm.r | 5.08 | 5.53 | 5.879 | 5.575 |
| R/symm.r | +0.248 | +0.461 | +0.136 | +0.257 |
| symm.r/symm.r' | +0.008 | +0.062 | +0.007 | +0.017 |
| asymm.r/asymm.r' | +0.007 | +0.008 | −0.025 | +0.082 |
| R/symm.bend | +0.244 | +0.266 | +0.242 | +0.222 |
| symm.r/symm.bend | −0.095 | −0.058 | −0.093 | −0.018 |
| symm.r/symm.bend' | +0.015 | +0.039 | +0.020 | +0.074 |
| asymm.r/rock | +0.198 | +0.221 | +0.161 | +0.111 |
| asymm.r/rock' | +0.049 | +0.061 | +0.065 | +0.285 |
| symm.bend | 0.579 | 0.332 | 0.556 | 0.470 |
| rock | 0.599 | 0.410 | 0.628 | 0.572 |
| symm.bend/symm.bend' | +0.027 | +0.020 | +0.024 | +0.018 |
| rock/rock' | +0.099 | +0.004 | +0.104 | +0.087 |
| wagging | 0.404 | 0.220 | 0.322 | 0.243 |
| wagging/wagging' | −0.070 | −0.061 | −0.050 | −0.039 |
| torsion | 0.204 | 0.077 | 0.163 | 0.136 |

[a] Ref. [1].
[b] Ref. [19].

Table 5. Force constants of acetylene in semi-symmetry coordinate representation

| Force constants | CNDO/2 | MINDO/2 | Ab initio[a] | Exp.[b] |
|---|---|---|---|---|
| R | 13.18 | 18.29 | 18.02 | 15.953 |
| symm.r | 5.72 | 6.33 | 6.977 | 6.391 |
| R/symm.r | + 0.158 | + 0.363 | − 0.134 | − 0.098 |
| symm.r/symm.r' | + 0.007 | + 0.035 | + 0.007 | − 0.010 |
| wagging | 0.669 | 0.267 | 0.367 | 0.258 |
| wagging/wagging' | + 0.187 | + 0.165 | + 0.126 | + 0.100 |

[a] Ref. [17].
[b] Ref. [20].

### 3.1. Diagonal Stretching Constants

Calculation of these constants is generally not very important because they can be determined reliably from vibrational spectra, and it is unlikely that quantum chemical calculations can improve upon the experimental values. Both the MINDO and the corrected CNDO results are in moderate agreement with experiment.

### 3.2. Stretch-Stretch Couplings

Agreement for this type of force constants is unsatisfactory: the corrected CNDO and also the MINDO calculations yield always positive values, and they tend to overestimate the coupling. Fortunately these constants are nearly in every case small relatively to the diagonal ones, so they are not of great importance with the exception of conjugated systems.

### 3.3. Stretch-Deformation Couplings

Agreement for this important class of force constants is good by both methods, as expected [9]. The results of the MINDO/2 and the corrected CNDO/2 method do not differ significantly (see Tables 3–5).

### 3.4. Diagonal Deformation Constants

Results for these constants are too high in the CNDO/2 and too low in the MINDO/2 method. The important point is, however, how well the relative magnitude of the force constants could be predicted. In this respect both methods perform moderately. E.g. CNDO overestimates the symmetric bending force constants both in ethane and ethylene relatively to the other bendings, as well as MINDO does in the case of ethane. Both methods, particularly CNDO, greatly overestimate the force constants of the out of plane deformations in the ethylene and acetylene relatively to other deformations. As the *ab initio* results also show this phenomenon [17] we suspect that it is not due to specific approximations of the semiempirical methods, but is caused by correlation effects. In $\pi$ systems, lowlying configurations of $\pi$ symmetry can mix to the Hartree-Fock determinant only in nonplanar or nonlinear geometry. This effect lowers the experimental force constant relatively to the one-determinant value.

Table 6. Calculated and experimental vibrational frequencies (in $cm^{-1}$)

| Molecules | Repr. | CNDO/2 | MINDO/2 | Exp.[a] |
|---|---|---|---|---|
| $C_2H_6$ | $A_{1g}$ | 1021 | 1056 | 995 |
|  |  | 1686 | 1328 | 1400 |
|  |  | 3003 | 3189 | 2920 |
|  | $A_{2u}$ | 1623 | 1287 | 1379 |
|  |  | 3010 | 3178 | 2910 |
|  | $E_u$ | 936 | 816 | 821 |
|  |  | 1714 | 1172 | 1472 |
|  |  | 3065 | 3193 | 2985 |
|  | $E_g$ | 1332 | 1010 | 1190 |
|  |  | 1704 | 1168 | 1469 |
|  |  | 3055 | 3174 | 2950 |
| $C_2H_4$ | $A_{1g}$ | 1406 | 1220 | 1342 |
|  |  | 1741 | 1592 | 1623 |
|  |  | 3032 | 3205 | 3026 |
|  | $B_{1g}$ | 1296 | 990 | 1220 |
|  |  | 3078 | 3202 | 3102 |
|  | $B_{2u}$ | 860 | 773 | 826 |
|  |  | 3092 | 3226 | 3105 |
|  | $B_{3u}$ | 1616 | 1221 | 1444 |
|  |  | 3025 | 3178 | (3020) |
|  | $B_{1u}$ | 1204 | 945 | 949 |
|  | $B_{2g}$ | 1174 | 812 | 940 |
|  | $A_u$ | 1264 | 777 | 1023 |
| $C_2H_2$ | $A_{1g}$ | 1828 | 2151 | 1974 |
|  |  | 3277 | 3458 | 3374 |
|  | $A_{2u}$ | 3229 | 3389 | 3282 |
|  | $E_u$ | 1180 | 839 | 730 |
|  | $E_g$ | 1099 | 499 | 613 |

[a] For $C_2H_6$ see Ref. [16], for $C_2H_4$ see Ref. [19], for $C_2H_2$ see Ref. [20].

### 3.5. Deformation-Deformation Couplings

This is an important class of force constants for there is usually little experimental information about them. Furthermore, these couplings may be quite large relatively to the corresponding diagonal force constants. Note that in semi-symmetry coordinates some bend-bend couplings, notably those acting within a $CH_3$ or $CH_2$ group, are absorbed into the diagonal bending force constants. The remaining constants are mainly connecting deformations on one group ($CH_3$, $CH_2$ or CH) with deformations on the other one.

As the tables show, CNDO/2 results are excellent for these constants. Not only do the signs agree with experiment and *ab initio* values, but the magnitudes are correctly reproduced as well. In the cases where the corresponding diagonal bending constants are overestimated, the couplings are also too high. This suggests that a simple scaling of the calculated deformation constants could further improve the results.

The MINDO/2 results are rather good with the exception of rock-rock type interactions. This is a serious deficiency of the MINDO method because

rock-rock type couplings are important (they are about 20% of the diagonal rocking force constants). We suspect that the cause of this discrepancy is the overemphasis of non-bonded interactions by MINDO method. It is easy to show that the non-bonded contribution to the rock-rock force constants is negative. Note that MINDO predicts linear geometry for water and planar one for ammonia: this also indicates too high non-bonded interactions.

Finally, we have also calculated the vibrational frequencies of the title compounds. The results compared to experiment are listed in Table 6.

## 4. Comparison with the Results of Dewar and Metiu

Recently Dewar and Metiu [8] have calculated the complete quadratic force field and some higher force constants of ethane by MINDO/2 method. These values are compared with ours (computed similarly at the calculated molecular geometry) only for CC stretching, CH stretching and CCH bending force constants because of the numerical errors in their torsional coordinates. Agreement is poor, especially for the coupling constants, as it can be seen in Table 7. For reasons quoted below we think our force constants are correct and the published figures of Dewar and Metiu are in error.

The force constant matrix of Dewar and Metiu is not positive definite, e.g. $|F_{14,16}| > \sqrt{F_{14,14} F_{16,16}}$. [Note that the diagonal force constants in Table 3 of their paper are not consistent with the potential function; either all diagonal constants must be multiplied by 0.5 or a factor 0.5 should be inserted in the first term of their Eq. (4)]. In fact we have calculated the vibrational frequencies with the force constant matrix of Dewar and Metiu and obtained three imaginary frequencies. It is worth mentioning that they quote also only 15 frequencies instead of 18.

Dewar and Metiu claim that the lack of symmetry in their force constants is caused only by the strange non-symmetrical choice of internal coordinates. Still, their force constants should obey some symmetry relationships. E.g. all torsion-torsion type force constants are deducible from three of the semi-symmetry force constants, from $F_{asymm.bend.}$, $F_{asymm.bend.,-asymm.bend.}$, and $F_{torsion}$. This gives rise to a number of linear equations for these force constants, which they do not obey. E.g. the following equations should hold: $F_{14,14} - F_{15,15} = 2(F_{14,16} - F_{15,17})$ and $F_{16,18} + F_{17,18} = F_{14,18} + F_{15,16}$. This points to a systematic error with the consequence that the degenerate frequencies split into components.

Our force constants are in good agreement with physical intuition. E.g. the $r/r_{gauche}$ and $r/r_{trans}$ couplings of our calculation are smaller than $r/r_{gem}$ coupling, in accordance with the greater spacial separation of the interacting CH bonds. Our MINDO $r/\beta$ couplings agree in sign with the predictions of the Hybrid Orbital Force Field [18]: $2F_{r/\beta_{same}} = -F_{r/\beta_{gem}} > 0$, while those of Dewar and Metiu do not. The agreement with the *ab initio* and experimental figures is also better for our force constants.

The conclusion is that the disagreement between our results and those of Dewar and Metiu is most likely caused by numerical errors in their calculation, for the larger diagonal force constants agree well.

Table 7. Comparison of the force constants of ethane with the results of Dewar and Metiu (in mdyn/Å, mdyn and mdynÅ, resp.)

| Coordinates | Dewar and Metiu MINDO/2[a] | Present work MINDO/2 | Ab initio[b] | Exp.[c] |
|---|---|---|---|---|
| R | 6.21 | 6.27 | 5.07 | 4.45 |
| r | 5.13 | 5.24 | 5.59 | 4.81 |
| $R/r$ | $+0.451$ | $+0.264$ | $+0.081$ | $0^d$ |
| $r/r_{gem.}$ | $+0.153$ | $+0.152$ | $+0.045$ | $+0.045$ |
| $r/r_{trans}$ | $+0.242$ | $+0.024$ | $-0.021$ | $-0.036$ |
| $r/r_{gauche}$ | $+0.169$ | $+0.022$ | $+0.014$ | $+0.014$ |
| $R/\beta$ | $+0.120$ | $+0.273$ | $+0.319$ | $+0.282$ |
| $r/\beta_{same}$ | $+0.280$ | $+0.092$ | $+0.079$ | $+0.027$ |
| $r/\beta_{gem.}$ | $+0.037$ | $-0.114$ | $-0.127$ | $-0.049$ |
| $r/\beta_{trans}$ | $+0.255$ | $+0.060$ | $+0.063$ | $0^d$ |
| $r/\beta_{gauche}$ | $+0.136$ | $+0.005$ | $-0.014$ | $0^d$ |
| $\beta$ | 0.600 | 0.667 | 1.071 | 0.859 |
| $\beta/\beta_{gem.}$ | $+0.031$ | $+0.142$ | $+0.221$ | $+0.177$ |
| $\beta/\beta_{trans}$ | $-0.094$ | $+0.029$ | $+0.151$ | $+0.115$ |
| $\beta/\beta_{gauche}$ | $-0.148$ | $+0.017$ | $-0.043$ | $-0.023$ |

[a] Ref. [8].
[b] Ref. [17].
[c] Ref. [16].
[d] Constrained value.

## 5. Conclusions

The results demonstrate that semiempirical quantum chemical calculations are capable of yielding force constants in satisfactory agreement with experiment. For the experimentally less accessible coupling force constants, especially for stretching-deformation and deformation-deformation such calculations give really new informations. In comparing CNDO/2 with MINDO/2 we have a slight preference for the former since MINDO reproduces the deformation-deformation coupling constants less well.

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