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TO THE REDUCED PARTITION FUNCTION OF
ISOTOPIC MOLECULES

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1. Introduction

The reduced partition function ratio of isotopic molecules introduced by Bigeleisen and Mayer [1] in the statistical mechanics of isotopic systems has the form

$$\frac{s}{s'} f = \prod_{i=1}^{3N-6} \frac{u_i}{u'_i} \frac{e^{-u_i/2}}{e^{-u'_i/2}} \frac{1 - e^{-u'_i}}{1 - e^{-u_i}} \quad /1.1/$$

where $u_i = hc\omega_i/kT$, ω_i is the i -th normal vibrational frequency /in cm^{-1} /, $3N-6$ is the number of internal degrees of freedom for a molecule with N atoms / $3N-5$ for a linear molecule/, while u'_i and u_i stand for light and heavy isotopic species, respectively.

The logarithm of the reduced partition function ratio

$$\ln s/s' f = \sum_i \left[\ln b(u'_i) - \ln b(u_i) \right] \quad /1.2/$$

where

$$\ln b(u) = -\ln u + u/2 + \ln(1 - e^{-u}) \quad /1.3/$$

can be expanded into appropriate power series which permit the quick numerical evaluation or the estimation of the equilibrium constants of isotopic exchange

reactions, the isotope effect on rate constants and the thermodynamic quantities of the isotopic systems. The approximation to $\ln s/s'f$ in terms of an even power series helped in the understanding of the nature of isotope effects.

The reduced partition function ratio and the isotope effect on the thermodynamic properties can be evaluated without actually solving the secular equation by using the method of moments [2,3] and an expansion in the even powers of u_i [2,4,5]. Bigeleisen and his coworkers used Chebyshev and Jacobi polynomials [4,5], which are interpolating polynomials, and yield a better approximation than the Bernoulli series [2] based on the Taylor expansion, while the convergence is not subject to the restriction $u'_{\max} < 2\pi$.

In the present work the different methods used for the expansion of Eq. /1.2/ are briefly reviewed and then a method which gives the best /minimax [6]/ approximation to $\ln b(u)$ will be described. The error curve of this approximation has as many extrema as possible at any given order of the expansion and the maxima and minima of the error curve have the smallest possible values. This high frequency and small amplitude oscillation of the absolute error is precisely the feature needed for a good approximation to $\ln s/s'f$.

2. The polynomial expansions of $s/s'f$ or $\ln s/s'f$

Usually it is not the reduced partition function ratio $s/s'f$ itself, but its logarithm $\ln s/s'f$ which is expanded into a power series [7].

Let us see first the expansions methods which permit the quick numerical evaluation or estimation of $\ln s/s'f$.

The expansion developed and used by Urey for the evaluation of the equilibrium constants of a number of isotopic exchange reactions [8] reads as

$$\ln s/s'f = \sum_i \ln \frac{u_i}{u_i'} + \sum_i \left[\delta_i \coth x_i + \frac{1}{12} \delta_i^3 \coth x_i (\coth^2 x_i - 1) + \dots \right] \quad /2.1/$$

where

$$x_i = \frac{u_i' + u_i}{4} ; \quad \delta_i = \frac{u_i' - u_i}{2} \quad \dots \quad /2.2/$$

This expansion converge rapidly /see Appendix I/ and can be used in most cases without the term in δ_i^3 . A similar expansion was formulated by Waldmann already in 1943 [9].

For the numerical evaluation of $\ln s/s'f$ the most successful seems to be the $G(u)$ expansion introduced by Bigeleisen and Mayer [1]. The result of the expansion which to first order has the form

$$\ln s/s'f = \sum_i G(u_i) \Delta u_i \quad /2.3/$$

was extended to third order [2] as

$$\ln s/s'f = \sum_i G(u_i) \left[1 + \frac{S(u_i)}{2G(u_i)} \frac{\Delta u_i}{u_i} + \frac{C(u_i) - 2S(u_i)}{6G(u_i)} \left(\frac{\Delta u_i}{u_i} \right)^2 \right] \Delta u_i \quad /2.4/$$

where

$$G(u_i) = \frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i} - 1} \quad /2.5/$$

$$S(u_i) = \frac{1}{u_i} - \frac{u_i e^{u_i}}{(e^{u_i} - 1)^2} \quad /2.6/$$

and

$$C(u_i) = \frac{2u_i^2 e^{2u_i}}{(e^{u_i} - 1)^3} - \frac{u_i(u_i + 2) e^{u_i}}{(e^{u_i} - 1)^2} \quad \dots \quad /2.7/$$

The functions $G(u_i)$, $S(u_i)$ and $C(u_i)$ have been tabulated for different values of u_i [10,1]. The convergence restriction on this series is that $\Delta u_i/u_i < 1$, thus it converges for all the physically possible values of u_i and Δu_i /see Appendix II/. The $G(u)$ expansion was extended by Vojta to order n [7,11] as

$$\ln s/s'f = \sum_i \sum_{k=1}^{\infty} (-1)^k G_k(u_i) (\Delta u_i)^k \quad /2.8/$$

$$G_1(u_i) = - \left(\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i} - 1} \right) \equiv -G(u_i) \quad /2.9/$$

$$G_k(u_i) = \frac{1}{ku^k} - \frac{1}{k!} \sum_{n=1}^{\infty} n^{k-1} e^{-nu_i} \quad k > 2 \quad /2.10/$$

An approximation in the form

$$\frac{e^{-hc\omega'_1/2kT} \left(1 - e^{-hc\omega_1/kT}\right)}{e^{-hc\omega_1/2kT} \left(1 - e^{-hc\omega'_1/kT}\right)} \approx \frac{\omega_1}{\omega'_1} \quad /2.11/$$

was introduced by Tatevskii [12,13]. This approximation works well at higher temperatures and the equilibrium constant of an isotopic exchange reaction can be evaluated in a simple manner from the ratios of the symmetry numbers of the participating isotopic molecules. If the zero point energy cannot be ignored the author used instead of Eq. /2.11/ the expression

$$\frac{e^{-hc\omega'_1/2kT} \left(1 - e^{-hc\omega_1/kT}\right)}{e^{-hc\omega_1/2kT} \left(1 - e^{-hc\omega'_1/kT}\right)} = \frac{\omega_1}{\omega'_1} \gamma_1 \left(\frac{\omega_1}{\omega'_1}, \frac{\omega_1}{T}\right) \quad /2.12/$$

The function γ_1 has been evaluated and tabulated for various values of ω_1/ω'_1 and ω_1/T . Since the exact meaning of the function γ_1 is not clear and the expressions are fairly complicated, the Bigeleisen-Mayer $G(u)$ approximation is preferably used for the calculations.

At lower temperatures the isotopic difference in the zero point energies plays an important role. The zero point energy difference was approximated by Bigeleisen and Goldstein [14] in terms of a Taylor series of even powers of the frequencies around an arbitrarily chosen point λ_0 as

$$\frac{1}{\omega_0} \sum_i (\omega'_i - \omega_i) = \frac{1}{2} \sum_i \frac{\delta\lambda_i}{\lambda_0} + \sum_i \sum_{p=2}^{\infty} \frac{(-1)^{p+1} (2p-2)!}{2^{2p-1} (p-1)!} \quad /2.13/$$

$$\sum_{j=0}^{p-1} \frac{(-1)^j}{j!(p-j)!} \frac{\delta\lambda_i^{p-j}}{\lambda_0^{p-j}}$$

where

$$\lambda_i = 4\pi^2 c \nu_i^2 \quad /2.14/$$

$$\delta\lambda_i^n = \lambda_i'^n - \lambda_i^n \quad /2.15/$$

The value of λ_0 must be selected from the frequency spectrum by considering that the condition of the convergence is that

$$\frac{\lambda'_1 - \lambda_0}{\lambda_0} \leq 1 \quad /2.16/$$

This expression was used for studying the relations between the zero point energies of isotopic homologues [15].

In the formulation of the relationships between the reduced partition function ratios of multiple isotope substituted molecules the Bernoulli series [2]

$$\ln s/s'f = \sum_i \sum_{j=1}^{\infty} (-1)^{j+1} \frac{B_{2j-1}}{2^j (2j)!} \delta(u_i^{2j}) \quad /2.17/$$

where B_{2j-1} are the Bernoulli numbers [16], $\delta(u_i^{2j}) = u_i'^{2j} - u_i^{2j}$, proved to be useful. Because of the convergence restriction $u'_{\max} < 2\pi$ on the Bernoulli series, this expansion can be applied only at higher temperatures and to molecules with not too high frequencies. Vojta [17] has given two new proofs of the Bernoulli series expansion. The first term in Eq./2.17/ is the first quantum correction to the reduced partition function ratio of isotopic molecules from which a fundamental expression for the description of the isotope effects of equilibrium systems can be obtained [2] as

$$\frac{1}{24} \left(\frac{hc}{kT} \right)^2 \sum_{i=1}^{3N} \left[(m'_i)^{-1} - (m_i)^{-1} \right] a_{ii} \quad /2.18/$$

where m'_i is the mass of the i -th atom in the light, m_i that in the heavy isotopic molecule and a_{ii} is the Cartesian force constant of the i -th atom in the molecule.

In the $\bar{\gamma}$ method [2] proposed for extending the validity of the Bernoulli expansion γ_i is defined as

$$\gamma_i = 12G(u_i)/u_i \quad /2.19/$$

which, introduced into Eq./2.3/ yields

$$\ln s/s'f = \sum_i \gamma_i \frac{u_i}{12} \Delta u_i \quad /2.20/$$

Since γ_i does not decrease very rapidly with u_i , an average value $\bar{\gamma}$ can be defined if the frequencies of the molecule lie within a narrow range and we can write

$$\ln s/s'f \cong \frac{\bar{Y}}{24} \sum_i \delta u_i^2 \quad /2.21/$$

The applicability of Eq. /2.21/ has been investigated by several authors [18,19,20,21,22].

The restriction $u'_{\max} < 2\pi$ to the convergence of the Bernoulli series was removed by Bigeleisen and Ishida [4] who used shifted Chebyshev polynomials of the first kind for the expansion into even powers of u'_i and u_i . They started from the expression of $\ln b(u)$ [23] as

$$\ln b(u) = \sum_{k=1}^{\infty} \ln \left[1 + \left(\frac{u}{2\pi k} \right)^2 \right] \quad /2.22/$$

This infinite series converges for all values of u . Applying the τ method proposed by Lanczos [24] Bigeleisen and Ishida obtained

$$\ln b(u) = \sum_{m=1}^n \frac{(-1)^{m+1} B_{2m-1} u^{2m}}{2m(2m)!} T(n,m,u_{\max}) \quad /2.23/$$

where

$$T(n,m,u_{\max}) = \frac{\left[\sum_{p=m}^n (-1)^p C_n^p / R^p \right]}{\left[\sum_{p=0}^n (-1)^p C_n^p / R^p \right]} \quad /2.24/$$

$$R = (u_{\max}/2\pi)^2 \quad /2.25/$$

and

$$C_n^p = (-1)^{n+p} 2^{2p} n(n+p-1)! / (n-p)! (2p)! \quad /2.26/$$

Then

$$\ln s/s'f = \sum_i \sum_{m=1}^n \frac{(-1)^{m+1} B_{2m-1} \delta u_i^{2m}}{2m(2m)!} T(n,m,u_{\max}) \quad /2.27/$$

The expansion /2.27/ differs from the Bernoulli series /2.17/ essentially only by that each term is multiplied by the modulating coefficient $T(n,m,u_{\max})$ and this causes the new series to converge much faster than the Bernoulli series.

The method was extended to the group of the Jacobi polynomials [5]

$$P_n^{(\gamma, \delta)}(x) = 1 + \sum_{m=1}^n x^m \prod_{k=0}^{m-1} \frac{(-n+k)(n+\gamma+\delta-1+k)}{(\gamma+k)(1+k)} \quad /2.28/$$

The expansion of the logarithmic terms in Eq. /2.22/ applying the τ method and using a common range $R = (u'_{\max}/2\pi)^2$, with u'_{\max} being the highest frequency of the light isotopic molecule, leads to the expression

$$\ln s/s'f = \sum_{m=1}^n \frac{(-1)^{m+1} B_{2m-1} \sum_1 \delta u_1^{2m}}{2m (2m)!} T^{\gamma, \delta}(n, m, u'_{\max}) \dots \quad /2.29/$$

The approximation to $\ln b(u)$ could be improved by subdividing the range of the expansion variable. On dividing the summation of Eq. /2.22/ into two parts they obtained

$$\ln b(u) = \sum_{k=1}^L \ln \left[1 + \left(\frac{u}{2\pi k} \right)^2 \right] + \sum_{k=L+1}^{\infty} \ln \left[1 + \left(\frac{u}{2\pi k} \right)^2 \right] \quad /2.30/$$

where L is a finite, positive integer. It was shown that the approximation to $\ln b(u)$ improves with increasing values of L , but the use of higher values than 5 does not seem to be worth while.

A search was made [5] for the "best" Jacobi polynomial by minimizing the weighted root-mean-square-error /RMSE/ expressed as

$$RMSE = \sqrt{\frac{\int_0^{u_{\max}} w(u) [\epsilon(u) - \bar{\epsilon}]^2 du}{\int_0^{u_{\max}} w(u) du}} \quad /2.31/$$

where $w(u)$ is the weighting function and $\bar{\epsilon}$ is the mean of the absolute errors of the expansion of $\ln b(u)$ expressed as

$$\bar{\epsilon} = \frac{\int_0^{u_{\max}} w(u) \epsilon(u) du}{\int_0^{u_{\max}} w(u) du} \quad /2.32/$$

With the assumption of $w(u) \propto u$ the RMSE was numerically evaluated for the systematically varied two parameters γ and δ of the Jacobi polynomial. By comparing the results the "best" Jacobi polynomial was obtained for every combination of the fixed range $u_{\max} = 1\pi, 2\pi, \dots, 8\pi$, and order $n = 1, 2, 3, 4$ for both $L = 0$ and $L = 5$. The parameters γ and δ of the "best" Jacobi polynomials were listed in tabulated form. Since the weighting function $w(u)$ depends on the frequency distribution in the molecule and on the values of the isotopic shifts on the frequencies in order to find the "best" Jacobi polynomial for a given molecule it might be necessary to establish a suitable weighting function in each case.

In the method to be described in the following for the approximation to $\ln b(u)$ polynomials in terms of the even powers of u are used, the convergence restriction $u'_{\max} < 2\pi$ on the Bernoulli series is removed and the amplitude of the error curve is as small as possible.

3. The minimax approximation to $\ln b(u)$

The so-called minimax approximation method [6] is based on some definitions and theorems which will be briefly recalled before showing its use for the function $\ln b(u)$. The aim is to expand the function $\ln b(u)$ into a series of even powers of u . Let H be a set of the polynomials

$$P_n(u) = \sum_{k=0}^n a_k u^{2k} \quad /3.1/$$

and $Q_n(u) \in H$ be the polynomial for which the expression

$$\max_{0 \leq u \leq u_{\max}} |\ln b(u) - P_n(u)| \quad /3.2/$$

has a minimum value $/u_{\max} = \frac{hc\omega_{\max}}{kT} /$. The polynomial $Q_n(u)$ is the minimax approximation to the function $\ln b(u)$. Using the notation

$$E_n = \max_{0 \leq u \leq u_{\max}} |\ln b(u) - Q_n(u)| \quad /3.3/$$

the error function obtained by the $Q_n(u)$ polynomial in the form

$$E_n(u) = \ln b(u) - Q_n(u) \quad /3.4/$$

takes by the Chebyshev theorem [25] its extreme values $\pm E_n$ at $n+2$ distinct points, with alternating sign in the interval $[0, u_{\max}]$, that is

$$E_n(u_1) = \alpha E_n, \quad E_n(u_2) = -\alpha E_n, \quad E_n(u_3) = \alpha E_n, \quad \dots \quad /3.5/$$

$$0 \leq u_1 < u_2 < u_3 \dots \leq u_{\max} \quad ; \quad \alpha = \pm 1$$

Conversely, if there is a polynomial which approximates the function with a deviation having its extreme values at $n+2$ distinct points, with alternating sign in the interval of the approximation, then this polynomial is the minimax approximation of the function in question. Unfortunately, no explicit formula can be given for the coefficients of the minimax approximation to a function, but there are some numerical processes by which they can be evaluated to a desired accuracy. By using these methods the error function of some initial approximations to a given functions can be improved so that it obtains the properties characterizing the error function of the minimax approximation. The partial sum of the Taylor expansion, some interpolating polynomials, the partial sum of some orthogonal expansions, the expansion formula for $\ln b(u)$ obtained by Bigeleisen and Ishida with the use of the Lanczos τ method [4] etc. can be regarded as initial approximation.

To formulate the minimax approximation to $\ln b(u)$, it is first expanded in terms of Chebyshev polynomials, second the Chebyshev coefficients are improved by the method of Hornecker [26] and finally a numerical test is performed to see whether the error function has the properties required by the Chebyshev theorem.

The Chebyshev expansion of the $\ln b(u)$ is written in the form

$$\ln b(u) = \frac{c_0}{2} + \sum_{k=1}^{\infty} c_k T_k^*(x^2) \quad 0 \leq x \leq 1 \quad /3.6/$$

where

$$x = \frac{u}{u_{\max}} \quad 0 \leq u \leq u_{\max} \quad /3.7/$$

$$c_k = \frac{4}{\pi} \int_0^1 \ln b(x \cdot u_{\max}) T_k^*(x^2) \frac{1}{\sqrt{1-x^2}} dx \quad /3.8/$$

and

$$T_k^*(x^2) = \cos [k \arccos (2x^2 - 1)] \quad k=0,1,2,\dots \quad /3.9/$$

stands for the orthogonal polynomials transformed to $[0,1]$ interval, the so-called Chebyshev polynomials [24]. Unfortunately, the integrals /3.8/ can be evaluated only by numerical processes.

For the calculation of the coefficients c_k , use is made of the expansion of $\ln b(u)$ given by Eq. /2.22/ and the equation

$$\ln(1+x) = x \int_0^1 \frac{dy}{1+xy} \quad /3.10/$$

Eq. /2.22/ can be thus rewritten as

$$\ln b(u) = \sum_{k=1}^{\infty} \frac{u^2}{4\pi^2 k^2} \int_0^1 \frac{1}{1 + \frac{u^2}{4\pi^2 k^2} y} dy \quad /3.11/$$

Using an even power series expansion of the function $1/\left(1 + \frac{u^2}{4\pi^2}\right)$ [27]

$$\frac{1}{1 + \frac{u^2}{4\pi^2}} = \sum_{m=0}^n b_m u^{2m} + h(u^2) \quad /3.12/$$

and substituting it in Eq. /3.11/ we obtained the polynomial approximation to $\ln b(u)$ as

$$\ln b(u) = \frac{u^2}{24} \sum_{m=0}^n b_m \frac{\zeta(2m+2)}{\zeta(2)} \frac{1}{m+1} u^{2m} + H \quad /3.13/$$

where

$$H = \frac{u^2}{24} \sum_{k=1}^{\infty} \frac{1}{\zeta(2)k^2} \int_0^1 h\left(\frac{u^2}{k^2} t\right) dt \quad /3.14/$$

and $\zeta(m) = \sum_{\ell=1}^{\infty} 1/\ell^m$ the Riemann zeta function. For the estimation of the error H of $\ln b(u)$ we get by /3.14/

$$|H| \leq \frac{u_{\max}^2}{24} |h| \quad /3.15/$$

On multiplying the coefficients b_m of the approximation /3.12/ by $\frac{\zeta(2m+2)}{\zeta(2)(m+1)}$ and by rearranging this polynomial approximation in terms of

Chebyshev polynomials [24] we get the approximate values of the coefficients c_k defined by Eq. /3.8/. On improving the approximate values of the coefficients c_k by the Hornecker method [26] we get the coefficients of the mini-max approximation of the function $\ln b(u)$.

The curves for the absolute error in $\ln b(u)$ obtained by the mini-max approximation over the ranges $[0, 4\pi]$ and $[0, 8\pi]$ as a function of u for orders $n = 1-4$ can be seen in Figs. 1 and 2, respectively. For comparison also the error curves plotted for the Chebyshev $[L=0, L=5]$, and the "best" Jacobi polynomial approximations of Bigeleisen et.al. [5] are shown. It is apparent from the figures that the shape of the error function for $\ln b(u)$ has the properties of the minimax approximation: it exhibits uniform small amplitude oscillations on both sides of the abscissa and has the number of extrema required by the Chebyshev theorem.

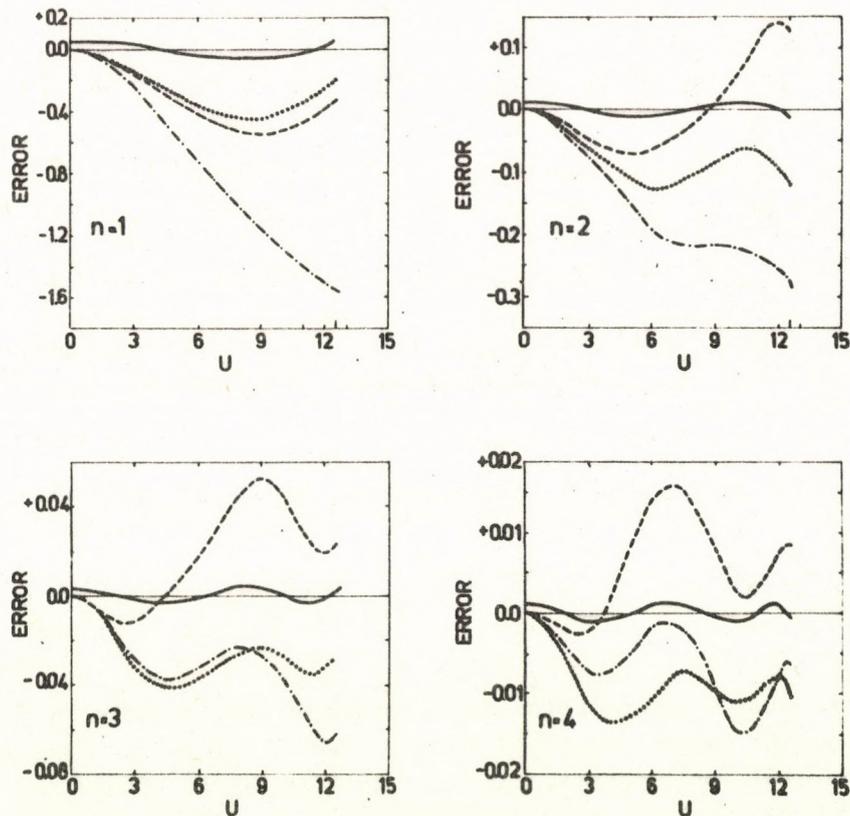


Fig. 1

Intercomparison of the absolute error in $\ln b(u)$ obtained by various approximations over the range $[0, 4\pi]$ as a function of u for orders $n = 1-4$

..... "Best" Jacobi polynomial $L=5$, ----- Chebyshev polynomial $L=5$, -.-.-.-. Chebyshev polynomial $L=0$ [5], _____ minimax approximation.

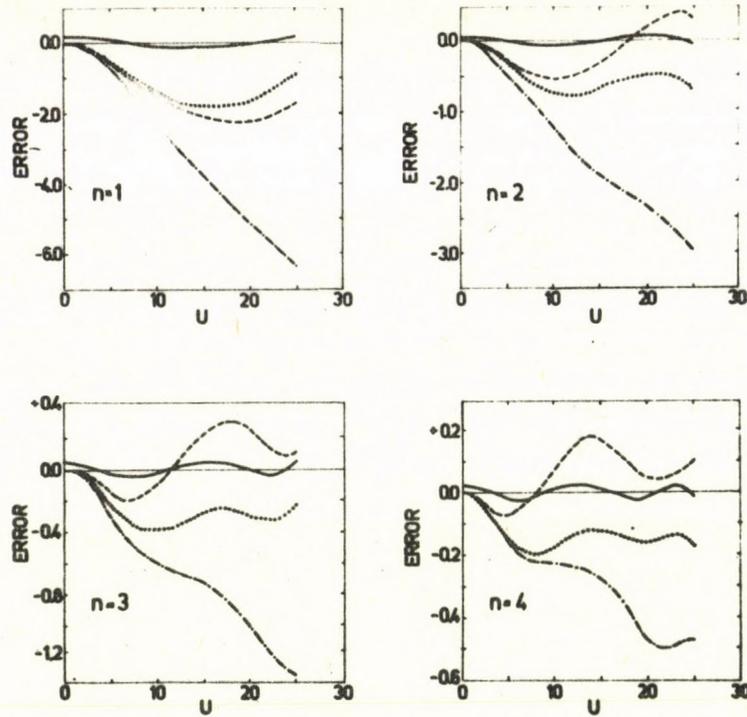


Fig. 2

Intercomparison of the absolute error in $\ln(u)$ obtained by various approximations over the range $[0, 8\pi]$ as a function of u for orders $n = 1-4$

..... "Best" Jacobi polynomial $L=5$, ----- Chebyshev polynomial $L=5$, -.-.-.-. Chebyshev polynomial $L=0$ [5], _____ minimax approximation.

The l th derivative of the expression /2.22/ can be written as

$$\frac{d^l}{d(u^2)^l} \ln b(u) = (-1)^l (l-1)! \sum_{k=1}^{\infty} \frac{1}{(4\pi^2 k^2)^l} \frac{1}{\left(1 + \frac{u^2}{4\pi^2 k^2}\right)^l} \quad /3.16/$$

It can be shown that the derivative of any order of the function $\ln b(u)$ is nonzero over the range $[0, u_{\max}]$ and thus two of the extrema are at the end of the interval [28], that is the constant term of the approximation is nonzero. This fact, however, does not give any trouble in the calculation of the reduced partition function ratio considering that owing to the difference $\ln b(u') - \ln b(u)$ in Eq. /1.2/ the constant terms cancel each other on expanding both $\ln b(u')$ and $\ln b(u)$ in the same power series using a common u'_{\max} determined by the highest frequency of the light isotopic molecule.

The coefficients $a(n, k, u_{\max})$ of the approximation

$$\ln b(u) = \sum_{k=0}^n a(n, k, u_{\max}) \cdot \left(u/u_{\max}\right)^{2k} \quad /3.17/$$

for $u_{\max} = 1, 2, \dots, 30$ and for $n = 1-4$ are listed in Table I. /As mentioned above, the coefficient $a(n, 0, u_{\max})$ of the approximation equals the amplitude of the error curve./

The coefficients $a(n, k, u_{\max})$ as a function of n and k are shown in Figures 3, 4, 5, while the absolute error as a function of n for $u_{\max} = 20$ and 30 can be seen in Fig. 6.

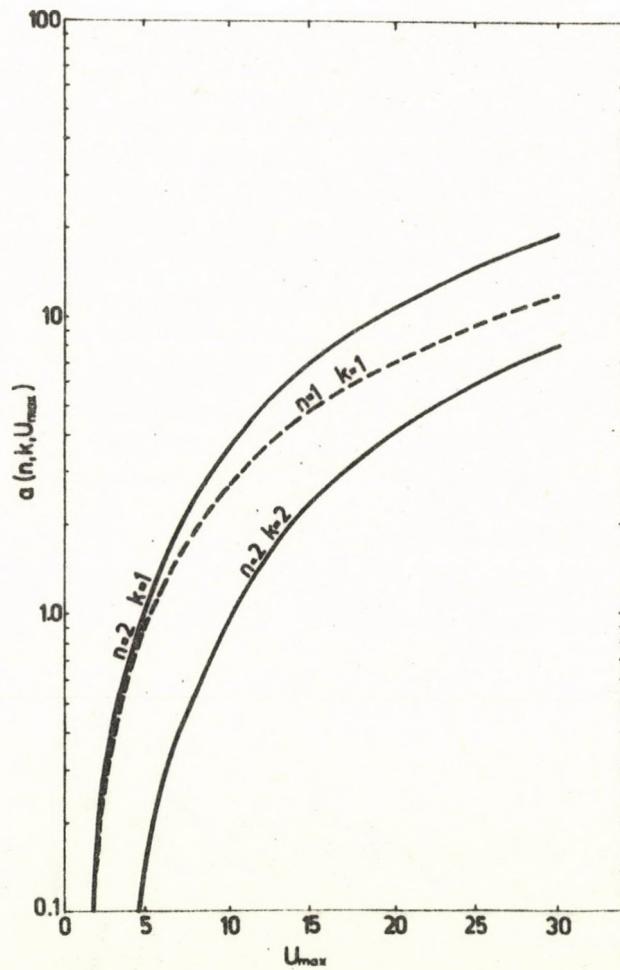


Fig. 3

Coefficients of the minimax approximation to $\ln b(u)$ as a function of u_{\max} for $n = 1, 2$.

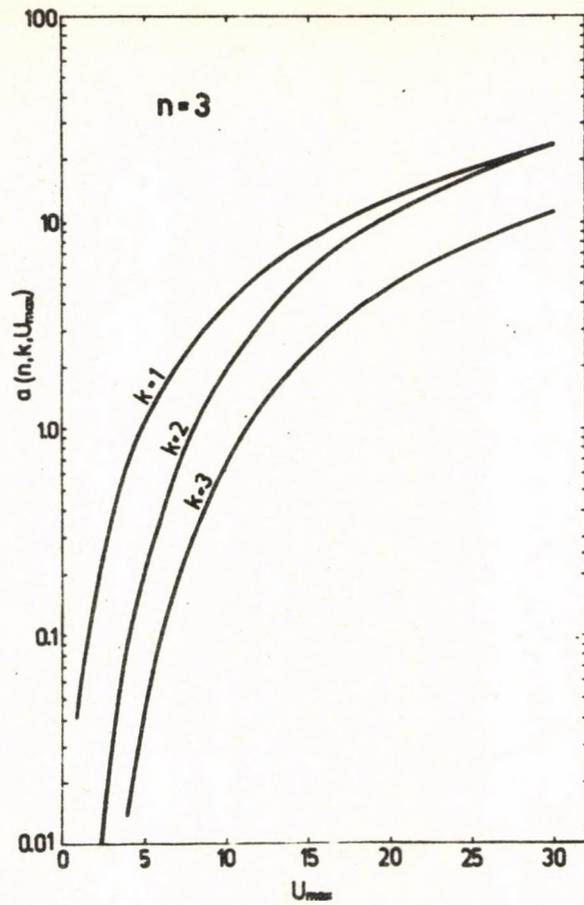


Fig. 4

Coefficients of the minimax approximation to $\ln b(u)$ as a function of u_{\max} for $n = 3$.

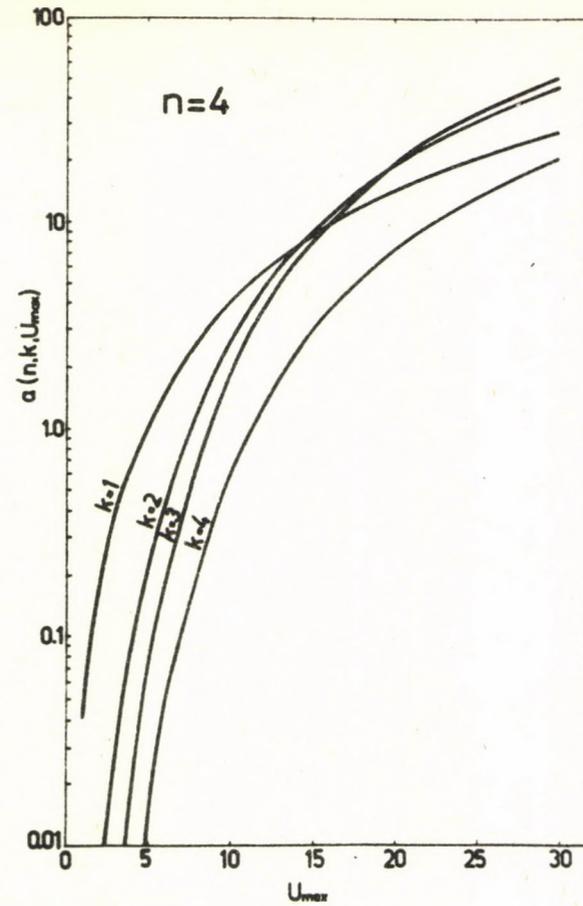


Fig. 5

Coefficients of the minimax approximation to $\ln b(u)$ as a function of u_{\max} for $n = 4$.

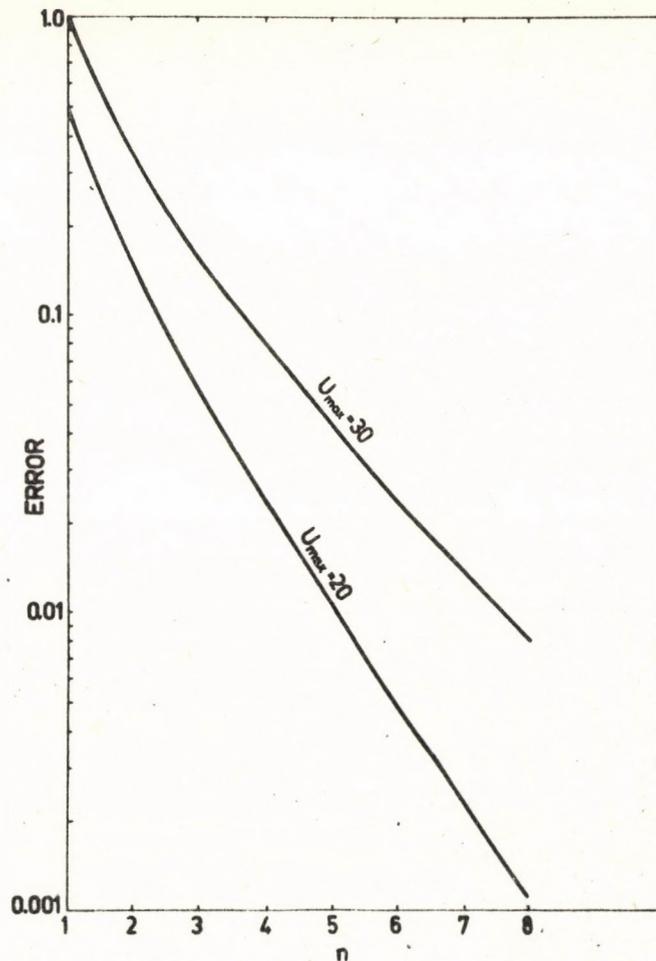


Fig. 6

Absolute error in $\ln b(u)$ obtained by the minimax approximation as a function of n , the order of the expansion for $u_{\max} = 20, 30$.

The variation of the absolute error with u_{\max} for different values of n is plotted in Fig. 7.

It can be shown that the error of the $(n+1)$ -th order approximation becomes for large orders equal to the error of the n -th order approximation multiplied by q , since

$$\lim_{n \rightarrow \infty} \frac{E_{n+1}}{E_n} = q = \frac{R}{(1 + \sqrt{1+R})^2}, \quad R = \left(\frac{u_{\max}}{2\pi}\right)^2 \quad /3.18/$$

/see Appendix III/. For large values of u_{\max} , q is close to unity. This means that the error decreases very slowly with increasing n , e.g. for $u_{\max} = 20$ and $u_{\max} = 30$, $q = 0.54$ and $q = 0.66$, respectively. Thus, the error is not reduced even by half if the order of the approximation is increased by one. Consequently for too large u_{\max} a few terms cannot give a good convergence.

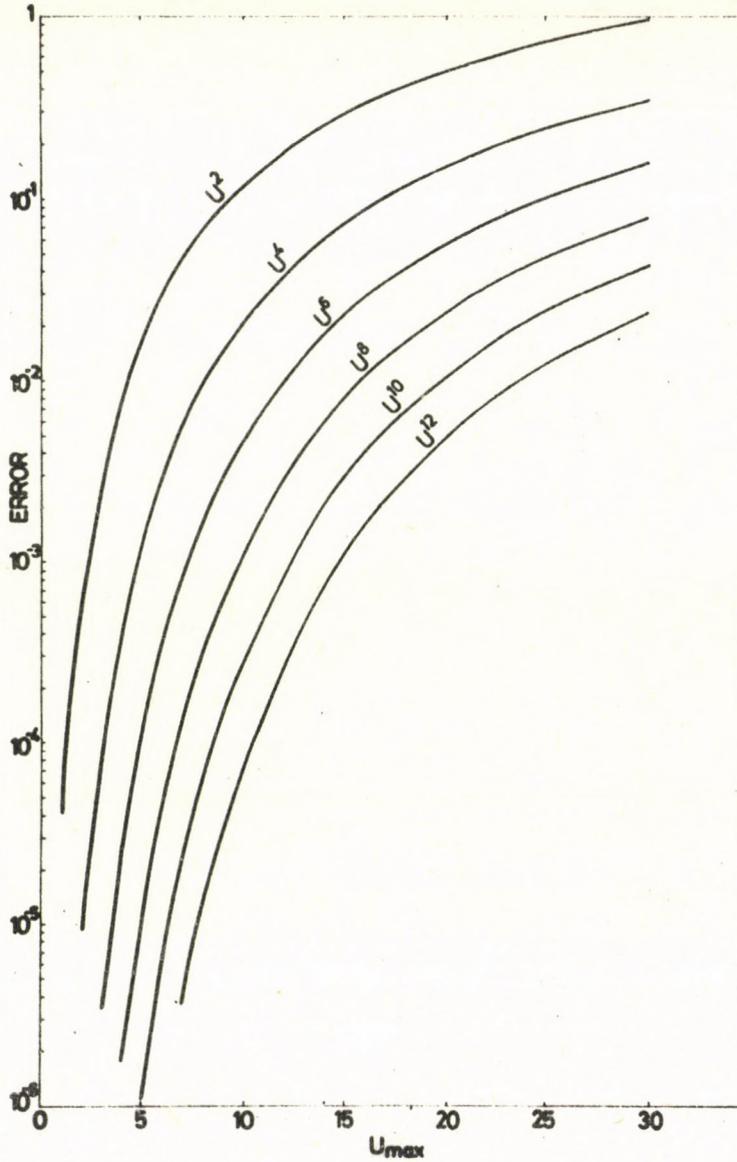


Fig. 7

Absolute error in $\ln b(u)$ obtained by the minimax approximation as a function of u_{\max} and n , the order of expansion.

The absolute values of the percent error of the approximation over the range $[0,20]$ as a function of $n = 2,4,6$ are shown in Fig.8.

On substituting Eq. /3.17/ into the expression /1.2/ we obtain

$$\ln s/s'f = \sum_{k=1}^n a(n,k,u'_{\max}) \sum_{i=1}^{3N-6} \delta(u_i/u'_{\max})^{2k} \quad /3.19/$$

where

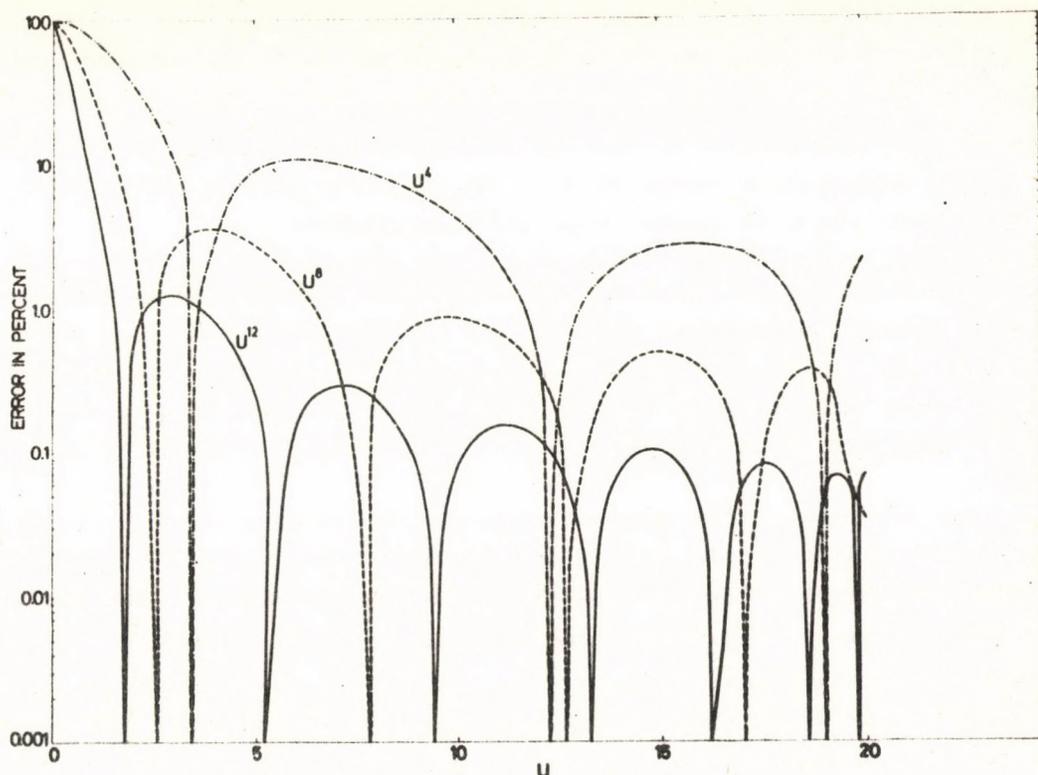


Fig. 8

Percent error in $\ln b(u)$ obtained by the minimax approximation over the range $[0, 6\pi]$ as a function of u and n , the order of expansion.

$$\delta \left(u_i / u'_{\max} \right)^{2k} = \frac{u_i^{2k} - u_i'^{2k}}{u_{\max}^{2k}} \quad /3.20/$$

ω'_{\max} can be estimated without actually solving the secular equation by applying the "row-sum and column-sum" method used by Bigeleisen et.al. [5].

In the next chapter some applications to polyatomic molecules, an analysis of the accuracy obtainable and a comparison of the results of the minimax approximation with those obtained by Bigeleisen et.al. [5] will be presented.

4. Application of the minimax method

The minimax approximation method was used for the evaluation of the reduced partition function ratios of some pairs of isotopic molecules and the approximations to the exact values were compared with those obtained by other methods. For the exact calculations of $\ln s/s'$ the individual molecular frequencies were evaluated by using the Wilson FG-matrix method [29]. The

value of u'_{\max} was computed at each temperature from the highest molecular frequency of the system and rounded off to the next higher integer. The coefficients of the polynomial for the rounded value of u'_{\max} were taken from Table I. The temperature range covered by the calculation was chosen to be wider than that which is experimentally significant.

In Tables II-IV the intercomparison of the Chebyshev expansion [4], the "best" Jacobi polynomials [5] and the minimax approximation with the exact values of $\ln s/s'f$ for isotopic pairs in ethylene and methane is presented. /The coefficients of the Chebyshev polynomials were evaluated by using the "running u" method [4]./

For the deuterated ethylene molecules /Table II/ the value of $\ln s/s'f$ of every isotopic pair was evaluated separately for the planar, non-planar and total vibrations of the molecule. It can be seen that the errors for the non-planar vibrations are smaller than those for the planar and total vibrational spectrum. This is due to the smaller value of u'_{\max} which determines in the first place the error of the minimax approximation, and to the narrower range of the non-planar vibrations. It can be seen that in the case of the total and planar vibrations the minimax method gives better results than the Chebyshev expansion, especially so, at room temperature and low values of the order n . The accuracy of the minimax approximation is not worsened if more protium are substituted by deuterium.

The intercomparison of the different approximations to the $\ln s/s'f$ for the planar vibrations of mono-deuteroethylene /Table III/ is difficult because of the fact that different Chebyshev / $L=0$, $L=5$ / and "best" Jacobi / $L=0$, $L=5$ / polynomials yield the best results at different temperatures and orders, i.e. the "best" Jacobi polynomials are not always the best. A detailed inspection of the values in Table III, however, shows that the minimax method gives in this particular example at least as good results as the other approximations. Similar conclusions can be made from Table IV for the mono-deuteromethane.

The results of the minimax approximation in the case of the deuterated methyl halide molecules /Table V / show that at lower temperatures even for high values of $\ln s/s'f$ the method works very well. The maximum error, 11.1% is obtained in the case of CD_3F-CH_3F at $200^{\circ}K$ and $n=1$.

In table VI the results obtained by using the actual value of u'_{\max} are compared with those obtained by using the rounded off value for the evaluation of the coefficients of the minimax approximation in the case of CD_3F-CH_3F . If one uses the actual values of u'_{\max} the occasional breaks in the monotonous trend of the approximation disappear but it may worsen to some extent. Consequently, it presents no special advantage to use the actual value

of u'_{\max} , not to mention the difficulty caused by the necessity of evaluating the minimax approximation coefficients of $\ln b(u)$ every time the actual value of u'_{\max} is used.

The results for isotopic methanols, summarized in Table VII show for the $^{13}\text{CH}_3\text{OH}-^{12}\text{CH}_3\text{OH}$ pair of isotopic molecules the results are not better but in some cases even worse than those obtained for the deuterated methanol molecules. This is not surprising if one considers that the error of the approximation is determined above all by the value of u'_{\max} which is the same for all the isotopic methanol molecules.

It can be seen from the intercomparison of the approximations in the case of deuterated water molecules /Table VIII / that about room temperature the Bigeleisen-Mayer $G(u)$ expansion gives the best, while the minimax method the second best results. The Bernoulli expansion cannot be applied at room temperatures at which the condition $u'_{\max} < 2\pi$ does not hold. At temperatures of 1200°K and 3000°K the Chebyshev and the minimax approximations yield similar results and both are better than those obtained from the Bernoulli series. It is of interest to note that the percent errors are about equal for the $\text{HDO}-\text{H}_2\text{O}$ and $\text{D}_2\text{O}-\text{H}_2\text{O}$ pairs of isotopic molecules although the value of $\ln s/s'f$ has doubled by the introduction of the second deuterium into the H_2O . It is apparent from Fig. 9 in which the errors of the minimax approximation for the different vibrations of the H_2O , HDO , D_2O molecules are shown, if one uses a polynomial corresponding to $u'_{\max} = 19$ and $n=1$, that the increase in the percent error on replacing protium by deuterium in HDO is due primarily to the shift in the ω_3 vibrational frequency.

As a general rule it is found that the accuracy of the approximation is sensitive to the distribution of the frequencies of a given pair of isotopic molecules. Therefore it can be hardly predicted how many terms of the polynomial are needed to obtain a given accuracy. An analysis of the calculated examples shows that at about room temperature / 300°K / the maximum error of the approximation is not more than 20% for $n=1$, 10% for $n=2$ and $\sim 1\%$ for $n=3$. In a favourable case the error of the approximation may be much smaller.

The relationship between the "rules of the mean" and the polynomial expansion of $\ln s/s'f$ is thoroughly discussed by Bigeleisen and Ishida [4]. Considering the minimax approximation from this point of view, we find that e.g. in the case of deuterated water molecules /using ω'_{\max} of H_2O for the evaluation of the coefficients of the polynomial for both isotopic pairs/ the minimax approximation predicts zero quantum correction to the first order, thus satisfying the first rule of the mean, /Table IX /. In order to approximate the exact value of the quantum correction it is necessary to use a polynomial with at least $n=3$.

Table I. The coefficients $a(n, k, u_{\max})$ of the minimax approximation

u_{\max}		1	2	3	4	5	6
	k						
n=1	0	0.000042	0.00063	0.0029	0.0080	0.017	0.030
	1	0.041325	0.16144	0.3503	0.5952	0.884	1.206
n=2	0	0.00000016	0.0000095	0.000092	0.00042	0.0013	0.0029
	1	0.04166366	0.1664907	0.373254	0.65842	1.0159	1.4378
	2	-0.00033914	-0.0050704	-0.023119	-0.06404	-0.1346	-0.2378
n=3	0	0.00000001	0.00000017	0.0000035	0.000026	0.00011	0.00034
	1	0.04166664	0.16666111	0.3748846	0.665765	1.03765	1.48737
	2	-0.00034710	-0.00553713	-0.0275124	-0.083972	-0.19416	-0.37467
	3	0.00000531	0.00030538	0.0029473	0.013427	0.04031	0.09306
n=4	0	0.00000000	0.00000000	0.00000014	0.0000018	0.000011	0.000044
	1	0.04166667	0.16666650	0.37499262	0.6665726	1.041067	1.497535
	2	-0.00034722	-0.00555420	-0.02806351	-0.0880828	-0.211705	-0.427338
	3	0.00000551	0.00034884	0.00384550	0.0200838	0.068876	0.179286
	4	-0.00000010	-0.00002178	-0.00044636	-0.0033569	-0.014458	-0.043812

Table I. (Continued)

u_{\max}		7	8	9	10	11	12	13	14
k									
n=1	0	0.047	0.067	0.091	0.119	0.149	0.181	0.216	0.252
	1	1.553	1.920	2.303	2.697	3.102	3.515	3.934	4.359
n=2	0	0.0056	0.0096	0.015	0.021	0.029	0.039	0.049	0.061
	1	1.9157	2.4416	3.008	3.610	4.241	4.898	5.577	6.275
	2	-0.3737	-0.5405	-0.735	-0.956	-1.198	-1.461	-1.741	-2.036
n=3	0	0.00082	0.0016	0.0029	0.0048	0.0072	0.010	0.014	0.018
	1	2.01030	2.6008	3.2528	3.9603	4.7173	5.519	6.360	7.236
	2	-0.63699	-0.9871	-1.4264	-1.9530	-2.5629	-3.251	-4.012	-4.840
	3	0.17986	0.3065	0.4762	0.6900	0.9476	1.247	1.587	1.965
n=4	0	0.00013	0.00031	0.00063	0.0011	0.0019	0.0030	0.0043	0.0061
	1	2.03413	2.64800	3.33542	4.0920	4.9131	5.7939	6.7296	7.7158
	2	-0.76157	-1.23604	-1.86596	-2.6602	-3.6221	-4.7507	-6.0421	-7.4900
	3	0.38498	0.71863	1.20778	1.8729	2.7273	3.7779	5.0262	6.4701
	4	-0.10462	-0.21099	-0.37585	-0.6097	-0.9201	-1.3119	-1.7874	-2.3470

Table I. (Continued)

u_{\max} k	15	16	17	18	19	20	21	22
n=1 0 1	0.290 4.790	0.330 5.224	0.371 5.662	0.414 6.104	0.457 6.548	0.502 6.994	0.548 7.443	0.595 7.894
n=2 0 1 2	0.074 6.990 -2.345	0.088 7.719 -2.666	0.103 8.461 -2.998	0.119 9.215 -3.340	0.136 9.978 -3.690	0.153 10.751 -4.048	0.172 11.531 -4.413	0.191 12.319 -4.785
n=3 0 1 2 3	0.023 8.144 -5.730 2.377	0.029 9.080 -6.676 2.823	0.035 10.042 -7.674 3.398	0.043 11.027 -8.719 3.801	0.050 12.032 -9.807 4.329	0.058 13.056 -10.934 4.881	0.067 14.096 -12.098 5.454	0.077 15.152 -13.294 6.047
n=4 0 1 2 3 4	0.0082 8.7483 -9.0872 8.1044 -2.9897	0.011 9.823 -10.826 9.922 -3.713	0.013 10.936 -12.697 11.915 -4.515	0.017 12.085 -14.692 14.074 -5.390	0.021 13.267 -16.804 16.389 -6.337	0.025 14.478 -19.023 18.853 -7.351	0.029 15.716 -21.344 21.455 -8.428	0.034 16.979 -23.759 24.187 -9.565

Table I. (Continued)

u_{\max}		23	24	25	26	27	28	29	30
k									
n=1	0	0.643	0.692	0.741	0.791	0.842	0.894	0.946	0.999
	1	8.346	8.800	9.256	9.712	10.170	10.629	11.089	11.549
n=2	0	0.211	0.232	0.253	0.275	0.297	0.320	0.344	0.368
	1	13.113	13.914	14.719	15.529	16.344	17.162	17.984	18.810
	2	-5.161	-5.543	-5.930	-6.320	-6.715	-7.113	-7.513	-7.917
n=3	0	0.087	0.097	0.108	0.119	0.131	0.144	0.156	0.170
	1	16.222	17.305	18.399	19.504	20.619	21.743	22.875	24.015
	2	-14.521	-15.775	-17.055	-18.358	-19.683	-21.028	-22.391	-23.772
	3	6.658	7.286	7.929	8.587	9.258	9.941	10.635	11.340
n=4	0	0.039	0.045	0.051	0.058	0.064	0.072	0.079	0.087
	1	18.266	19.573	20.900	22.245	23.607	24.984	26.376	27.781
	2	-26.261	-28.844	-31.503	-34.232	-37.027	-39.884	-42.798	-45.765
	3	27.041	30.009	33.083	36.257	39.525	42.880	46.317	49.831
	4	-10.758	-12.003	-14.397	-14.638	-16.023	-17.448	-18.911	-20.411

Table II. Comparison of the minimax method with the Chebyshev expansion of $\ln s/s'f$ for ethylene.¹

Class of vibrations	T °K	Exact $\ln s/s'f$	Percent error							
			n=1	n=2	n=3	n=4	C_2H_3D/C_2H_4			
Planar	300	2.09490	-40.4 ²	-14.0	-10.5	5.5	-3.8	-0.13	0.58	-0.52
	1200	0.261075	-3.0	-1.9	-0.031	-0.040	-0.019	0.020	0.001	-0.001
	3000	0.0465407	-0.38	0.79	-0.000	-0.015	-0.000	-0.000	0.000	0.000
Non-planar	300	0.225675	-2.3	-7.6	-0.000	0.27	-0.11	0.039	0.008	-0.003
	1200	0.0176614	0.017	1.3	0.001	-0.011	-0.000	-0.001	0.000	-0.000
	3000	0.00287159	0.005	0.51	0.000	0.001	-0.000	-0.000	0.000	-0.000
Total	300	2.32057	-42.9	-10.1	-11.8	6.0	-3.9	0.021	0.54	-0.54
	1200	0.278736	-3.6	-1.2	-0.071	0.010	-0.019	0.022	0.001	-0.000
	3000	0.0494123	-0.50	0.91	-0.001	-0.010	-0.000	-0.000	0.000	0.000
$cis-C_2H_2D_2/C_2H_4$										
Planar	300	4.19392	-40.4	-13.9	-10.4	5.2	-3.8	-0.007	0.55	-0.54
	1200	0.522391	-3.0	-1.8	-0.022	-0.048	-0.020	0.020	0.001	-0.001
	3000	0.0930907	-0.39	0.80	0.000	-0.015	-0.000	-0.000	0.000	0.000
Non-planar	300	0.453482	-2.8	-7.2	0.089	0.16	-0.11	0.048	0.008	-0.004
	1200	0.0353384	-0.027	1.3	0.001	-0.010	-0.000	-0.001	0.000	-0.000
	3000	0.00574359	-0.002	0.52	0.000	0.001	-0.000	-0.000	0.000	0.000
Total	300	4.64740	-43.0	-10.0	-11.7	5.8	-4.0	0.15	0.51	-0.55
	1200	0.557730	-3.7	-1.1	-0.064	0.004	-0.020	0.022	0.001	-0.000
	3000	0.0988343	-0.51	0.92	-0.001	-0.010	-0.000	-0.000	0.000	0.000

Table II. (Continued)

Class of vibrations	T °K	Exact ln s/s'f	Percent error							
			n=1	n=2	n=3	n=4				
trans-C ₂ H ₂ D ₂ /C ₂ H ₄										
Planar	300	4.19273	-40.4	-13.9	-10.5	5.5	-3.8	-0.12	0.59	-0.54
	1200	0.522211	-3.0	-1.8	-0.031	-0.040	-0.020	0.020	0.001	-0.001
	3000	0.0930835	-0.38	0.79	-0.000	-0.015	-0.000	-0.000	0.000	0.000
Non-planar	300	0.456029	-3.4	-6.7	0.16	0.067	-0.11	0.046	0.006	-0.002
	1200	0.0353562	-0.078	1.4	0.002	-0.007	-0.000	-0.001	0.000	-0.000
	3000	0.00574407	-0.010	0.53	0.000	0.002	-0.000	-0.000	0.000	-0.000
Total	300	4.64875	-43.0	-10.0	-11.9	6.1	-4.0	0.071	0.54	-0.54
	1200	0.557567	-3.6	-1.2	-0.073	0.012	-0.020	0.022	0.001	-0.000
	3000	0.0988275	-0.50	0.92	-0.001	-0.010	-0.000	-0.000	0.000	0.000
gem-C ₂ H ₂ D ₂ /C ₂ H ₄										
Planar	300	4.19744	-40.5	-13.8	-10.5	5.4	-3.9	-0.047	0.62	-0.59
	1200	0.522325	-3.0	-1.8	-0.029	-0.041	-0.020	0.021	0.001	-0.001
	3000	0.0930875	-0.38	0.80	0.000	-0.015	-0.000	-0.000	0.000	0.000
Non-planar	300	0.451755	-2.4	-7.6	-0.023	0.29	-0.100	0.031	0.009	-0.004
	1200	0.0353247	0.011	1.3	0.001	-0.011	-0.000	-0.001	0.000	-0.000
	3000	0.00574322	0.004	0.51	0.000	0.001	-0.000	-0.000	0.000	0.000
Total	300	4.64920	-43.0	-10.0	-11.9	6.0	-4.0	0.10	0.58	-0.60
	1200	0.557650	-3.7	-1.2	-0.070	0.010	-0.020	0.023	0.001	-0.000
	3000	0.0988307	-0.50	0.92	-0.001	-0.010	-0.000	-0.000	0.000	0.000

Table II. ((Continued))

Class of vibrations	T °K	Exact ln s/s'f	Percent error							
			n=1		n=2		n=3		n=4	
			C_2HD_3/C_2H_4							
Planar	300	6.29919	-40.5	-13.8	-10.5	5.3	-3.9	0.016	0.60	-0.60
	1200	0.783702	-3.0	-1.8	-0.024	-0.046	-0.020	0.021	0.001	-0.001
	3000	0.139639	-0.39	0.80	0.000	-0.015	-0.000	-0.000	0.000	0.000
Non-planar	300	0.684142	-3.4	-6.7	0.17	0.062	-0.11	0.047	0.006	-0.003
	1200	0.0530351	-0.079	1.4	0.002	-0.007	-0.000	-0.001	0.000	-0.000
	3000	0.00861612	-0.011	0.53	0.000	0.002	-0.000	-0.000	0.000	-0.000
Total	300	6.98333	-43.1	-9.9	-11.8	5.9	-4.0	0.20	0.54	-0.59
	1200	0.836737	-3.7	-1.1	-0.066	0.006	-0.020	0.023	0.001	-0.000
	3000	0.148256	-0.51	0.92	-0.001	-0.009	-0.000	-0.000	0.000	0.000
			D_4/C_2H_4							
Planar	300	8.40818	-40.6	-13.7	-10.4	5.2	-3.9	0.094	0.60	-0.63
	1200	1.04525	-3.1	-1.8	-0.020	-0.049	-0.021	0.021	0.001	-0.001
	3000	0.186197	-0.40	0.81	0.000	-0.015	-0.000	-0.000	0.000	0.000
Non-planar	300	0.916751	-3.8	-6.2	0.27	-0.059	-0.11	0.056	0.004	-0.002
	1200	0.0707474	-0.13	1.4	0.003	-0.006	-0.000	-0.001	0.000	-0.000
	3000	0.0114891	-0.019	0.54	0.000	0.002	-0.000	-0.000	0.000	0.000
Total	300	9.32493	-43.2	-9.7	-11.8	5.9	-4.1	0.29	0.54	-0.61
	1200	1.11600	-3.7	-1.1	-0.064	0.004	-0.021	0.023	0.001	-0.000
	3000	0.197687	-0.52	0.93	-0.001	-0.009	-0.000	-0.000	0.000	0.000

¹F matrix elements taken from [30], geometry parameters from [31].

²For each temperature and order the figure on the left is the error of the Chebyshev expansion [4] and that on the right the error of the minimax method.

Table III. Intercomparison of various expansions of $\ln s/s'f$ for planar vibrations of ethylene $-d_1$.¹

T °K	Exact $\ln s/s'f$	Percent error							
		n=1		n=2		n=3		n=4	
200	3.42613	-57.3 ² 10.2 -15.6	0.69 11.3	-24.6 -7.1 6.4	5.0 -7.0	-11.0 -4.7 1.0	-1.66 0.177	-0.75 1.58 -2.2	2.1 0.119
300	2.09490	-40.4 12.2 -14.0	3.8 10.8	-10.5 -4.1 5.5	4.0 -4.9	-3.8 -2.5 -0.13	-1.23 0.061	0.58 0.92 -0.518	0.85 0.017
400	1.44128	-28.0 11.2 -8.2	5.0 9.8	-4.6 -2.6 0.46	2.9 -3.3	-1.60 -0.178 1.21	-0.81 0.033	0.35 0.39 -0.34	0.33 -0.005
600	0.812063	-13.9 4.9 -5.4	5.2 6.5	-0.99 -1.62 0.005	1.38 -1.41	-0.41 0.002 0.38	-0.30 -0.023	0.073 0.040 -0.050	0.057 -0.004
800	0.519383	-7.6 5.4 -3.6	4.3 5.3	-0.27 -0.60 -0.065	0.67 -0.70	-0.129 -0.001 0.13	-0.106 -0.002	0.016 0.008 -0.009	0.012 -0.001

Table IV. Intercomparison of various expansions of $\ln s/s'f$
for methane $-d_1$.

T °K	Exact $\ln s/s'f$	Percent error							
		n=1		n=2		n=3		n=4	
200	4.00170	-58.3 ² 8.4 -15.8	-0.43 10.1	-24.5 -6.3 6.2	6.2 -5.8	-9.7 -3.1 -2.0	0.60 1.74	-0.52 2.2 -1.8	2.7 0.6
300	2.45632	-41.7 10.4 -10.1	2.5 9.4	-10.6 -3.8 1.3	4.6 -4.3	-3.0 -1.72 0.76	-0.017 0.89	0.73 1.21 -1.21	1.11 0.23
400	1.69197	-29.5 9.5 -7.9	3.7 8.4	-4.7 -2.5 0.80	3.2 -3.1	-1.15 0.36 0.53	-0.195 0.46	0.43 0.36 -0.48	0.44 0.078
600	0.952670	-15.1 3.8 -5.1	4.2 5.5	-1.07 -1.66 0.27	1.46 -1.42	-0.28 0.148 0.21	-0.136 0.088	0.089 0.031 -0.082	0.076 0.011
800	0.608673	-8.4 4.7 -3.5	3.7 4.6	-0.31 -0.64 0.089	0.70 -0.72	-0.09 0.045 0.077	-0.059 0.033	0.019 0.006 -0.017	0.016 0.001

Table IV. (Continued)

T °K	Exact ln s/s'f	P e r c e n t e r r o r							
		n=1		n=2		n=3		n=4	
1000	0.419890	-5.2	3.0	-0.109	0.36	-0.034	-0.025	0.005	0.004
		2.4	3.1	-0.41	-0.36	0.022	0.009	0.001	0.000
		-1.4		-0.15		0.046		-0.003	
1200	0.305650	-3.4	2.4	-0.045	0.20	-0.014	-0.011	0.002	0.001
		2.2	2.5	-0.21	-0.20	0.009	0.004	0.000	0.000
		-1.8		0.012		0.013		-0.001	
3000	0.0544606	-0.46	0.52	-0.001	0.007	-0.000	-0.000	0.000	0.000
		0.55	0.53	-0.007	-0.007	0.000	0.000	0.000	0.000
		0.79		-0.013		-0.000		0.000	

¹ F matrix elements and geometry parameters taken from [32]

² See footnote 2 of Table III. for the arrangement of the results of the various expansions.

Table V. Approximation to $\ln s/s'f$ by the minimax method for deuterated methyl halide molecules.⁴

T °K	Exact $\ln s/s'f$	Percent error			
		n=1	n=2	n=3	n=4
CD_3F/CH_3F					
200	13.016222	-11.1	6.3	-1.6	-2.3
300	7.901031	-6.1	2.0	0.93	-1.21
400	5.391878	-4.8	1.3	0.66	-0.46
1200	0.948549	-1.08	0.045	0.016	-0.001
3000	0.167998	0.93	-0.008	-0.000	0.000
CD_3Cl/CH_3Cl					
200	12.822894	-8.8	4.8	1.16	-2.9
300	7.769187	-6.9	3.2	1.03	-1.1
400	5.299955	-5.6	2.0	0.71	-0.41
1200	0.937514	-1.4	0.081	0.016	-0.001
3000	0.166523	0.85	-0.009	0.000	0.000
CD_3Br/CH_3Br					
200	12.668759	-9.1	5.2	1.5	-2.7
300	7.670660	-7.3	3.4	1.19	-1.0
400	5.233233	-6.0	2.1	0.78	-0.38
1200	0.928145	-1.56	0.082	0.017	-0.001
3000	0.165016	0.83	-0.010	0.000	0.000
CD_3I/CH_3I					
200	12.566487	-9.8	6.1	1.4	-2.5
300	7.609738	-8.0	3.9	1.1	-0.94
400	5.195229	-6.6	2.4	0.75	-0.35
1200	0.925714	-1.8	0.098	0.016	-0.001
3000	0.164877	0.79	-0.011	0.000	0.000

F matrix elements taken from [33], geometry parameters used are given in [33] too.

Table VI. Comparison of the approximations to $\ln s/s'f$ for CD_3F/CH_3F with the actual u_{max} and the rounded u_{max} .¹

T °K	u_{max}	Exact $\ln s/s'f$	Percent error			
			n=1	n=2	n=3	n=4
200	22.78	13.016222	-11.1 ²	6.3	-1.6	-2.3
			-11.7	7.3	-2.3	-1.8
300	15.19	7.901031	-6.1	2.0	0.93	-1.2
			-9.3	4.9	-0.83	-0.7
400	11.39	5.391878	-4.8	1.3	0.66	-0.46
			-7.6	3.2	-0.28	-0.26
1200	3.80	0.948549	-1.08	0.045	0.016	-0.001
			-2.0	0.17	0.001	-0.001
3000	1.52	0.167998	0.93	-0.008	-0.000	0.000
			-0.39	0.006	0.000	-0.000

¹See footnote 1 of Table V.

²For each temperature and order the upper number is calculated by rounded u_{max} the lower by the actual value of u_{max} .

Table VII. Approximation to $\ln s/s'f$ for isotopic methanol molecules.¹

T °K	Exact ² $\ln s/s'f$	Percent error			
		n=1	n=2	n=3	n=4
$\text{CH}_3\text{OD}/\text{CH}_3\text{OH}$					
200	4.139935	-19.0	14.3	0.035	-1.9
300	2.562505	-16.5	9.2	0.48	-0.72
400	1.786176	-12.4	3.3	1.8	-0.55
1200	0.352451	-2.1	-0.24	0.073	0.002
3000	0.065525	-0.35	-0.013	0.001	0.000
$\text{CD}_3\text{OH}/\text{CH}_3\text{OH}$					
200	12.299398	5.3	-4.4	1.8	0.22
300	7.428451	6.0	-2.9	1.2	0.37
400	5.045085	8.3	-2.1	0.46	0.41
1200	0.866466	5.4	-0.12	-0.015	0.004
3000	0.151970	1.18	-0.003	-0.000	0.000
$\text{CD}_3\text{OD}/\text{CH}_3\text{OH}$					
200	16.444358	-2.1	-0.36	1.4	-0.34
300	9.993444	-0.86	-0.069	1.05	0.081
400	6.832797	2.1	-0.78	0.82	0.16
1200	1.219061	3.1	-0.16	0.010	0.004
3000	0.217501	0.72	-0.006	0.000	0.000
$^{13}\text{CH}_3\text{OH}/^{12}\text{CH}_3\text{OH}$					
200	0.213980	12.6	4.1	1.7	-4.2
300	0.127058	11.4	3.7	1.9	-1.65
400	0.084978	12.2	2.6	1.7	-0.39
1200	0.014089	5.3	0.21	0.061	0.007
3000	0.002470	1.1	0.008	0.000	0.000

¹ F matrix elements taken from [34], geometry parameters from [35].

² The contribution from the hindered rotation of the OH group is not included in $\ln s/s'f$ exact.

Table VIII. Intercomparison of various approximations to $\ln s/s'f$ for deuterated water molecules.¹

T °K	Exact $\ln s/s'f$	Percent error								Percent error							
		Bigeleisen-Mayer				Chebyshev				Bernoulli				Minimax method ²			
		n=1	n=2	n=3	n=1	n=2	n=3	n=4	n=1	n=2	n=3	n=4	n=1	n=2	n=3	n=4	
		HDO/H ₂ O								HDO/H ₂ O							
300	2.58246	-2.4	0.49	-0.13	-47.9	-16.3	-7.5	0.16					-20.2	-6.9	0.026	-0.95	
1200	0.377830				-4.2	0.012	-0.069	0.005	22.9	-8.9	3.9	-1.77	-4.1	-0.11	0.055	-0.003	
3000	0.0714062				-0.45	0.004	-0.001	0.000	4.1	-0.26	0.018	-0.001	-0.78	-0.007	0.000	-0.000	
		D ₂ O/H ₂ O								D ₂ O/H ₂ O							
300	5.20178	-3.2	0.72	-0.18	-48.3	-16.7	-7.8	0.17					-19.6	7.3	0.24	-1.02	
1200	0.756234				-4.3	-0.005	-0.072	0.005	22.8	-8.9	3.9	-1.76	-4.0	-0.095	0.059	-0.003	
3000	0.142830				-0.46	0.004	-0.001	0.000	4.1	-0.26	0.018	-0.001	-0.77	-0.007	0.000	-0.000	

¹ The results of the Bigeleisen-Mayer, Chebyshev and Bernoulli approximations taken from [4].

² F matrix elements and geometry parameters taken from [36].

Table IX. Deviation from the first rule of the mean for water :

$$2 \ln s/s'f \left(\frac{\text{HDO}}{\text{H}_2\text{O}} \right) - \ln s/s'f \left(\frac{\text{D}_2\text{O}}{\text{H}_2\text{O}} \right)^1$$

T OK	Exact	Order	Bigeleisen-Mayer ²	Chebyshev(L=5) ²	Chebyshev(L=0) ²	Minimax method
300	$-3.687 \cdot 10^{-2}$	1	$4.900 \cdot 10^{-3}$	0	0	0
		2	$-4.906 \cdot 10^{-2}$	$-1.286 \cdot 10^{-2}$	$-8.994 \cdot 10^{-3}$	$-1.490 \cdot 10^{-2}$
		3	$-3.410 \cdot 10^{-2}$	$-2.630 \cdot 10^{-2}$	$-2.181 \cdot 10^{-2}$	$-2.568 \cdot 10^{-2}$
1200	$-5.741 \cdot 10^{-4}$	1		0	0	0
		2		$-4.588 \cdot 10^{-4}$	$-4.441 \cdot 10^{-4}$	$-4.43 \cdot 10^{-4}$
		3		$-5.516 \cdot 10^{-4}$	$-5.482 \cdot 10^{-4}$	$-5.46 \cdot 10^{-4}$

¹ F matrix elements and geometry parameters taken from [31].

² Values taken from [4].

APPENDIX I

It will be shown that the series expansion /2.1/ converges at the rate of the geometric progression. For convenience, the consideration is restricted to the general term in u_1

$$S = \ln \frac{\text{sh}\left(x_1 + \frac{1}{2} \delta_1\right)}{x_1 + \frac{1}{2} \delta_1} - \ln \frac{\text{sh}\left(x_1 - \frac{1}{2} \delta_1\right)}{x_1 - \frac{1}{2} \delta_1} = \sum_{k=0}^{\infty} \frac{1}{4^k} \delta_1^{2k+1} \frac{1}{(2k+1)!} F^{(2k+1)}(x_1) \quad /1/$$

where

$$F(x_1) = \ln \frac{\text{sh } x_1}{x_1} = \sum_{\ell=1}^{\infty} \ln \left(1 + \frac{x_1^2}{4\pi^2 \ell^2} \right) \quad /2/$$

It can be readily shown that

$$F^{(2k+1)}(x_1) = (2k)! \sum_{\ell=1}^{\infty} \frac{2}{\left(x_1^2 + 4\pi^2 \ell^2\right)^{k+1/2}} \cos \left[(2k+1) \arctg \frac{2\pi\ell}{x_1} \right] \quad /3/$$

Substituting expression /3/ into /1/, we get

$$S = \sum_{k=1}^{\infty} \frac{\delta_1^{2k+1}}{4^k} \frac{2}{2k+1} \sum_{\ell=1}^{\infty} \frac{1}{\left(x_1^2 + 4\pi^2 \ell^2\right)^{k+1/2}} \cos \left[(2k+1) \arctg \frac{2\pi\ell}{x_1} \right] \quad /4/$$

that is, a series convergent for $q = \frac{\delta_1^2}{4(x_1^2 + 4\pi^2)} < 1$ at a rate q^k .

APPENDIX II

It will be shown that the series /2.8/ converges faster than one can expect from condition $\frac{\Delta u_1}{u_1} < 1$ given by Vojta.

We consider the Eq. /2.8/ of the form

$$\ln s/s'f = \sum_i \sum_{k=1}^{\infty} (-1)^k G_k(u_i) (\Delta u_i)^k \quad /1/$$

where

$$G_k(u_i) = \frac{(-1)^k}{k!} G_1^{(k)}(u_i) \quad /2/$$

from which in the same manner as in APP.I. we get the expression

$$G_k(u_i) = \sum_{\ell=1}^{\infty} \frac{1}{(u_i^2 + 4\pi^2 \ell^2)^{k+1/2}} \cos \left[(k+1) \arctg \frac{2\pi \ell}{u_i} \right] \quad /3/$$

On substituting /3/ into /1/ we obtain a series which is convergent for every value of i , at a rate q^k , where

$$q = \frac{\Delta u_i}{(u_i^2 + 4\pi^2)^{1/2}} .$$

APPENDIX III

The formula /3.18/ can be obtained by expanding the function $\ln b(u)$ in terms of Chebyshev polynomials as follows:

$$\ln b(u) = \sum_{\ell=0}^{\infty} A_{\ell} T_{\ell}^*(x^2) \quad 0 \leq x \leq 1 \quad /1/$$

where

$$x = \frac{u}{u_{\max}} \quad /2/$$

The coefficients A_{ℓ} can be formulated in terms of a Chebyshev expansion of the function $\ln(1 + sx^2)$ as

$$\ln(1 + sx^2) = \sum_{\ell=0}^{\infty} B_{\ell}(s) T_{\ell}^*(x^2) \quad , \quad s = \left(\frac{u_{\max}}{2\pi k} \right) \quad /3/$$

where

$$B_0(s) = 2 \ln \frac{1 + \sqrt{1+s}}{2} \quad , \quad B_{\ell}(s) = \frac{2(-1)^{\ell+1}}{\ell} \frac{s^{\ell}}{(1 + \sqrt{1+s})^{2\ell}} \quad \ell=1,2,\dots \quad /4/$$

and the coefficients A_{ℓ} can be expressed as

$$A_{\ell} = \sum_{k=1}^{\infty} B_{\ell} \left(\frac{u_{\max}^2}{4\pi^2 k^2} \right) \quad /5/$$

Let

$$\epsilon_n = \max_{0 \leq u \leq u_{\max}} |\ln b(u) - S_n(u)| \quad /6/$$

and

$$E_n = \max_{0 \leq u \leq u_{\max}} |\ln b(u) - Q_n(u)| \quad /7/$$

where S_n is the n -th partial sum of Eq. /1/ and Q_n is the minimax approximation to $\ln b(u)$.

It can be shown that

$$\epsilon_n = \sum_{\ell=n+1}^{\infty} |A_{\ell}| \quad /8/$$

which by /4/ can be rewritten in the form

$$\epsilon_n = \sum_{k=1}^{\infty} \sum_{\ell=n+1}^{\infty} \frac{2}{\ell} q_k^{\ell}, \quad q_k = \frac{s}{(1 + \sqrt{1+s})^2} \quad /9/$$

For large n , we find

$$\epsilon_n \sim \frac{2}{n+1} \frac{q_1^{n+1}}{1 - q_1} \quad /10/$$

Instead of /10/ one can use the expression

$$\epsilon_n^{1/n} = q_1 \left[1 + O\left(\frac{\ln n}{n}\right) \right] \quad /11/$$

According to Lebesgue's theorem [25], for large n

$$E_n \leq \epsilon_n \leq c \ln n E_n \quad /12/$$

where c is a positive constant. Thus we can write

$$\frac{1}{c \ln n} \epsilon_n \leq E_n \leq \epsilon_n \quad /13/$$

Applying now the formula /11/ to this equation, it can be seen that an equation of the form /11/ holds also for $E_n^{1/n}$

$$E_n^{1/n} = q_1 \left[1 + O\left(\frac{\ln n}{n}\right) \right] \quad /14/$$

Hence

$$\frac{E_{n+1}}{E_n} = q_1 \frac{\left[1 + O\left(\frac{\ln(n+1)}{n+1}\right) \right]^{n+1}}{\left[1 + O\left(\frac{\ln n}{n}\right) \right]^n} \quad /15/$$

in which the ratio tends to 1 if n goes to infinity and therefore

$$\lim_{n \rightarrow \infty} \frac{E_{n+1}}{E_n} = q_1 = \frac{s_1}{(1 + \sqrt{1+s_1})^2} ;$$

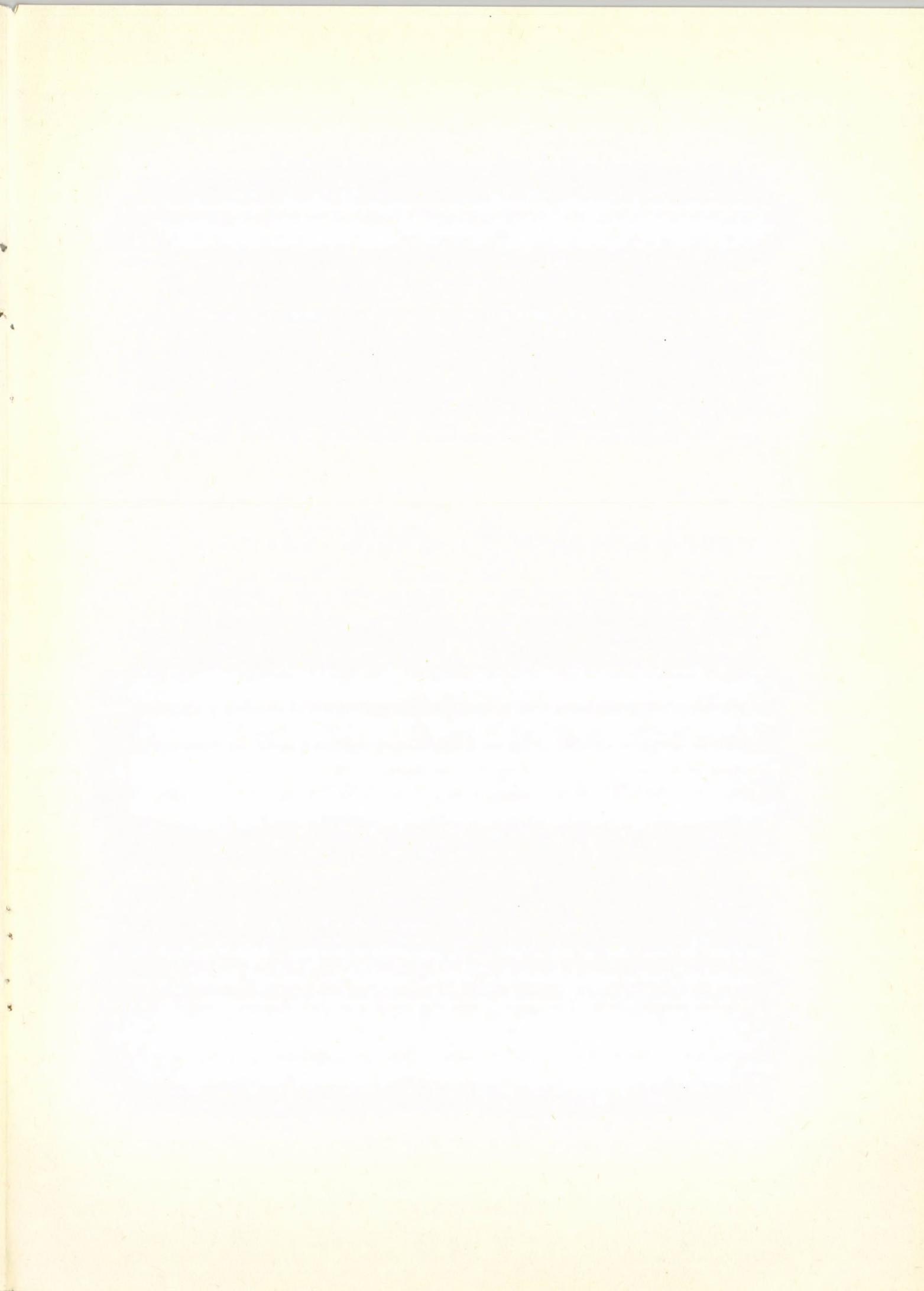
$$/q_1 = q ; s_1 = R/$$

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