Note on the Calculation of Zero-Point Energies and Isotopic Zero-Point Energy Differences by a Taylor's Series Expansion*

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KLAUS CLUSIUS *zum 60. Geburtstag gewidmet*

The series expansion for the zero-point energy of a system of harmonic oscillators derived by BIGELEISEN and GOLDSTEIN has been examined in detail. The convergence properties have been tested as a function of the reduced frequency, and the error produced in truncating the series has been found. Calculations of zero-point energy sums by solving the secular equations for isotopically substituted series of hydrogen, methane, ethylene, ethane, and benzene molecules have been made and the results are discussed in terms of the first- and second-order isotope sum rules.

In the preceding paper [1], it has been shown that the reduced harmonic zero-point energy of an n-atomic molecule

$$\varepsilon_0 = \tfrac{1}{2} \sum^{3n-6} \omega_k/\omega_0$$

(where ω_k refers to the eigenfrequencies of the molecule and ω_0 is a characteristic frequency to be chosen) can be expressed in terms of a power series

$$2\,\varepsilon_0 = \frac{3n-6}{2} + \frac{\sum^{3n-6} x_k}{2} + \sum_{k}^{3n-6} \sum_{p=2}^{\infty} \frac{(-1)^{p+1}\,(2p-2)!}{2^{2p-1}\,(p-1)!\,p!}\,(x_k-1)^p, \quad (1)$$

where $x_k = (\omega_k/\omega_0)^2$. This series is absolutely convergent for $|x_k - 1| \leqq 1$, $k = 1, \ldots, 3n-6$. The purpose of this paper is to examine the convergence properties of this series for various values of x, to determine the errors produced by truncating the series at various terms, and to show the behavior of equation (1) when some representative molecules are considered. Furthermore, the effect of changes in certain vibrational force constants on the terms of equation (1) will be discussed. Particular interest is attached to the calculation of zero-point energy differences between isotopically substituted molecules. In the present context, series (1) has been evaluated by means of calculated values of $x_k^{1/2}$ (i. e. frequencies). From the practical point of view this would obviously be completely useless because a knowledge of $x_k^{1/2}$ $(k = 1, \ldots, 3n-6)$ is equivalent to a knowledge of the zero-point energy ε_0. The practical usefulness of (1) arises from the fact that $\sum^{3n-6}_k x_k^n$ (or $\sum \omega_k^{2n}$) can be obtained from the secular determinant in terms of force constants and atomic masses by means of the sum rules [2] without explicit calculation of the individual frequencies.

I. Individual Frequencies

Figures 1 and 2 show the convergence of the series (1) for an individual frequency (i. e. $3n-6=1$) as a function of x. The convergence criterion sets limits on x of $0 \leqq x \leqq 2$. We see from the figures that the rapidity and the type of the convergence do show a dependence on x. It is to be observed, however, that if we restrict our attention to the range $0.25 \leqq x \leqq 2$, the maximum error made at $p=2$ in the summation is of the order of 10%. We should consider this in the light of the fact that we want to use the series (1) to calculate the zero-point energy of a polyatomic molecule (i. e. several frequencies) with a single value of ω_0. (It is obvious, of course, that the sum rules can be used in conjunction with series (1) only if a single characteristic frequency, ω_0, is employed [1].) Thus for a molecular species having frequencies which differ by as much as a factor of 2.83 (i. e. $\sqrt{2}/\sqrt{0.25}$), it is possible to pick a value of ω_0 such that the zero-point energy is given by the first three terms of series (1) to better than 10%. For organic molecules containing

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[1] J. BIGELEISEN and P. GOLDSTEIN, Z. Naturforschg. **18 a**, 205 [1963].

[2] J. BIGELEISEN, "Proceedings of the International Symposium on Isotope Separation", edited by J. KISTEMAKER, J. BIGELEISEN and A. O. C. NIER, North-Holland Publ. Co., Amsterdam 1958, pp. 122—125.

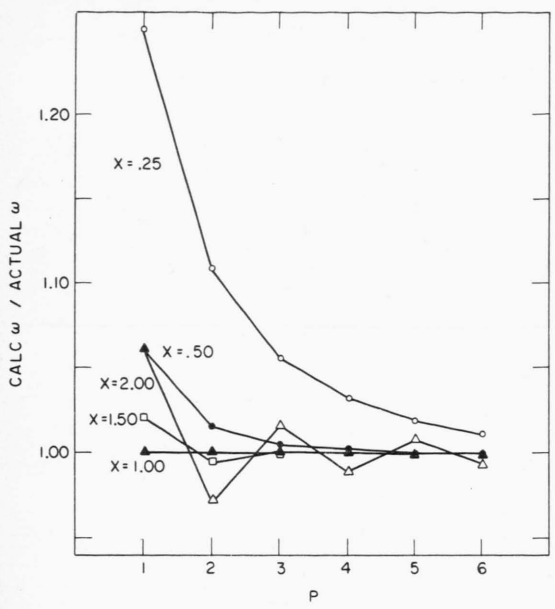

Fig. 1.

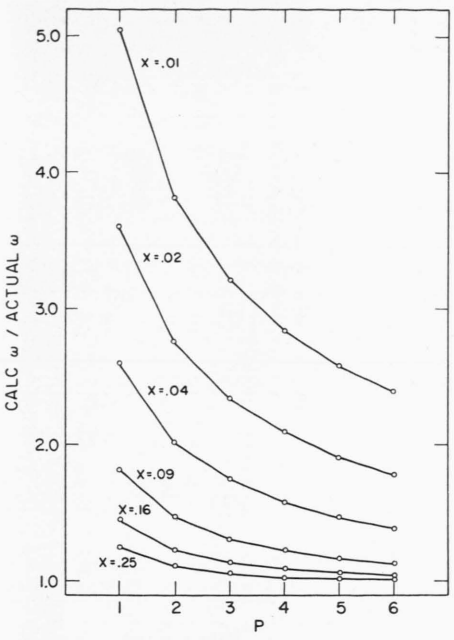

Fig. 2.

Figs. 1 and 2. Ratio of calculated frequency to actual frequency as a function of x ($x=\omega^2/\omega_0^2$) at various terms in the series expansion (equation 1).

carbon-hydrogen bonds, the maximum frequencies are about 3000 cm^{-1}. Then with $\omega_0 = 3000/\sqrt{2}$, we are assured of the above 10% convergence if there are no frequencies in the molecule less than 1000 cm^{-1}. The 10% figure actually applies only to the smaller frequencies in the above range and there may be some cancellation of errors. Hence, we would expect to be able to pick a value of ω_0 such that the series (1) converges to the zero-point energy to better than 10% for the first three terms over a much larger range of frequencies than 1000 cm^{-1} to 3000 cm^{-1}. The contribution of extremely low frequencies may be estimated quite incorrectly by the series (1) but such frequencies tend to contribute proportionally rather little to the total zero-point energy.

These considerations are demonstrated in Fig. 3, in which the differences between actual frequencies and those calculated from equation (1) are plotted. With a choice of $\omega_0 = 2000$ cm^{-1} (corresponding approximately to the value needed in a molecule with a C – H bond), frequencies in the range 1000 to 2800 cm^{-1} are in error by no more than 100 cm^{-1} when the first three terms of the series are

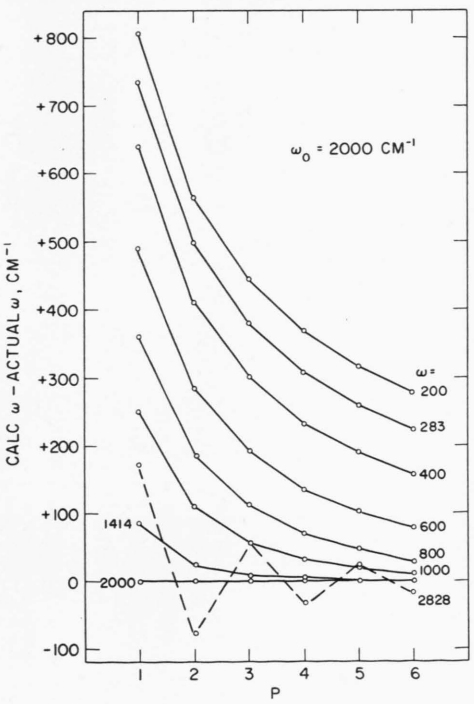

Fig. 3. Error in calculated frequency with $\omega_0 = 2000$ cm^{-1} at various terms in the series.

used. The errors become larger for frequencies below 1000 cm^{-1}.

Fig. 4 shows the error which results when equation (1) is used to approximate the change in frequency produced by isotopic substitution. The ordinate is the error in the difference $\omega_1 - \omega_2$, where we have used the ratio $\omega_1/\omega_2 = 2^{1/2}$, i. e. the maximum isotope effect to be expected in a molecule where a hydrogen atom has been replaced by deuterium. The maximum error (for $p \geqq 2$) is found when $\omega_2 \approx 400$ cm^{-1}. Fortunately, molecular vibrations with frequencies below 1000 cm^{-1} are usually skeletal vibrations which are relatively insensitive to isotopic substitution of a hydrogen atom.

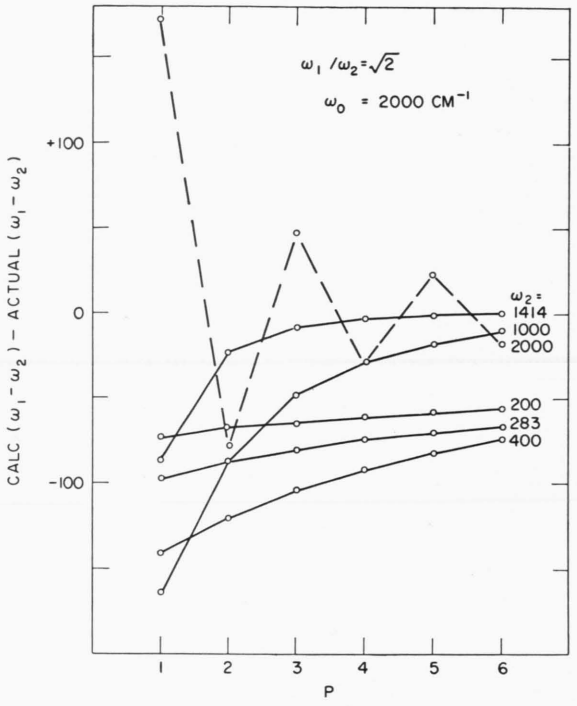

Fig. 4. Error in frequency difference, $\omega_1 - \omega_2$, with $\omega_1/\omega_2 = \sqrt{2}$ and $\omega_0 = 2000$ cm^{-1} at various terms in the series.

It should be pointed out that in the comparison of frequencies of different isotopic species, a somewhat more stringent requirement is placed on the choice of ω_0. In order to take advantage of the convenient form of the isotopic sum rules [1], one must use the same ω_0 for the different isotopic molecules. The use of the minimum value allowed by the high frequencies of the light isotopic species will lead to smaller values of ω/ω_0 in the heavy isotopic species, and thus to less rapid convergence of the series.

The behavior of series (1) for an actual molecule is shown in Table 1, which gives results obtained for the H_2, HD, and D_2 molecules. This system is expected to show the largest deviation from the linear zero-point energy rule (law of the mean), i. e. the largest difference between $\omega(H_2) - \omega(HD)$ and $\omega(HD) - \omega(D_2)$. It is seen that convergence is extremely rapid for the three values of ω_0 which were used.

II. Polyatomic Molecules

Tables 2 through 6 contain the zero-point energies and zero-point energy differences for several isotopically substituted series of larger molecules. These values were obtained from exact solutions of the secular determinants for the vibrational frequencies. In addition, some comparisons are made with zero-point energies calculated with the series expansion (1).

Methane. – The zero-point energies of CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4 were calculated

$p =$		1	2	3	4	5	6	Exact
$\omega_0 =$ 3788.19 [b]	$\omega_{H2} - \omega_{HD}$	640.54	581.75	592.13	589.79	590.35	590.22	590.28
	$\omega_{HD} - \omega_{D2}$	640.54	690.05	698.08	699.71	700.06	700.17	700.19
	$2\omega_{HD} - (\omega_{H2} + \omega_{D2})$	0	108.30	105.96	109.92	109.70	109.95	109.90
$\omega_0 =$ 3760.00 [c]	$\omega_{H2} - \omega_{HD}$	645.40	580.36	592.58	589.72	590.47	590.26	590.28
	$\omega_{HD} - \omega_{D2}$	645.40	691.12	698.38	699.77	700.11	700.19	700.19
	$2\omega_{HD} - (\omega_{H2} + \omega_{D2})$	0	110.77	105.81	110.06	109.64	109.93	109.90
$\omega_0 =$ 3815.61 [d]	$2\omega_{HD} - (\omega_{H2} + \omega_{D2})$	0	106.00	106.00	109.66	109.66	109.90	109.90

[a] Based on calculations by P. GOLDSTEIN. [b] $\omega_0 = (\omega_{H_2} + \omega_{D_2} + 2\omega_{HD})/4$. [c] $\omega_0 = (\omega_{H_2}\omega_{D_2}\omega^2_{HD})^{1/4}$. [d] $\omega_0 = \omega_{HD}$.

Table 1. Frequency differences (in cm^{-1}) for H_2, HD, and D_2 Molecules Calculated by Series Expansion [a].

Molecule	$p=0$	1	2	3	4	5	6	Exact
CH_4	5062.50	10641.66	9877.33	10054.69	9876.68	9966.29	9887.78	9913.56
Δ		646.96	559.25	642.17	615.29	646.91	632.20	646.07
CH_3D	5062.50	9994.69	9318.08	9412.52	9261.39	9319.38	9255.58	9267.49
Δ		646.96	561.53	646.24	621.01	653.82	640.13	657.00
CH_2D_2	5062.50	9347.73	8756.55	8766.28	8640.38	8665.56	8615.45	8610.49
Δ		646.96	563.82	650.32	626.74	660.68	647.95	667.37
CHD_3	5062.50	8700.76	8192.73	8115.96	8013.64	8004.88	7967.50	7943.12
Δ		646.96	566.10	654.40	632.42	667.43	655.63	677.12
CD_4	5062.50	8053.80	7626.63	7461.56	7381.22	7337.45	7311.87	7266.00

Table 2. Zero-point Energies and Differences (in cm^{-1}) for Isotopic Methanes, $\omega_0=2250\ cm^{-1}$.

with force constants given by JONES [3]. These values (from solution of the secular determinant) are compared with the approximate values calculated by equation (1) in Table 2, together with zero-point energy differences between successive pairs in the isotopically substituted series. The choice of $\omega_0 = 2250\ cm^{-1}$ is approximately the minimum value which obeys the convergence requirement. The second-order approximation ($p=2$) in the series is seen to produce a maximum error of about five percent in the zero-point energies, but the error in the change of zero-point energy upon isotopic substitution of one hydrogen is about 20%. The comments in the preceding paper [1] concerning this system are confirmed: the difference in zero-point energies between successive pairs increases with increasing deuterium substitution. Also, the difference between successive pairs which would be obtained from a linear interpolation between CH_4 and CD_4 is 661.89 cm^{-1}. The differences between the actual zero-point energies and those obtained with this linear interpolation are: CHD_3, 15.23 cm^{-1}; CH_2D_2, 20.71 cm^{-1}; CH_3D, 15.82 cm^{-1} (cf. Fig. 1 of reference [1]). According to Table 1 of the preceding paper [1], the ratio of these differences should be 20.71/15.57, in good agreement with the above values.

Similar calculations were made with this same set of isotopically substituted molecules in which the force constants for H – C – H bending vibrations (and any interaction terms involving this motion) were set equal to zero. In this case, only four frequencies are found, corresponding to C – H stretching vibrations. The results are shown in Table 3,

[3] L. H. JONES and R. S. MCDOWELL, J. Mol. Spectroscopy **5**, 632 [1959].

Molecule	$p=0$*	1	2	Exact
CH_4	2250.00	6701.68	6162.95	6329.66
Δ	0	513.85	379.95	421.53
CH_3D	2250.00	6187.83	5783.00	5908.13
Δ	0	513.85	380.06	421.68
CH_2D_2	2250.00	5673.98	5402.94	5486.45
Δ	0	513.85	380.18	421.84
CHD_3	2250.00	5160.14	5022.76	5064.61
Δ	0	513.85	380.30	421.99
CD_4	2250.00	4646.29	4642.46	4642.62

* $(3n-6)/2$ is set equal to 2 since there are only 4 non-zero frequencies.

Table 3. Zero-point Energies and Differences (in cm^{-1}) for Isotopic Methanes with Bending Force Constants Neglected, $\omega_0=2250\ cm^{-1}$.

and it is immediately evident that the zero-point energy differences between successive pairs are very nearly equal although there is still a slight increase with increasing heavy atom substitution. The table also shows that the series expansion through second-order terms leads to a similar result. To this order of approximation, this is to be expected from the type of force field employed, since a difference of the type

$$\sum \omega(CH_4) - \sum \omega(CH_3D) - \left[\sum \omega(CH_3D) - \sum \omega(CH_2D_2)\right]$$

is proportional to $\sum_{i \neq j} a^2_{H_iH_j}$ (cf. the last section of the preceding paper). These force constants are for the mutual motion of two hydrogen atoms and the only contribution to this term here arises from the interaction force constant between carbon-hydrogen stretches which, it should be noted, has not been set equal to zero in these calculations.

Molecule	$\sum^{12}\omega_i$	$\sum^{12}\Delta\omega_i$ [b]	$\sum^{9}\omega_i$ (planar)	$\sum^{9}\Delta\omega_i$ (planar)	$\sum^{3}\omega_i$ (non-planar)	$\sum^{3}\Delta\omega_i$ (non-planar)
$H_2C{=}CH_2$	21650.47		18730.67		2919.80	
		1287.71		1120.05		167.66
$H_2C{=}CHD$	20362.76		17610.62		2752.14	
		1300.24		1122.32		177.92
trans-$HDC{=}CHD$	19062.52		16488.30		2574.22	
		1295.24		1123.11		172.13
cis-$HDC{=}CDH$	19067.52		16487.51		2580.01	
		1295.27		1126.13		169.14
gem-$D_2C{=}CH_2$	19067.49		16484.49		2583.00	
		1305.18		1127.42		177.76
$HDC{=}CD_2$	17760.66		15359.35		2401.31	
		1312.81		1130.77		182.04
$D_2C{=}CD_2$	16447.85		14228.58		2219.27	

[a] Frequencies from M. J. STERN, W. A. VAN HOOK, and M. WOLFSBERG, J. Chem. Phys., to be published.

[b] $\sum\Delta\omega_i = \sum\omega_i(C_2H_nD_{4-n}) - \sum\omega_i(C_2H_{n-1}D_{5-n})$, Barred $(\sum\Delta\omega_i)_K = \sum\omega_i(C_2H_nD_{4-n})_{Av.} - \sum\omega_i(C_2H_{n-1}D_{5-n})_K$.

Table 4. Vibrational Frequency Sums for the Isotopic Ethylenes [a].

Ethylene. – Table 4 shows zero-point energies calculated by solving the secular equations for the isotopic ethylenes with the force constants of CRAWFORD and ARNETT and of BRODERSEN [4]. There are again small deviations from the law of the mean with larger isotopic zero-point energy differences between successive pairs on increasing deuteration. The percentage deviation is much smaller for the planar vibrations than for the out-of-plane ones since the major contribution to the planar zero-point energy results from the carbon-hydrogen stretches which would not be expected to lead to any deviations in the truncated expansion (1). It is seen that the *gem* compound shows larger deviations than either *cis* or *trans* for the planar vibrations. This effect may be rationalized in terms of the H_iH_j interaction which arises from the HCH bending force constant. The out-of-plane motions correspond to bending motions which involve interactions between hydrogens.

Ethane. – For some of the members of the deuterated ethane series, vibrational frequencies have been calculated with force constants based on (but not identical with) those used by SCHACHTSCHNEIDER and SNYDER [5] and with modifications of this force field. The resulting zero-point energies are given in Table 5. The neglect of off-diagonal terms in the force constant matrix (Force Field II) leads to changes of $\sim 50\ cm^{-1}$ in the zero-point energies, but the differences between successive members of the series is practically unaffected by this change in force fields. There is a small difference between the isotopic isomers H_2DCCDH_2 and H_3CCHD_2 in either

Molecule	Force Field I	Force Field II	Force Field III
H_3CCH_3	15725.57	15774.08	9395.09
Δ	657.80	658.06	393.01
H_3CCH_2D	15067.77	15116.02	9002.08
Δ	658.26	658.42	393.01
H_2DCCH_2D	14409.51	14457.60	8609.07
Δ*	666.62	666.79	393.14
H_3CCHD_2	14401.15	14449.23	8608.94
HD_2CCD_3	12399.92	12447.54	7429.52
Δ	675.59	675.65	393.28
D_3CCD_3	11724.33	11771.89	7036.24

* Difference between H_3CCH_2D and H_3CCHD_2.

Table 5. Zero-point Energies and Differences (in cm^{-1}) for Isotopic Ethanes.

Force Field I: Complete SCHACHTSCHNEIDER type force field.
Force Field II: SCHACHTSCHNEIDER force field with no interaction force constants.
Force Field III: Only stretching force constants.

[4] R. L. ARNETT and B. L. CRAWFORD, J. Chem. Phys. **18**, 118 [1950]. – S. BRODERSEN, Mat. Fys. Skr. Dan. Vidensk. Selsk. **1**, no. 4 [1957].

[5] J. H. SCHACHTSCHNEIDER and R. G. SNYDER, private communication.

Molecule	$\sum^{30}\omega_i$	$\sum^{30}\Delta\omega_i$	$\sum^{21}\omega_i$ (planar)	$\sum^{21}\Delta\omega_i$ (planar)	$\sum^{9}\omega_i$ (non-planar)	$\sum^{9}\Delta\omega_i$ (non-planar)
C_6H_6	43109.2		36317.2		6792.0	
		1377.8		1163.9		213.9
C_6H_5D	41731.4		35153.3		6578.1	
		1378.3		1164.3		214.0
o-$C_6H_4D_2$	40353.1		33989.0		6364.1	
		1377.8		1164.1		213.7
m-$C_6H_4D_2$	40353.6		33989.2		6364.4	
		1377.8		1164.1		213.7
p-$C_6H_4D_2$	40353.6		33989.2		6364.4	
		1379.1[a]		1164.6		214.5
1,2,3-$C_6H_3D_3$	38974.4		32824.6		6149.8	
		1378.6		1164.4		214.2
1,2,4-$C_6H_3D_3$	38974.9		32824.8		6150.1	
		1378.1		1164.3		213.8
1,3,5-$C_6H_3D_3$	38975.4		32824.9		6150.5	
		1380.0		1165.1		214.9
o-$C_6H_2D_4$	37594.9		31659.7		5935.2	
		1379.1		1164.7		214.4
m-$C_6H_2D_4$	37595.9		31660.2		5935.7	
		1379.2		1164.6		214.6
p-$C_6H_2D_4$	37595.8		31660.3		5935.5	
		1379.7		1164.9		214.8
C_6HD_5	36215.8		30495.2		5720.6	
		1380.0		1165.0		215.0
C_6D_6	34835.8		29330.2		5505.6	

[a] For the meaning of the bars, reference should be made to Table 4.

Table 6. Vibrational Frequency Sums of the Deutero-benzenes.

case. Once again, one observes that successive deuterium substitution leads to larger differences as the extent of substitution increases. The effect of neglecting all but stretching force constants is similar to that found in the case of methane, and the change in zero-point energy is almost exactly a linear function of the number of substituted atoms.

Benzene. – Table 6 shows zero-point energies which were calculated for the isotopic benzenes by solving the relevant secular equations with the use of the force constants of CRAWFORD and MILLER [6]. The law of the mean is valid to a high degree here. The isotopic hydrogens are separated from each other by at least two carbon atoms and this leads to very small interactions between them. The latter is also evidenced by the fact that the various sets of isotopic isomers (e. g. *o*-, *m*-, and *p*-$C_6H_4D_2$) have very closely the same zero-point energies.

[6] F. A. MILLER and B. L. CRAWFORD, J. Chem. Phys. **14**, 282 [1946]. – B. L. CRAWFORD and F. A. MILLER, J. Chem. Phys. **17**, 727 [1949].

Conclusion

The expansion (1) for the zero-point energy has been examined. Special emphasis has been placed on the effect of the proper choice of ω_0 on the convergence of the series. An argument has been advanced for making a reasonable choice of ω_0 in a polyatomic molecule. With proper choice of ω_0, the convergence for the series is reasonably good at $p=2$. Isotope effects are also calculated quite well by means of differences in the truncated series. The results of the series expansion have been shown for methane. Secular equation solutions for zero-point energies in the isotopic methanes, ethanes, ethylenes, and benzenes have been presented to demonstrate some of the factors on which the validity of the law of the mean rests.

Acknowledgement

It is a pleasure to thank Dr. J. H. SCHACHTSCHNEIDER for making available to us his computer programs for calculating frequencies of polyatomic molecules. These programs were employed in making most of the "secular equation" type of calculations.