

# The Validity of Different Approximations in the Determination of Molecular Force Fields

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(Z. Naturforsch. 23 a, 1029—1033 [1968]; received 31 March 1968)

Various approximate solutions to the second order secular equation  $((G \cdot F)L = L\Lambda)$  in molecular spectroscopy are considered. New relations between them are developed and their validities tested empirically. It is found that the methods are decreasingly valid in the following order:

- „Verfahren der nächsten Lösung“ which considers the point on the surface of all real allowed solutions of  $F$  nearest to that corresponding to completely uncoupled oscillators.
- A distribution of the potential energy in  $\nu_1$  of  $V_{22} = -V_{12}$  or  $V_{11} = 100\%$ .
- $F_{22}$  a minimum, equivalent to  $L_{12} = 0$ ,  $V_{12} = -2V_{22}$  in  $\nu_1$  and in  $\nu_2$   $V_{22} = 100\%$ . This is the easiest solution to calculate ( $L$  matrix approximation method).
- The “Modified Valence Force Field” where  $F_{12} = 0$ .
- $L$  matrix of maximum trace, equivalent to  $L = G^{1/2}$ , having  $L_{12} = L_{21}$ .
- $F_{11}$  a maximum, equivalent to  $L_{21} = 0$ ;  $V_{12} = -2V_{11}$  in  $\nu_2$  and in  $\nu_1$ ,  $V_{11} = 100\%$ , being the second root of a quartic equation in  $F_{22}$  of which solution (b) is the first.

Owing to the impossibility of solving exactly the secular equation  $(G \cdot F)L = L\Lambda$  in molecular spectroscopy just using frequency data, even in the case of only  $2 \times 2$  matrices, attention has been drawn to providing further conditions, either from a physical force field or from mathematical constraints, to remove the indeterminacy from the solutions. In this paper the validity of some of the latter methods are examined for the second order secular equation for molecules of the type  $XY_m$ . There the frequency connected mainly with the stretching motion lies

above that of the bending. The allowed solutions form ellipses<sup>1</sup> connecting each pair of the three force constants ( $F_{11}$ ,  $F_{12}$  and  $F_{22}$ ), the eccentricities of which depend on the mass ratio  $M_Y/M_X$ , the smaller this the more nearly circular they being (see Fig. 1).

In Fig. 2 are shown the mean deviations of the solutions of the methods to be discussed from the actual solutions fixed by additional data, they being given as a function of  $M_Y/M_X$ . For the measure of the deviation the obvious parameter to use, independent of the individual force constants, is the proportion of the ellipse circumference by which the cal-

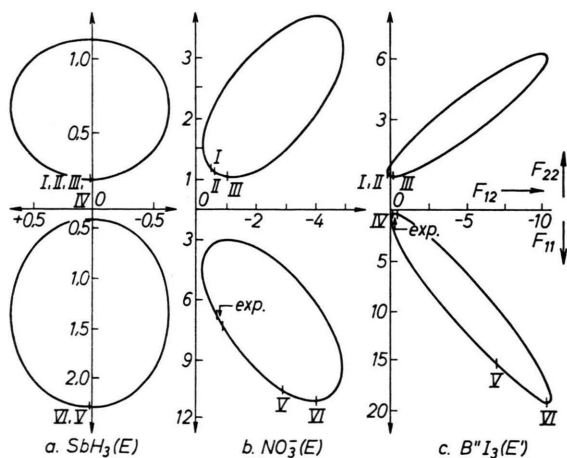


Fig. 1. Variation of  $F_{11}$  and  $F_{22}$  as a function of  $F_{12}$  in  $\text{mdyn}/\text{\AA}$  for a.  $\text{SbH}_3(\text{E})$ , b.  $\text{NO}_3^-(\text{E}')$ , c.  $\text{BI}_3(\text{E}')$ . Approximate solutions marked: I: Verfahren der nächsten Lösung; II:  $V_{22} = -V_{12}$ ; III:  $L_{12} = 0$ ; IV:  $F_{12} = 0$ ; V:  $L$  matrix of maximum trace; VI:  $F_{11}$  a maximum.

<sup>1</sup> P. TORRINGTON, J. Chem. Phys. 17, 357 [1949].

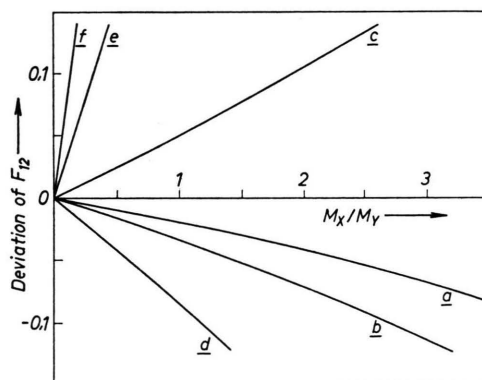


Fig. 2. Deviations of the approximations as function of the mass ratio  $M_Y/M_X$  for  $XY_m$  molecules. Deviation measured as the ratio of the difference in  $F_{12}$  between the approximate solution and that fixed by additional data, to the total range of  $F_{12}$  allowing real solutions: a. „Verfahren der nächsten Lösung“; b.  $V_{22} = -V_{12}$ ; c.  $L_{12} = 0$ ; d.  $F_{12} = 0$ ; e.  $L$  matrix of maximum trace; f.  $F_{11}$  a maximum.



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culated and experimental values differ. However whilst this is difficult to calculate, if the deviation be relatively small it may be approximated by the ratio of the difference in  $F_{12}$  to the total range of  $F_{12}$  allowing real solutions. From Fig. 2 it is immediately seen that as the mass ratio tends to zero all the approximations become accurate, because the mixing between the normal vibrations (the cause of the difficulties in characterizing the exact solution) becomes very small, the oscillators being almost independent of each other. Unfortunately this obvious fact has often been disregarded and to test approximations frequently only their applications to various hydride molecules have been considered. With these not only is the mass ratio so low that all approximations work, but also the anharmonicity corrections are so large and illdefined that all methods based on using frequencies alone are doomed to failure because of the large errors the frequencies carry<sup>2</sup>.

We have calculated the various approximate solutions for a series of some 40 molecules whose constants using additional data have been published, a representative selection of which are given in Table 1. Fig. 2 shows the best fit curves of the mean deviations of the approximate solutions as a function of  $M_Y/M_X$ .

However the scatter of the points is such as to obviate any attempt to correct an approximate result from the graph. This scatter may be a true physical phenomenon but judging by some of the molecules where several reported "exact" force fields have been published (e.g.  $\text{BF}_3$   $E'$  species;  $F_{11} = 6.75^3$ ,  $6.56^4$ ,  $7.82^{5?}$  mdyne/Å) much arises from this latter source.

## Discussion of the Approximations Examined

### a) $F_{11}$ a Maximum

STREY<sup>6</sup> has suggested that for hydrides  $F_{11}$  a maximum gives the correct solution. However as discussed above one cannot really apply any of the

methods solely dependent on the frequencies to hydrides. Fig. 2 shows it to be quite hopeless for other molecules where the stretching frequency is higher than the bending, always seriously over-estimating  $F_{12}$ . However from similar arguments to those of PEACOCK and MÜLLER<sup>7</sup> which showed that  $F_{22}$  a minimum means  $L_{12} = 0$ ,  $F_{11}$  a maximum can be shown to mean  $L_{21} = 0$ . This expression appears to be reasonably valid for cases where the bending mode is at higher frequency than the stretching (see<sup>8</sup> where after a high frequency separation this has been applied to  $\text{ReO}_3\text{Cl}$ ,  $\nu\text{ReCl} < \delta_{\text{a1}}\text{ReO}_3$ ).

### b) $L$ Matrix of Maximum Trace

HERRANZ and CASTANO<sup>9</sup> have proposed a method in which the  $L$  matrix has maximum trace, this corresponding to the most characteristic set of assignments. PULAY and TÖRÖK<sup>10</sup> have also suggested a method using this best assignment technique, giving the condition that  $L = G^{\frac{1}{2}}$ . It has been pointed out by STREY<sup>6</sup> that the two methods are identical. As  $G$  is symmetric, so hence is  $L$ , i.e.  $L_{12} = L_{21}$ . This is physically unreasonable for, as shown in ref.<sup>12</sup>  $L_{12}$  is always much less than  $L_{21}$ .

### c) "Modified Valence Force Field"

This often used force field just ignores the interaction term in the  $F$  matrix i.e. here  $F_{12}$  is set equal to zero. This means it can only work if there is little coupling between vibrations, otherwise the interactions are always underestimated. Indeed from Table 1 and Fig. 2b it can be seen that often, when the mass ratio is above 1, no real solutions exist at this point.

### d) $F_{22}$ a Minimum or $L_{12} = 0$ ( $L$ matrix approximation method of MÜLLER)

This solution has been proposed several times. As  $F_{22}$  a minimum it was one of the solutions favoured by TORKINGTON<sup>1</sup>, STREY<sup>6</sup> suggested it was applicable for molecules not containing hydrogen and BECHER

<sup>2</sup> J. L. DUNCAN and I. M. MILLS, *Spectrochim. Acta* **20**, 523 [1964].

<sup>3</sup> L. BECKMANN, L. GUTJAHR, and R. MECKE, *Spectrochim. Acta* **21**, 141 [1965].

<sup>4</sup> J. L. DUNCAN, *J. Mol. Spectr.* **13**, 338 [1964].

<sup>5</sup> I. LEVIN and S. ABRAMOWITZ, *J. Chem. Phys.* **43**, 4213 [1965].

<sup>6</sup> G. STREY, *J. Mol. Spectr.* **24**, 87 [1967].

<sup>7</sup> C. J. PEACOCK and A. MÜLLER, *J. Mol. Spectr.* (in press).

<sup>8</sup> A. MÜLLER, B. KREBS, and C. J. PEACOCK, *Spectrochim. Acta* (in press).

<sup>9</sup> J. HERRANZ and F. CASTANO, *Spectrochim. Acta* **22**, 1965 [1966].

<sup>10</sup> P. PULAY and F. TÖRÖK, *Acta Chim. Acad. Sci. Hungaricae* **44**, 287 [1965]; **47**, 274 [1966].

Molecule	Experimental		FADINI		P. E. D. Method		$L_{12} = 0$		$F_{12} = 0$		$L$ max. trace		$F_{11}$ max.	
SO <sub>2</sub> (A <sub>1</sub> )	10.41 ± 0.20 0.32 ± 0.21	a) 0.815 ± 0.007	10.42 0.37	0.819	10.26 0.22	0.821	10.45 0.40	0.818	9.99 0	0.839	11.11 1.40	0.932	11.22 1.94	1.083
NO <sub>2</sub> (A <sub>1</sub> )	13.18 0.66	b) 1.109	12.72 0.45	1.138	13.00 0.67	1.121	13.72 0.95	1.106	11.49 0	1.242	15.34 2.40	1.31	15.54 3.03	1.510
PF <sub>3</sub> (E)	4.96 0.21	c) 0.49	4.96 0.21	0.490	4.88 0.13	0.491	4.98 0.23	0.489	4.74 0	0.503	5.44 0.91	0.590	5.56 1.46	0.814
NF <sub>3</sub> (E)	3.40 ± 0.10 0.33 ± 0.04	d) 0.90 ± 0.02	3.36 0.31	0.907	3.55 0.40	0.876	3.99 0.65	0.845	no real solution		4.94 1.54	1.075	5.19 2.19	1.492
SO <sub>3</sub> (E')	10.52 - 0.30	e) 0.623	10.33 - 0.18	0.626	10.44 - 0.25	0.621	10.76 - 0.46	0.618	10.01 0	0.643	12.48 - 2.19	0.898	12.76 - 3.19	1.303
B <sup>11</sup> F <sub>3</sub> (E')	6.52, 6.75, 7.82	f, g, h)	6.45		6.61		7.37		5.51		12.65		13.74	
	- 0.31, - 0.39, - 0.81	0.51, 0.51, 0.50	- 0.31	0.522	- 0.34	0.515	- 0.62	0.500	0	0.591	- 3.88	1.450	- 5.72	2.619
B <sup>11</sup> Cl <sub>3</sub> (E')	4.19 ± 0.05 ? - 0.51 ± 0.02	h) 0.25 ± 0.002	3.18 - 0.16	0.262	3.27 - 0.19	0.256	3.77 - 0.36	0.248	2.53 0	0.318	9.28 - 3.44	1.364	10.39 - 5.00	2.486
SnH <sub>4</sub> (F <sub>2</sub> )			2.247 0.003	0.140	2.242 0.003	0.140	2.242 0.002	0.140	2.242 0	0.140	2.242 0.015	0.140	2.242 0.024	0.140
OsO <sub>4</sub> (F <sub>2</sub> )	7.72 ± 0.03 - 0.03 ± 0.07	i) 0.427 ± 0.003	7.75 0.03	0.425	7.76 0.05	0.424	7.78 0.09	0.424	7.74 0	0.425	7.88 0.46	0.445	7.90 0.72	0.482
GeCl <sub>4</sub> (F <sub>2</sub> )	2.73 ± 0.13 0.13 ± 0.08	j) 0.170 ± 0.003	2.71 0.12	0.170	2.63 0.07	0.171	2.73 0.13	0.170	2.50 0	0.178	3.24 0.65	0.264	3.38 0.96	0.406
SiCl <sub>4</sub> (F <sub>2</sub> )	2.96 ± 0.09 0.14 ± 0.03	j) 0.237 ± 0.005	2.91 0.13	0.238	3.00 0.16	0.233	3.34 0.28	0.227	2.47 0	0.273	5.43 1.59	0.590	5.77 2.20	0.959
CF <sub>4</sub> (F <sub>2</sub> )	6.21 0.83	k) 1.02	5.85 0.75	1.056	6.09 0.80	1.028	7.67 1.29	0.948	no real solution		12.33 4.00	1.742	13.11 5.29	2.57
RhF <sub>6</sub> (F <sub>1u</sub> )	4.30 ± 0.1 - 0.10 ± 0.1	l) 0.29 ± 0.01	4.22 - 0.03	0.296	4.29 - 0.09	0.292	4.37 - 0.16	0.291	4.18 0	0.298	4.78 - 0.73	0.370	4.84 - 1.03	0.477
SeF <sub>6</sub> (F <sub>1u</sub> )	4.88 ± 0.1 - 0.44 ± 0.03	l) 0.64 ± 0.01	4.40 - 0.13	0.680	4.63 - 0.25	0.657	4.87 - 0.42	0.648	4.13 0	0.721	5.38 - 1.00	0.738	5.47 - 1.34	0.874
SF <sub>6</sub> (F <sub>1u</sub> )	4.75 ± 0.15 - 0.74 ± 0.03	l) 1.10 ± 0.03	4.71 - 0.73	1.104	4.84 - 0.76	1.085	5.79 - 1.10	1.016	no real solution		7.18 - 2.08	1.251	7.43 - 2.59	1.53

Table 1. Values of the  $2 \times 2$   $F$  matrix elements for various approximations in units of mdyne/Å, frequencies taken from experimental references.

a) Y. MORINO and K. KUCHITSU, J. Mol. Spectr. **13**, 95 [1964]. b) G. R. BIRD, J. C. BAIRD, A. W. JACHE, J. A. HODGESON, R. F. CURL, JR., A. C. KUNKLE, J. W. BRANFORD, J. RASTRUP-ANDERSEN, and J. ROSENTHAL, J. Chem. Phys. **40**, 3378 [1964]. c) ANNA M. MIRRI, J. Chem. Phys. **47**, 2823 [1967]. d) W. SAWODNY, A. RUOFF, C. J. PEACOCK, and A. MÜLLER, Mol. Phys. (in press). e) R. STØLEVIK, B. ANDERSEN, S. J. CYVIN, and J. BRUNVOLL, Acta Chem. Scand. **21**, 1581 [1967]. f) See ref. <sup>3</sup>. g) See ref. <sup>4</sup>. h) See ref. <sup>5</sup>. i) Using  $\zeta_3$  from I. W. LEVIN and S. ABRAMOWITZ, Inorg. Chem. **5**, 2024 [1966]. See also R. S. MacDOWELL, Inorg. Chem. **6**, 1760 [1967]. j) R. KEBABCIOGLU, A. MÜLLER, and C. J. PEACOCK, Z. Naturforsch. **23a**, 703 [1968]. k) T. SHIMANUCHI, I. NAKAGAWA, J. HIRASHI, and M. ISHII, J. Mol. Spectr. **19**, 78 [1966]. l) H. KIM, P. A. SOUDER, and H. H. CLAASEN, J. Mol. Spectr., in press.

and BALLEIN<sup>11</sup> have also suggested it. MÜLLER<sup>12</sup> put forward the solution  $L_{12}=0$  giving a series of physical reasons for its applicability. Later PEACOCK and MÜLLER<sup>7</sup> showed that the two solutions were identical and derived simple equations allowing ready evaluation of the  $\mathbf{F}$  matrix elements without solution of the secular equation, making it the easiest of the approximations to apply:

$$F_{11} = \frac{\lambda_1}{G_{11}} + \frac{\lambda_2 G_{12}^2}{G_{11} \det \mathbf{G}}; \quad F_{12} = \frac{-G_{12} \lambda_2}{\det \mathbf{G}}; \quad F_{22} = \frac{G_{11} \lambda_2}{\det \mathbf{G}}$$

By the use of this approximation MÜLLER<sup>12</sup> was able to explain the mass dependence of Coriolis coupling constants. From Fig. 2 it is however seen that it is only really valid when  $M_Y < M_X$  otherwise it tends to overestimate the interaction term.

### e) Potential Energy Distribution Method

BECHER and BALLEIN<sup>11</sup> have proposed from empirical observation, a method in which a definite

potential energy distribution (P.E.D.) is favoured. In ref. <sup>11</sup> it is given as, in  $\nu_1$   $V_{12} = -2 V_{22}$ . However using the normal definition of P.E.D.<sup>13</sup> from the definition of the potential energy in the  $i^{\text{th}}$  normal mode:

$$V_i = \frac{1}{2} Q_i \sum_{j,k} F_{jk} L_{ji} L_{ki}$$

the distribution is given by the ratio of terms of this equation. Hence for the  $2 \times 2$  case in  $\nu_1$ <sup>13a</sup>:

$$V_{11} = F_{11} L_{11}^2; \quad V_{12} = 2 F_{12} L_{11} L_{21}; \quad V_{22} = F_{22} L_{21}^2.$$

Using this definition it has been shown<sup>7</sup> that the distribution in  $\nu_1$ :  $V_{12} = -2 V_{22}$  is identical to solution d. From the calculations in ref. <sup>11</sup> it would appear that P.E.D. is used without the factor 2 in the  $V_{12}$  term, and hence the approximation should read  $V_{22} = -V_{12}$  (when for a normalized distribution  $V_{11} = 100\%$ ). It must be noted that this can correspond to up to four different sets of constants, for using this constraint one may derive a compli-

Force constants			L-Matrix					Higher freq. P.E.D.			Lower freq. P.E.D.		
	$F_{12}$	$F_{11}$	$F_{22}$	$L_{11}$	$L_{12}$	$L_{21}$	$L_{22}$	$V_{11}$	$V_{12}$	$V_{22}$	$V_{11}$	$V_{12}$	$V_{22}$
a)	0.179	1.135	0.293	0.340	0.055	-0.670	0.108	72.5	-45.0	72.5	38.1	23.7	38.2
b)	0.329	2.063	0.198	0.345	0.006	-0.648	0.201	135.2	-81.0	45.8	0.8	9.0	90.2
	0.479	2.602	0.204	0.345	-0.014	-0.634	0.239	170.3	-115.5	45.2	6.1	37.2	131.1
c)	5.433	13.066	2.282	0.232	-0.255	-0.277	0.619	388.6	-384.9	96.3	9525.7	-19243.8	9818.1
	5.583	13.303	2.365	0.227	-0.260	-0.263	0.625	376.6	-366.7	90.2	10087.6	-20361.6	10374.0
	5.733	13.536	2.450	0.221	-0.265	-0.249	0.631	363.4	-347.0	83.6	10665.6	-21511.0	10945.4
	7.234	15.408	3.416	0.136	-0.317	-0.060	0.675	158.2	-64.9	6.7	17343.3	-34738.1	17494.8
	7.384	15.496	3.538	0.122	-0.323	-0.028	0.678	126.6	-28.2	1.6	18104.6	-36234.1	18229.6
d)	7.534	15.518	3.677	0.102	-0.329	0.012	0.678	89.6	10.1	0.3	18886.2	-37761.8	18975.5
	7.684	15.149	3.918	0.055	-0.340	0.108	0.669	25.0	49.9	25.1	19710.4	-39320.7	19710.3
	7.534	14.222	4.012	0.006	-0.345	0.201	0.648	0.3	10.1	89.6	18975.6	-37761.8	18886.3
	7.384	13.683	4.007	0.014	-0.345	-0.239	0.634	1.6	-28.2	126.6	18229.6	-36234.3	18104.6
	7.234	13.210	3.984	0.030	-0.343	-0.268	0.623	6.7	-64.9	158.2	17494.8	-34738.1	17343.3
	5.433	8.825	3.378	0.141	-0.315	-0.457	0.501	96.3	-384.9	388.6	9818.1	-19243.9	9525.8
e)	5.283	8.507	3.316	0.147	-0.312	-0.468	0.491	102.0	-401.5	399.6	9277.6	-18157.5	8980.0
	5.132	8.193	3.252	0.154	-0.308	-0.478	0.481	107.2	-416.6	409.4	8752.5	-17102.7	8450.2
	2.130	2.749	1.760	0.265	-0.221	-0.631	0.249	106.4	-392.6	386.2	1502.8	-2625.7	1222.9
e)	1.980	2.522	1.674	0.270	-0.215	-0.636	0.234	101.3	-375.2	373.8	1302.6	-2232.8	1030.2
	1.830	2.301	1.586	0.275	-0.208	-0.642	0.219	95.9	-356.2	360.2	1117.8	-1871.4	853.6
	1.680	2.087	1.497	0.280	-0.201	-0.647	0.203	90.2	-335.6	345.4	948.3	-1541.5	693.2
	0.629	0.876	0.795	0.317	-0.136	-0.675	0.060	48.5	-148.4	200.0	183.2	-114.9	31.7
	0.479	0.788	0.673	0.233	-0.122	-0.678	0.028	45.2	-115.5	170.3	131.1	-37.2	6.1
	0.329	0.767	0.533	0.329	0.102	-0.678	0.012	45.8	-81.0	135.2	90.2	9.0	0.8
	0.179	1.134	0.293	0.340	0.055	-0.670	0.108	72.5	-45.0	72.5	38.2	23.7	38.1

Table 2. Values of force constants in mdyne/Å, Matrix elements in (a.m.u.)<sup>-1/2</sup> and potential energy distribution in % for  $\text{Cl}_4$  ( $F_2$  species). The various points mentioned in the text are marked as follows: a) „Verfahren der nächsten Lösung“, potential energy distribution method. b)  $L_{12}=0$ ,  $F_{22}$  a minimum. c)  $\mathbf{L}$  matrix of maximum trace,  $L_{12}=L_{21}$ . d)  $F_{11}$  a maximum,  $L_{21}=0$ . e) 3rd and 4th solutions of the quartic equation of which „a” and „d” are the first two.

<sup>11</sup> H. J. BECHER and K. BALLEIN, Z. Phys. Chem. Frankfurt **54**, 302 [1967].

<sup>12</sup> A. MÜLLER, Z. Phys. Chem. Leipzig (in press).

<sup>13</sup> Y. MORINO and K. KUCHITSU, J. Chem. Phys. **20**, 1809 [1952].

cated quartic equation in  $F_{22}$ , the smallest root of which represents this solution, whilst the next root is when  $F_{11}$  is a maximum. This is obvious from the equations above, for as  $L_{21}=0$  when  $F_{11}$  is a maximum,  $V_{12}$  and  $V_{22}$  in  $v_1$  are both zero. Although explicit evaluation of the quartic equation is not possible it may be seen that when the ratio  $M_Y/M_X$  is very high (e. g.  $\text{BI}_3$ ,  $\text{CI}_4$ ) there are four real roots (see Table 2), normally only two, but when  $M_Y/M_X$  tends to zero these coincide (see  $\text{SiH}_4$  in Table 1).

This approximation is seen from Fig. 2 to be an improvement on the others, though generally representing too small a value of  $F_{12}$ .

f) „Verfahren der nächsten Lösung“

FADINI<sup>14</sup> has proposed a method which, unlike most of the above, is applicable to problems other than the  $2 \times 2$ . In the  $n(n+1)/2$  dimensional space represented by the force constants of the  $n \times n$  problem the nearest point on the hypersurface representing the infinity of real solutions to the point corresponding to completely uncoupled oscillators (i. e. diagonal  $\mathbf{F}$  and  $\mathbf{G}$  matrices) is chosen as the cor-

rect solution. Whereasyet no physical reasons have been advanced for its validity, it may be seen from Fig. 2 that it is the best of the approximate methods yet developed although  $F_{12}$  is generally underestimated. Unfortunately the method is rather difficult to evaluate.

From the selection of examples in Table 1 it can be seen that the trends shown in Fig. 2 are obeyed although in individual cases variation exists e. g. whereas  $\text{SF}_6$  shows the P.E.D. method to be much better than  $L_{12}=0$ , in  $\text{SeF}_6$  this is reversed, possibly meaning that the force field for  $\text{SeF}_6$  is not accurately determined. However it is obvious that provided their limitations are realized, when no additional data are available mathematical approximation methods may be successfully used, or alternatively when additional data are available they may give an added check, for if their deviation be far outside that in Fig. 2 more critical examination of the data would be called for.

We would like to thank Prof. Dr. O. GLEMSER for his generous encouragement.

<sup>13a</sup> This usually being normalised so that the sum of  $V_{ij}=100\%$ .

<sup>14</sup> A. FADINI, Z. Naturforsch. **21 a**, 426 [1966].