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APPROXIMATION METHODS FOR THE PARTITION FUNCTIONS OF ANHARMONIC SYSTEMS.

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APPROXIMATION METHODS
FOR
THE PARTITION FUNCTIONS OF ANHARMONIC SYSTEMS

by

Peter T. Lew

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ABSTRACT

The analytical approximations for the classical , quantum mechanical and reduced partition functions of the diatomic molecule oscillating internally under the influence of the Morse potential have been derived and their convergences have been tested numerically . This successful analytical method is used in the treatment of anharmonic systems . Using Schwinger perturbation method in the framework of second quantization formulism , the reduced partition function of polyatomic systems can be put into an expression which consists separately of contributions from the harmonic terms , Morse potential correction terms and interaction terms due to the off-diagonal potential coefficients . The calculated results of the reduced partition function from the approximation method on the 2-D and 3-D model systems agree well with the numerical exact calculations .

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I would like to express all my thanks to my mentor for giving me the guidance throughout my graduate study and thanks to everyone that enables me to enjoy and treasure this unique span of time in my life .

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CHAPTER I

INTRODUCTION

The main objective of this thesis research is to find a new method in accounting for the anharmonicity in the reduced partition functions of polyatomic molecules, one that utilizes the Morse potential as has been successfully applied to the diatomic molecule. The reduced partition function represents the theoretical basis for equilibrium isotope effects as well as the isotope effect on the population of transition states, which is a major factor in kinetic isotope effects. Various methods of approximation for the reduced partition function of a pair of isotopic molecules within the framework of harmonic oscillator approximation have been developed in the last two decades, some of them primarily designed to permit quick and accurate numerical evaluation of the function, and others are particularly suited to give insight into the understanding of isotope effect, to give explicit relationships between the isotope separation factor and molecular structure and molecular forces. For the present status of accounting for the anharmonicity, one can refer to Chapter II A for a brief discussion of Wolfsberg's result. The advantage of this new approach to be discussed later is that one can readily calculate the contributions due to the quadratic and cubic diagonal terms which are later identified with the Morse potential terms, and due to off-diagonal cubic terms separately. In case the contribution from the off-diagonal terms is negligible, we can justify to employ the diagonal terms alone in accounting for the anharmonicity involved and thus gain more insight in understanding the role of different diagonal terms in affecting the anharmonicity.

Part II of the thesis deals with the pertinent theories upon which the present research has been built, that is, with a discussion of the vibrational reduced partition function of the Morse oscillator and the second quantization formalism with operator technique for Schwinger's perturbation theory.

Part III is the research results of this study on the approximations for partition functions of diatomic systems. Results on approximations for the classical quantum-mechanical and reduced partition functions will be presented.

Part IV deals with the approximations for partition functions of polyatomic systems. Due to the complexity of the problem involved, a model system which simulates the two stretching modes of carbon dioxide is investigated with the exact numerical results compared to the approximate and the harmonic results. Then the results of a successful approximation on a linear triatomic system are presented.

In the Appendix, some results of other approximation methods which have been attempted during the course of this research are presented. Padé Approximant method has been applied to the diatomic partition function. Orthogonal polynomial methods have also been explored. Nielsen's formulae and some essential details leading to simplified perturbation results of quantum partition function Eqs.(90) and (91) are also given. Listings of computer programs used for numerical evaluation of 2-D model systems and 3-D systems are also included.

CHAPTER II

BACKGROUND THEORY

A. VIBRATION REDUCED PARTITION FUNCTION OF THE MORSE OSCILLATOR

a. Introduction

The Born-Oppenheimer (BO) approximation is the underlying basic principle in most theoretical works on isotope effect. The isotope effect is a quantum mechanical effect and is most often described in terms of the reduced partition function ratio $\frac{s}{s'}f$, whereas

$$\frac{s}{s'} f = \frac{(Q/Q')_{qm}}{(Q/Q')_{cl}} = \frac{(Q_{qm}/Q_{cl})}{(Q'_{qm}/Q'_{cl})} = \frac{Q_r}{Q_r'} \qquad (1)$$

with s and s' as the symmetry numbers of a pair of isotopic molecules. Q and Q' are the partition functions of the heavier and the lighter isotopic molecules, and the subscripts qm, cl, and r refer to the quantum mechanical, classical, and the reduced partition functions, respectively. Note that the validity of Eq. (1) does not depend on BO.

Under the harmonic oscillator treatment, and to the extent that the molecular translational and rotational motions are classical and separable from the internal vibrational motions, the reduced partition function ratio is expressed as

$$\frac{s}{s'}\, f = \prod_i \frac{u_i e^{\frac{-u_i}{2}}(1 - e^{-u_i'})}{u_i' e^{\frac{-u_i'}{2}}(1 - e^{-u_i})} = \prod_i \frac{b(u_i)}{b(u_i')} \qquad (2)$$

where each product is taken over all degrees of freedom, u is the energy of a normal vibration $hc\omega_e$ in the units of kT, and b(u) is the reduced partition function of a single harmonic oscillator,

$$b(u) = \frac{ue^{\frac{-u}{2}}}{1-e^{-u}} \qquad (2a)$$

One usually accounts for the anharmonicity of vibration of a polyatomic molecule by a correcton term $\prod_i \exp(u_i\chi_i/4)$ to the zero-point energy term $\Pi e^{-u_i/2}$ in Eq. (2) and ignores any effect of anharmonicity to the vibrational excitation. In 1969 Wolfsberg pointed out the presence of a mass dependent G_0 term in the energy terms of a diatomic molecule

$$\frac{E_\nu}{hc} = G_0 + w_e(\nu + \tfrac{1}{2}) - w_e\chi_e(\nu + \tfrac{1}{2})^2 \qquad (3)$$

In extending to simple polyatomic molecules, the G_0 term which comes from non-rotating anharmonic terms and interaction between rotation and vibration terms was found to make significant contribution to the zero-point energy of isotopic water and ammonia and its inclusion in the calculation of the equilibrium constant yields good agreement between experimental and theoretical values. G_0 exactly vanishes for the Morse potential. Also the effect of anharmonicity due to its interaction with the rotational motions of a real molecule is generally significant but dealing with this effect would be out of the scope of this present study.

b. Formulations

The potential parameters of the Morse oscillator

$$U(q) = D(1 - e^{-\alpha q})^2 \tag{4}$$

are related[6] to the parameters of the vibrational energy levels by

$$\omega_e = \alpha\sqrt{\frac{D}{2\pi^2c^2\mu}} \tag{5}$$

and

$$\omega_e\chi_e = \frac{h\alpha^2}{8\pi^2c\mu} \tag{6}$$

where μ is the reduced mass. The classical partition function Q_{cl} of the bound state of the oscillator is given by

$$Q_{cl} = \frac{1}{u_e} \frac{1}{\sqrt{\pi}} \int_{-\rho \ln 2}^{\infty} \exp\left[-\rho^2 (1-e^{-z/\rho})^2\right] \operatorname{erf} y_2 \, dz, \quad (7)$$

where ρ is a dimensionless quantity defined as

$$\rho \equiv \sqrt{\frac{D}{kT}} = \frac{1}{2}\sqrt{\frac{u_e}{\chi_e}} , \quad (8)$$

erf is the error function,

$$\operatorname{erf} y_2 = \frac{2}{\sqrt{\pi}} \int_0^{y_2} e^{-t^2} \, dt , \quad (9)$$

and z and y_2 are dimensionless functions given by

$$z = \alpha \rho q \quad (10)$$

and $$y_2 = \rho [1 - (1-e^{-z/\rho})^2]^{\frac{1}{2}} \quad (11)$$

The anharmonicity correction factor γ_{cl} for the classical partition function is expressed as

$$\gamma_{cl} = \frac{Q_{cl}}{Q^0_{cl}} = \frac{1}{\sqrt{\pi}} \int_{-\rho \ln 2}^{\infty} \exp[-\rho^2 (1-e^{-z/\rho})^2] \operatorname{erf} y_2 \, dz , \quad (12)$$

where Q_{cl} and Q^0_{cl} are the partition functions of the anharmonic and harmonic systems respectively. Note that γ_{cl} is a function of ρ only and does not depend on u_e and χ_e separately.

The quantum mechanical partition function is exactly given by

$$Q_{qm} = S \exp\left(-\frac{u_e}{2} + \frac{u\chi}{4}\right) , \tag{13}$$

with

$$S = \sum_{V=0}^{V_D} \exp\left[-u_e V + u\chi(V + V^2)\right] \tag{14}$$

where V_D is the largest integer not exceeding c,

$$c \equiv \frac{\omega_0}{2\omega_0\chi_0} = \frac{\omega_e - \omega\chi}{2\omega\chi} = \frac{u_e - u\chi}{2u\chi} = \frac{1-\chi_e}{2\chi_e} \tag{15}$$

Eq. (13) gives the exact value of Q_{qm} for the allowed vibrational energy of the Morse oscillator expressed as

$$\frac{E_V}{hc} = \omega_e(v + \tfrac{1}{2}) - \omega e\chi e(v + \tfrac{1}{2})^2 \tag{16}$$

The sum S can be equivalently expressed in terms of u or u_0 by using relations $u_e\chi_e = u_0\chi_0 = u\chi$ and $u = u_0 - u\chi = u_e - 2u\chi$.

Then γ_{qm}, the anharmonic correction factor for the quantum mechanical partition function is

$$\gamma_{qm} = \frac{Q_{qm}}{Q^0_{qm}} = Se^{u\chi/4} \; [1 - \exp(-u_e)] \tag{17}$$

which depends on ue and χe individually.

γ_r, the anharmonicity correction factor for the reduced partition function follows

$$\gamma_r = \frac{Q_r}{Q_r^0} = \frac{Q_{qm}/Q_{cl}}{Q_{qm}^0/Q_{cl}^0} = \frac{\gamma_{qm}}{\gamma_{cl}} \tag{18}$$

c. Discussion

What I have attempted in this research is an improvement of the classical partition function Q_{cl} and quantum partition function Q_{qm} over the above presentation of the vibrational reduced partition function of the Morse oscillator. An approximation of partition functions for a system of anharmonic oscillators will help solve various thermodynamic problems that are currently being thwarted partly due to the lack of adequate ways to account for the anharmonicities in thermodynamic functions. Wolfsberg and his group have calculated the equilibrium constants of hydrogen isotope exchange reactions involving several simple molecules, such as water and ammonia. Their calculations were based on a quartic potential function and included all other nonideal effects such as interactions of the anharmonic part of internal vibration with rotational motions, coriolis forces and are exact but tedious. It is hoped that a suitable approximation for the anharmonicity effect may provide some simplification of such calculations.

Partly to facilitate calculation of exact values to which one can compare any approximation, exact effects of anharmonicity of a single Morse oscillator to the classical, quantum mechanical, and reduced partition functions were calculated numerically. The anharmonicity correction factor for the classical partition function depends on a single parameter rather than on two potential parameters and temperature.[1] Several approximation methods have been investigated for the classical, quantum partition functions of a Morse oscillator. Only the method adopted will be presented in the main text and some other methods of interest will be relegated to the appendix.

B. SECOND QUANTIZATION WITH OPERATOR TECHNIQUE

a. General Formulation of the Schwinger Perturbation Theory[8,9]

The problem is to derive an expression for $e^{-H_0+H_1}$ in which H_0 is regarded as a large operator and H_1 a small one. Let

$$\phi(t) = e^{-(H_0+H_1)t} \tag{19}$$

$$\frac{\partial}{\partial t} \phi(t) = - (H_0 + H_1)\phi(t) \tag{20}$$

Introduce $\psi(t)$ defined by

$$\phi(t) = e^{-H_0 t} \psi(t) \tag{21}$$

which satisfies the differential equation

$$\frac{\partial}{\partial t}\Psi(t) = - e^{+H_0 t} H_1 e^{-H_0 t} \Psi(t) \tag{22}$$

subject to the boundary condition $\psi(0) = 1$. We replace Eq. (22) by an integral equation which incorporates the boundary condition and which may be solved by iteration:

$$\psi(t) = 1 - \int_0^t dt' \; e^{H_0 t'} H_1 e^{-H_0 t'} \psi(t') \tag{23}$$

Carrying out the iteration, we have

$$\psi(t) = 1 - \int_0^t dt' e^{H_0 t'} H_1 e^{-H_0 t'} + \int_0^t dt' \int_0^{t'} dt'' \; e^{H_0 t'} H_1 e^{-H_0 t'} e^{H_0 t''} H_1 e^{-H_0 t''} + \ldots \tag{24}$$

A somewhat neater form is obtained by making the substitutions $t' = tt_1$, $t'' = t't_2$, ... Making this change and forming $\phi(1)$ from Eq.(21) we find

$$\phi(1) = e^{-(H_0+H_1)} = e^{-H_0} + (-1) \int_0^1 dt_1 \, e^{-(1-t_1)H_0} \, H_1 e^{-t_1 H_0}$$

$$+ (-1)^2 \int_0^1 t_1 dt_1 \int_0^1 dt_2 e^{-(1-t_1)H_0} \, H_1 e^{-t_1(1-t_2)H_0} \, H_1 e^{-t_1 t_2 H_0}$$

$$+ \ldots + (-1)^n \int_0^1 t_1^{n-1} \, dt_1 \int_0^1 t_2^{n-2} \, dt_2 \ldots$$

$$\int_0^1 dt_n e^{-(1-t_1)H_0} \, H_1 e^{-t_1(1-t_2)H_0} \, H_1$$

$$\ldots H_1 e^{-t_1 t_2 \ldots t_n - 1(1-t_n) H_0} \, H_1 \, e^{-t_1 t_2 \ldots t_n H_0}$$

$$+ \ldots \tag{25}$$

If one is faced with the problem of taking the trace or the average value of $\phi(1)$, a further simplification can be made by virtue of the fundamental property of a trace, viz.,

$$\mathrm{Tr}(AB \ldots YZ) + \mathrm{Tr}(ZAB \ldots Y) = \mathrm{Tr}(B \ldots YZA), \text{ etc.} \tag{26}$$

Using Eq.(26) one may easily verify the following equation

$$T_r\left[e^{-(H_0+H_1)t}\right] - T_r\left[e^{-H_0 t}\right] = -t \int_0^1 d\alpha T_r\left[H_1 e^{-(H_0+\alpha H_1)t}\right] \tag{27}$$

Substituting the series of Eq.(25) for $e^{-(H_0+H_1\alpha)t}$ we find

$$\mathrm{Tr}\left[e^{-(H_0+H_1)}\right] = \mathrm{Tr}\left[e^{-H_0}\right] + (-1)\mathrm{Tr}\left[H_1 e^{-H_0}\right]$$

$$+ \frac{(-1)^2}{2} \int_0^1 dt_1 \mathrm{Tr}\left[H_1 e^{-(1-t_1)H_0} H_1 e^{-tH_0}\right]$$

$$+ \ldots + \frac{(-1)^{n+1}}{n+1} \int_0^1 t_1^{n-1} dt_1 \int_0^1 t_2^{n-2} dt_2$$

$$\ldots \int_0^1 dt_n \, \mathrm{Tr}\left[H_1 e^{-(1-t_1)H_0} H_1 \, e^{-t_1(1-t_2)H_0} H_1\right.$$

$$\left.\ldots H_1 e^{-t_1 t_2 \ldots t_n H_0}\right] + \ldots \qquad (28)$$

Later on, the above result will be set in the framework of second quantization, and the reduced partition function of polyatomic system can be put into an expression which consists of contributions from the harmonic terms, Morse potential correction terms, and interaction terms due to off-diagonal cubic coefficients.

b. Occupation Number Formalism for Harmonic Oscillators

The Hamiltonian operator for a harmonic oscillator is[10]

$$\hat{H} = \frac{1}{2m} (\hat{p}^2 + m\ ^2\hat{q}^2) \ , \qquad (29)$$

with $\hat{p}$ and $\hat{q}$ as the momentum and coordinate operators obeying the commutator rule.

$$[\hat{p}, \hat{q}]_- = -i\hbar \tag{30}$$

where

$$\hat{p} = i\left(\frac{m\hbar\omega}{2}\right)^{1/2} (a^\dagger - a) \tag{31a}$$

and

$$\hat{q} = \left(\frac{\hbar}{2m\omega}\right)^{1/2} (a^\dagger + a) \ . \tag{31b}$$

With the introduction of the creation and destruction operators $a^\dagger$ and a, the Hamiltonian operator becomes

$$\hat{H} = \hbar\omega(a^\dagger a + 1/2) \tag{32}$$

The $a^\dagger$, a are boson creation and destruction operators fulfilling the commutation relations

$$[a_i, a_j^\dagger]_- = \delta_{ij} \ . \tag{33}$$

For a multidimensional harmonic oscillator, the Hamiltonian H is

$$\hat{H} = \sum_{i=1}^{n} \hat{H}_i \ . \tag{34}$$

with

$$\hat{H}_i = \frac{1}{2m} (\hat{p}_i{}^2 + m\omega^2 \hat{q}_i{}^2) \tag{35}$$

Although, as Pauli has observed, all results derived from the occupation number formalism can also be obtained by the wave mechanical calculation, the advantage of the occupation number formalism lies in the simplicity of the algebraic manipulation of the destruction and creation operators. In a later section we will see the unfolding of the occupation number formalism in the framework of Schwinger's perturbation theory.

CHAPTER III

APPROXIMATIONS FOR PARTITION FUNCTIONS OF DIATOMIC SYSTEMS

A. APPROXIMATION FOR CLASSICAL PARTITION FUNCTIONS

a. Classical Parition Function of Oscillator in Finite Harmonic Well

The Hamiltonian of a harmonic oscillator in an infinitely deep harmonic well is given by

$$H = \frac{p_\xi^{\ 2}}{2\mu} + \frac{1}{2} a\xi^2 \tag{36}$$

where ξ is the displacement coordinate, μ the reduced mass and a the force constant. As for the classical partition function Q_{cl}^{harm}, we have

$$Q_{cl}^{harm} = \frac{1}{h} \int_{-\infty}^{\infty} dp_\xi \int_{-\infty}^{\infty} e^{-H/kT}\, d\xi$$

$$= \frac{1}{h} \int_{-\infty}^{\infty} e^{-\frac{a\xi^2}{2kT}}\, d\xi \int_{-\infty}^{\infty} e^{-\frac{p_\xi^{\ 2}}{2\mu kT}}\, dp\xi$$

$$= \frac{1}{h}\sqrt{\frac{2\pi kT}{a}}\, \sqrt{2\pi\mu kT}$$

$$= \frac{2\pi kT}{h} \frac{1}{2\pi\nu_e} = \frac{kT}{h\nu_e} = \frac{1}{u_e}$$

with

$$\nu_e = \frac{1}{2\pi}\sqrt{\frac{a}{\mu}} \ .$$

One is interested in developing a formula for the finite harmonic oscillator because it may exhibit features that are characteristic of a bound oscillator system. For an oscillator in a harmonic well of a finite depth, we have,

$$Q_{cl} = \frac{2}{h}\int_{-\sqrt{\frac{2D}{a}}}^{\sqrt{\frac{2D}{a}}} d\xi e^{-\frac{1}{2}\frac{a\xi^2}{kT}} \int_0^{\sqrt{2\mu(D-\frac{a\xi^2}{2})}} e^{\frac{p^2}{2\mu kT}} dp \ . \qquad (38)$$

By setting

$$\frac{p^2}{2\mu kT} \equiv y^2 \ , \qquad \frac{a\xi^2}{2kT} \equiv x^2 \qquad (39)$$

we obtain

$$Q_{cl} = \frac{1}{u_e}\frac{2}{\pi}\int_{-\sqrt{\frac{D}{kT}}}^{\sqrt{\frac{D}{kT}}} e^{-x^2} dx \int_0^{\sqrt{\frac{D}{kT}(1-\frac{a\xi^2}{2D})}} e^{-y^2} dy \ . \qquad (40)$$

Integrating by parts (IBP), it can be shown that

$$\int_0^x e^{-t^2}\,dt = e^{-x^2}\left[x + \frac{2}{3}x^3 + \frac{2}{3}\frac{2}{5}x^5 + \ldots\right.$$
$$\left.\left(\frac{2}{3}\frac{2}{5}\cdots\frac{2}{2n-1}\right)x^{2n-1}\right] + En(x) \qquad (41)$$

where

$$En(x) = \left(\frac{2}{1}\frac{2}{3}\frac{2}{5}\cdots\frac{2}{2n-1}\right)\int_0^x e^{-t^2}\,t^{2n}\,dt\,. \qquad (42)$$

It can easily be verified from Eq.(42) that the infinite series obtained above converges for all x.

An application of the series expansion, IBP, above to the harmonic oscillator problem of Eq.(40) leads to a very simple and exact result, which is the following closed form:

$$Q_{cl} = \frac{1}{u_e}\left(1 - e^{-\rho^2}\right) \qquad (43)$$

where $\rho^2 = \frac{D}{kT}$.

The Q_{cl} of Eq.(43) tends to $\frac{1}{u_e}$ as $\rho\to\infty$, as expected. What we need is a modification of Eq.(41), or its equivalent, which would account for the anharmonicity. Since the finite harmonic oscillator is the simplest of its kind, the next bound oscillator to look into is the Morse oscillator.

b. Approximation for the Vibrational Classical Partition Function of the Morse Oscillator

For a small x value, Eq.(41) converges well, but in general x is not small and most of the results based on an expansion like Eq.(41) will not yield satisfactory results for real diatomic molecules. Further investigation leads to another expansion of the error function:[11]

$$\operatorname{erf} x = 1 - \frac{e^{-x^2}}{\sqrt{\pi}} \left[\frac{1}{x} - \frac{1}{2}\frac{1}{x^3} + \frac{1}{2}\frac{3}{2}\frac{1}{x^5} \cdots \right.$$

$$\left. + (-1)^n \left(\frac{1}{2}\frac{3}{2} \cdots \frac{2n-1}{2} \right) \frac{1}{x^{2n+1}} \right] + En(x) \ , \qquad (44)$$

where

$$En(x) = (-1)^n \left(\frac{2}{\sqrt{\pi}} \right) \left(\frac{1}{2}\frac{3}{2} \cdots \frac{2^{n+1}}{2} \right) \int_x^\infty e^{-t^2} \frac{dt}{t^{2n+2}} \ , \qquad (45)$$

and values of En(x) have been tabulated in Table 1.

Difficulties arise in using Eq.(44) for the inner integral of Eq.(12) in the following manner. The outer integral of Eq.(12) obtained by substituting Eq.(44) for erf y_2 in it is found to be unbound at both limits of integration, i.e., at $z = -\rho \ln 2$ and $z = \infty$. Schematically the exact integrand of the outer integral of Eq.(12) looks like Figure 1. It is seen that the value of the integrand is very small near the limits of the integral. It is

Table 1 : Remainder $E_n(x)$ for Eqn.(45)

	x=1	x=2	x=3	x=4	x=5
n=1	$1.411*10^{-1}$	$2.204*10^{-3}$	$1.935*10^{-4}$	$3.444*10^{-5}$	$9.027*10^{-5}$
n=2	$2.645*10^{-1}$	$1.033*10^{-3}$	$4.031*10^{-5}$	$4.035*10^{-6}$	$6.770*10^{-7}$
n=3	$7.405*10^{-1}$	$7.231*10^{-4}$	$1.254*10^{-5}$	$7.062*10^{-7}$	$7.583*10^{-8}$
n=4	$2.777*10^{0}$	$6.780*10^{-4}$	$5.225*10^{-5}$	$1.655*10^{-7}$	$1.137*10^{-8}$
n=5	$1.309*10^{1}$	$7.990*10^{-4}$	$2.737*10^{-6}$	$4.877*10^{-8}$	$7.238*10^{-9}$

feasible to conduct a study of chopping off both extremities of the range of the integral. The more one moves away from the end points, the more one reduces the error of integration due to the singularity. However, the more one moves away from the true limits of the integral, the more error one acquires due to the increase in the neglected area. There must be an optimum set of points z_1 and z_2 to be used in place of $-\rho \ln 2$ and ∞, respectively.

One chooses to let z_1 and z_2 depend on each other as follows: choose a value for the ratio, R, of the level of y_2 called $y_{2,min}$ and the maximum possible value of y_2, which is ρ;

$$R \equiv \frac{y_{2,min}}{\rho} \tag{46}$$

Referring to Figure 1B, one obtains z_1 and z_2 as two real solutions of

$$R = \sqrt{1 - (1-e^{-z/\rho})^2} \tag{47}$$

They are:

$$z_1 = -\rho \ln \left(2 - \frac{R^2}{2}\right)$$

$$z_2 = \rho \ln \left(\frac{2}{R^2}\right) \tag{48}$$

As can be seen in Figure 2, the lop-off error is negligible even at as large a value of R as 0.3 when ρ is 2 or larger. This plot has been obtained by approximating the integrand of Eq.(12) by using Eq.(41) for erf y_2 in the lop-off regions of the integral.

Substituting Eq.(44) into Eq.(12), one obtains

$$\gamma_{cl} = \gamma_{cl}^0 - \Delta_1\gamma_{cl} + \Delta_2\gamma_{cl} - \cdots\cdots , \tag{49}$$

where

$$\gamma_{cl}^0 = \frac{1}{\sqrt{\pi}} \int_{-\rho \ln 2}^{\infty} e^{-\rho^2(1-e^{-z/\rho})^2} dz \quad , \tag{50}$$

$$\Delta_1\gamma_{cl} = \frac{1}{\pi} \int_{-\rho \ln 2}^{\infty} \frac{e^{-y_2^2} \exp[-\rho^2(1-e^{-z/\rho})^2]}{y_2} \tag{51}$$

and

$$\Delta_2\gamma_{cl} = \frac{1}{2\pi} \int_{-\rho \ln 2}^{\infty} \frac{e^{-y_2^2} \exp[-\rho^2(1-e^{-z/\rho})^2]}{y_2{}^3} \tag{52}$$

It has been found that γ_{cl}^0 is the dominant term. A transformation of Eq.(50) leads to

$$\gamma_{cl}^0 \simeq \frac{\rho}{\sqrt{\pi}} \int_{y_1}^{y_2} \frac{e^{-\rho^2 y^2} dy}{1-y^2} \quad , \tag{53}$$

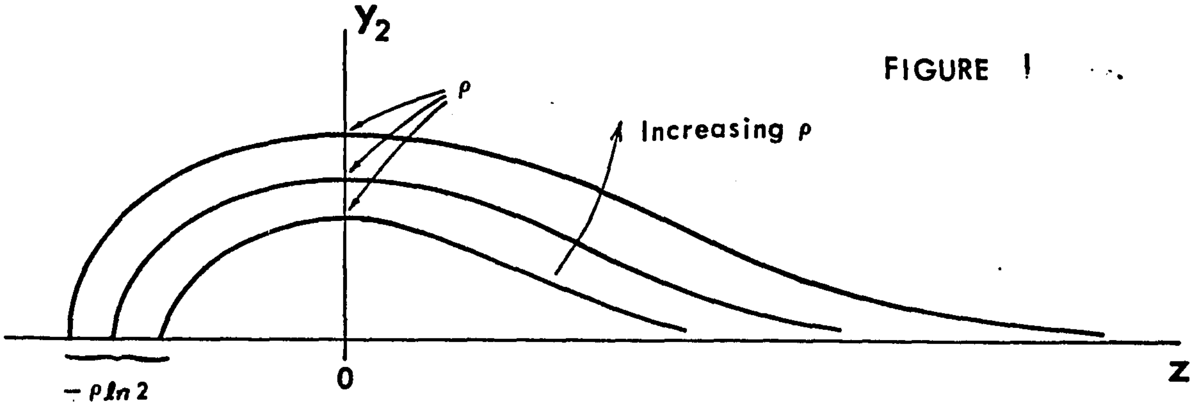


FIGURE 1

Integrand of Outer Integral of Classical Partition Function

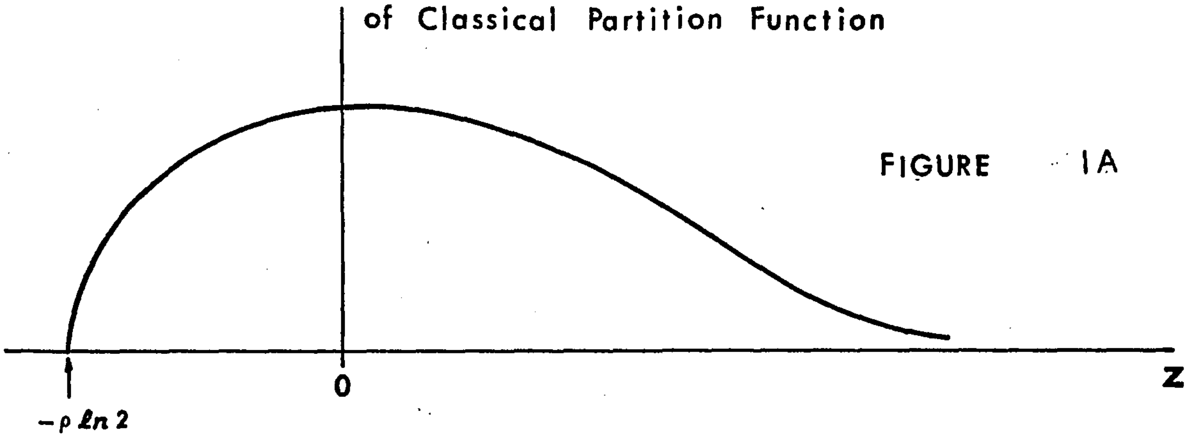


FIGURE 1A

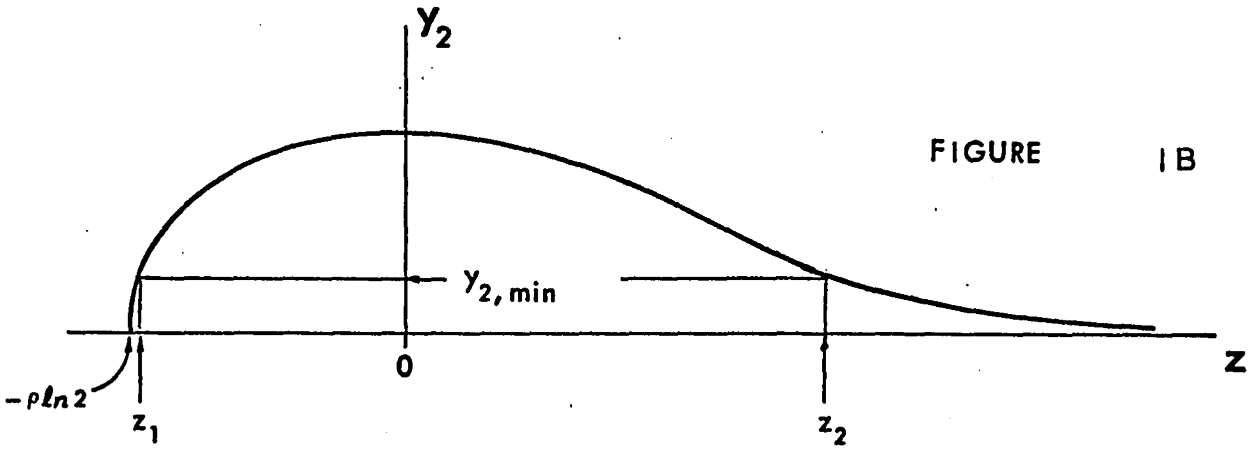
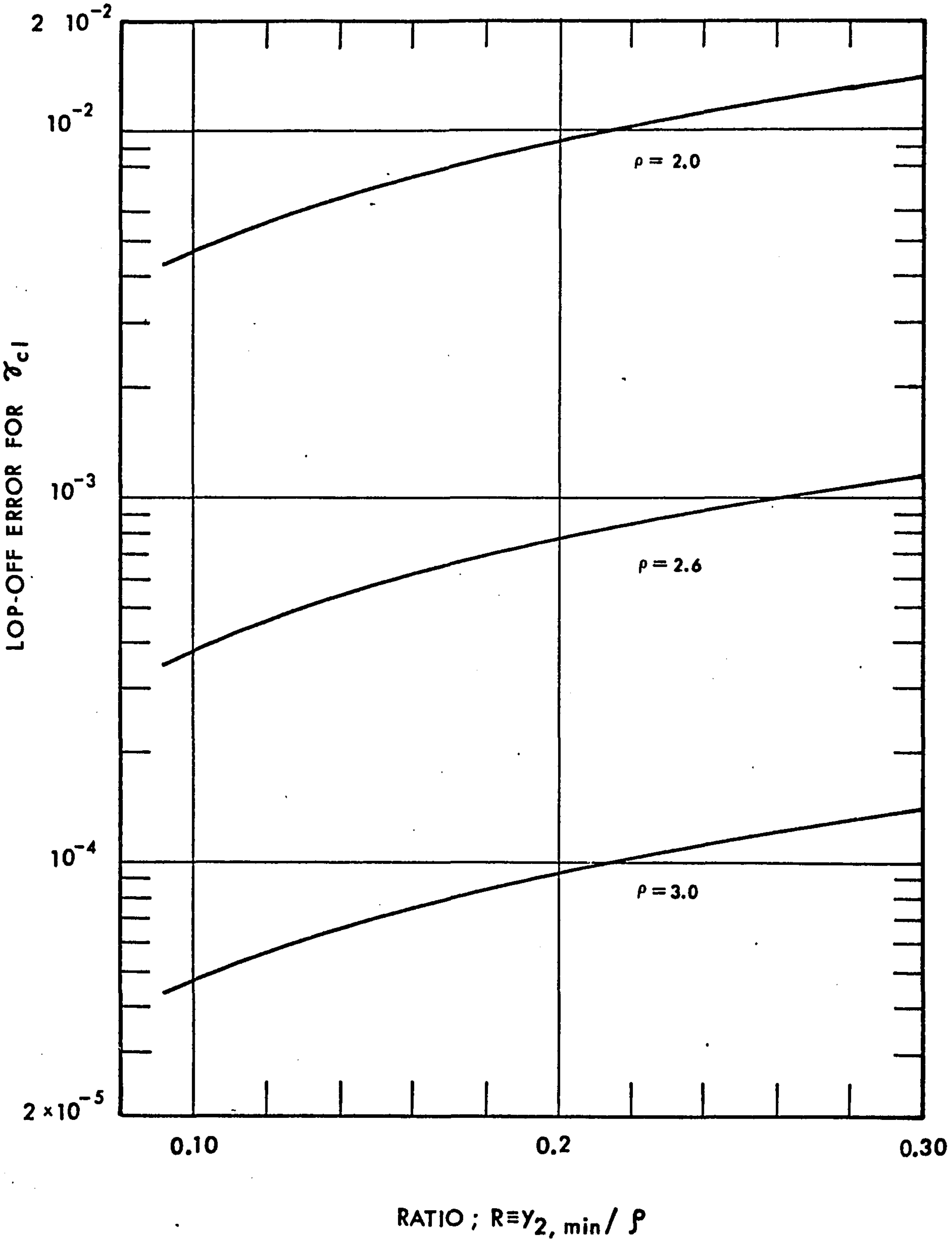


FIGURE 1B

FIGURE 2 LOP-OFF ERROR



where

$$y \equiv e^{-z/\rho} - 1 \quad . \tag{54}$$

The Taylor expansion of $1/(1-y^2)$ in Eq.(53) further leads to

$$\gamma_{cl}^{0}(m) = 1 + \gamma_{cl_0}{}^{0}(m) + \frac{2\rho}{\sqrt{\pi}} \sum_{k=1}^{m} \Delta f_k \tag{55}$$

where

$$\gamma_{cl_0}{}^{0}(m) = \sum_{k=1}^{m} R_k(\rho) = \sum_{k=1}^{m} \frac{1}{2^{k-1}(2\rho^2)^k} \frac{(2k-1)!}{(k-1)!} \quad , \tag{56}$$

$$\Delta f_k = \frac{-e^{-\rho^2 x^2}}{2\rho^2} \frac{(2k-1)!}{(k-1)!} \sum_{j=1}^{k} \frac{(j-1)!}{(2j-1)!} \frac{x^{2j-1}}{(4\rho^2)^{k-j}}$$

$$+ \frac{2(2k-1)!}{(4\rho^2)^k (k-1)!} \Delta f_0 \quad , \tag{57}$$

in which

$$\Delta f_0 = - \int_x^{\infty} e^{-\rho^2 y^2} dy \quad , \tag{58}$$

and

$$x = 1 - \frac{R^2}{2} \quad . \tag{59}$$

In Figure 3 I compare various approximations represented by Eq. (55) with the exact value of γ_{cl} obtained from Ref. (1). In this Figure,

$$cl_0^0\ (1) = 1 + \gamma_{cl_0^0}\ (1) = 1 + \frac{1}{2\rho^2} \tag{60}$$

and the curves labelled as $cl^0(1)$, $cl^0(2)$, $cl^0(3)$ are given by Eq. (55), including the terms of Δf_k, with m = 1,2, and 3, respectively. Figure 4 is a plot of relative errors obtained by

$$\gamma_{cl^0}(m) \simeq 1 + \gamma_{cl_0^0}(m) \tag{61}$$

Figure 5 is a similar plot obtained by including terms of Δf_k as well. The $cl^0(3)$ approximation, or Eq. (55) with m = 3, seems to give a generally satisfactory approximation. The apparently strange behavior of the $cl^0(4)$ approximation is a consequence of the lop-off procedure forced in obtaining Eq. (53).

Figure 6 shows the effects of inclusion of higher terms of Eq. (49). These higher terms come from the higher order terms of small anharmonicity approximation for the error function, Eq. (44). The behavior of these plots are

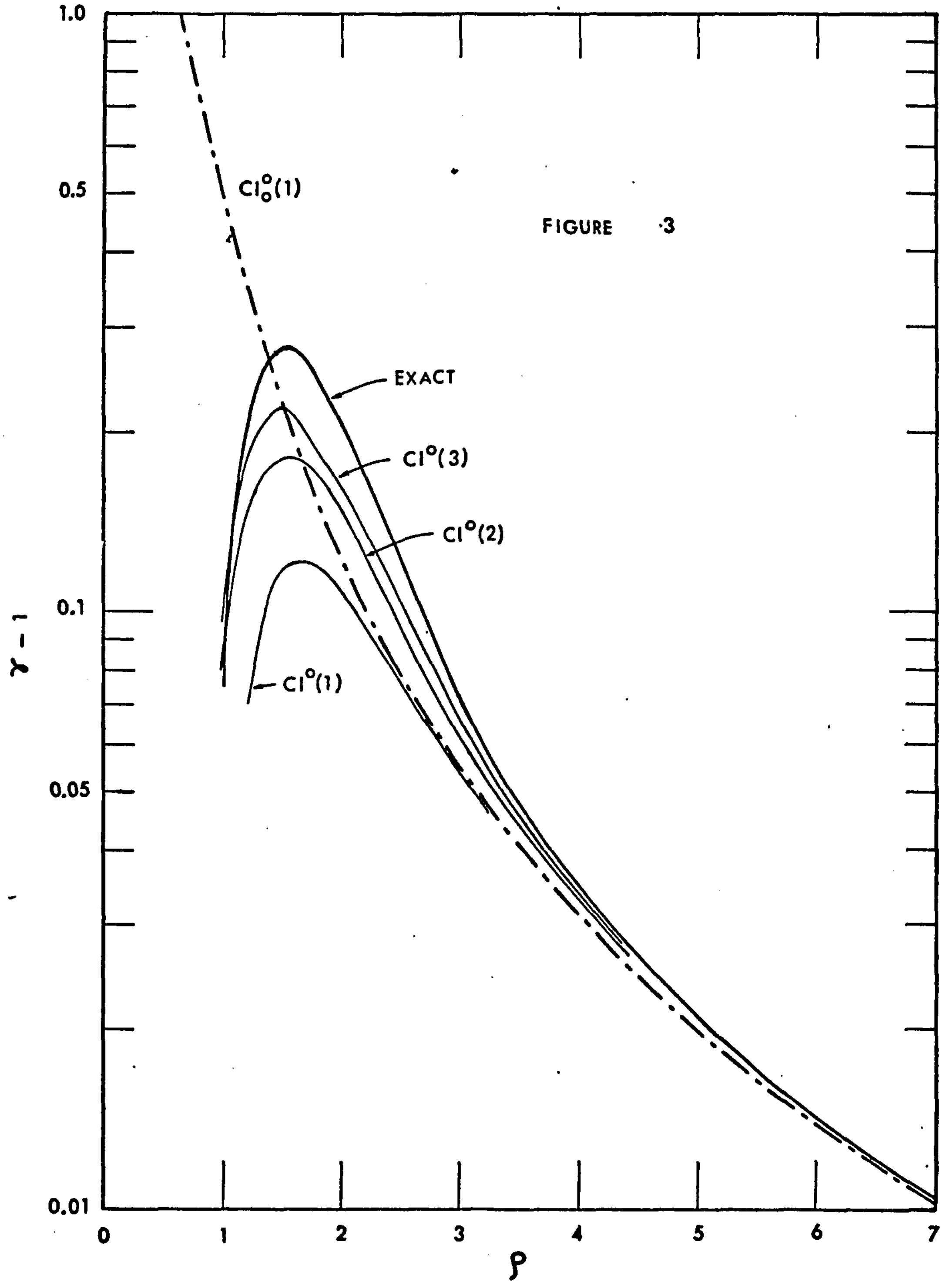


FIGURE ·3
EXACT
$CI^o(3)$
$CI^o(2)$
$CI^o(1)$
$CI^o_o(1)$
1.0
0.5
0.1
0.05
0.01
$\gamma - 1$
0
1
2
3
4
5
6
7
ρ

FIGURE 4 $\gamma_{CI_o^o}$-APPROXIMATION WITH R=0.3

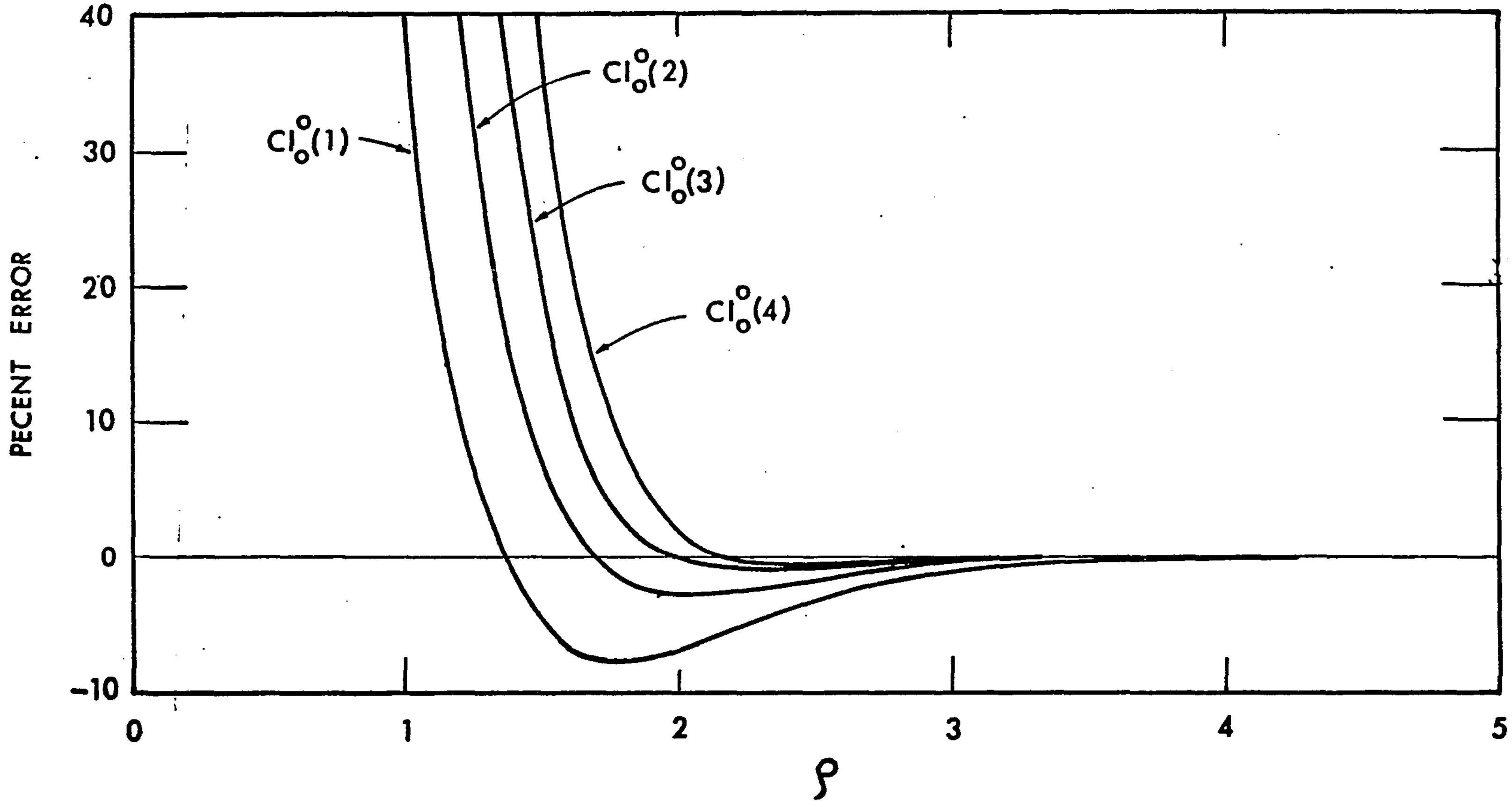


FIGURE 5 $\gamma_{cl^o}(m)$-APPROXIMATION WITH R=0.3

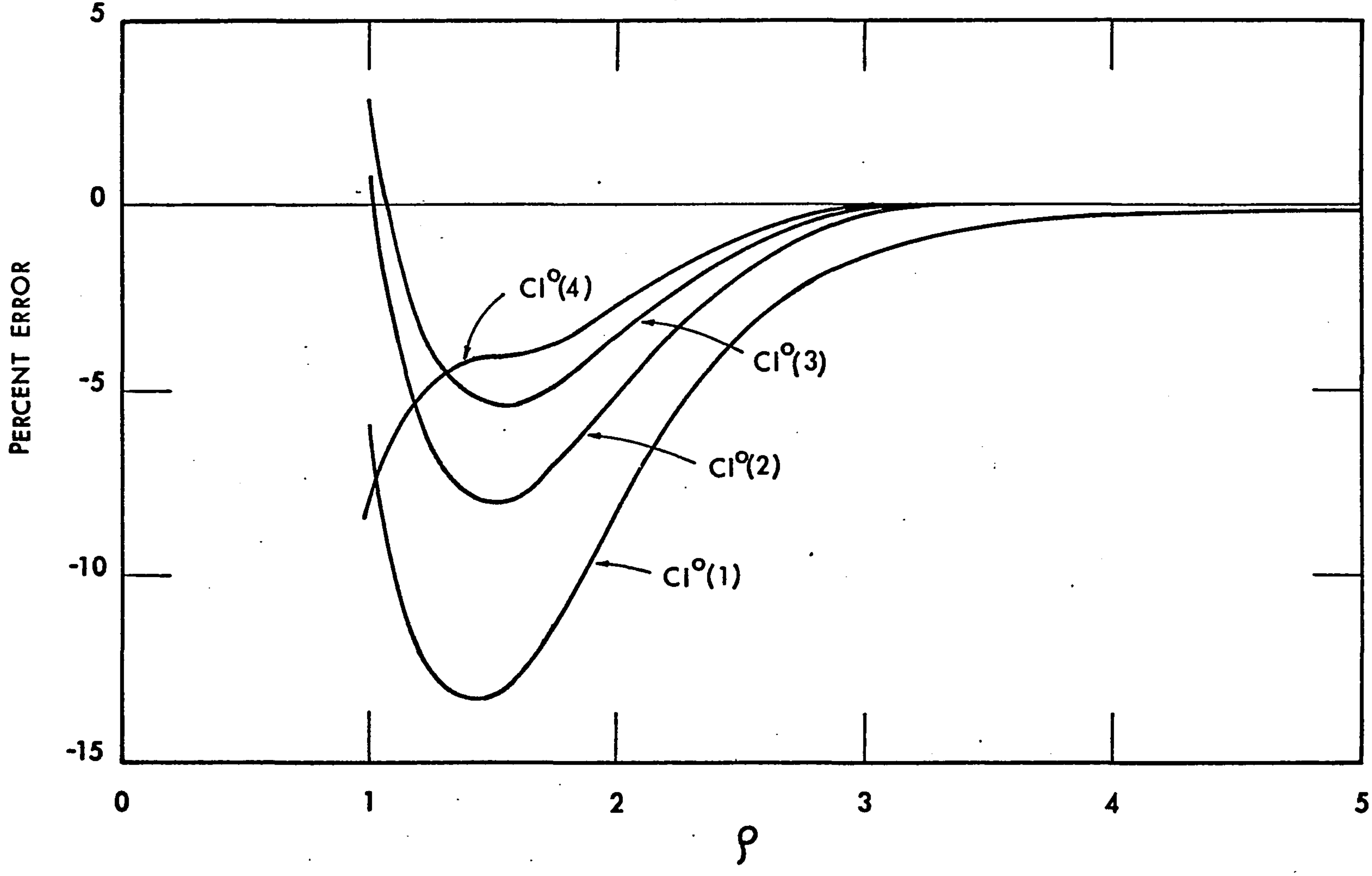
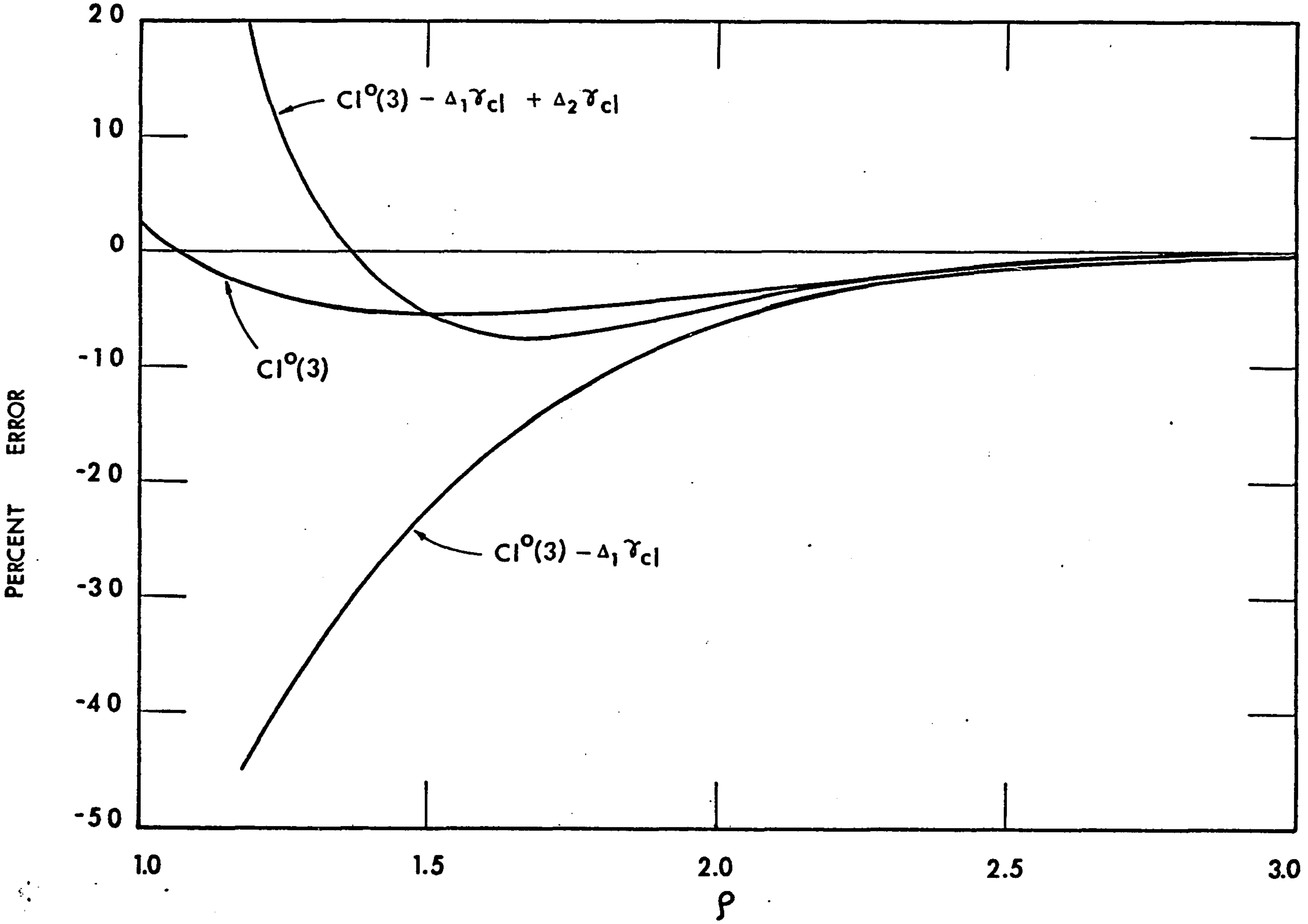


FIGURE 6 APPROXIMATION BY $\gamma_{Cl^{o}}(m) + \sum_{n} \Delta_{n} \gamma_{Cl}$



the results of the divergent nature of the series of Eq.(44).

B. APPROXIMATION FOR THE QUANTUM MECHANICAL VIBRATIONAL PARTITION FUNCTION OF THE MORSE-OSCILLATOR

For a Morse oscillator, the quantum mechanical partition function is exactly expressed as

$$Q_{qm} = S \exp \left[- \frac{u_e}{2} + \frac{ux}{4} \right] \qquad (62)$$

as it has been shown by Eqs.(13)-(16).

The best approximation obtained for S is by extending the upper limit of summation of Eq.(14) from the finite value V_D to ∞ and by grouping of exponents as $e^{-uv} e^{u\chi v^2}$ rather than as $e^{-u_e v} e^{u\chi(v+v^2)}$. The orthogonal polynomial expansion method has been tried besides the usual series type of expansion, but no improvement has been found.

Let $b = u\chi$. Then,

$$S \simeq \frac{1}{1-e^{-u}} \left\{ 1 + \frac{2b}{(e^{u}-1)^2} + \frac{b^2}{2} \left[\frac{e^{-u}}{(1-e^{-u}} + \frac{2e^{-2u}}{(1-e^{-u})^2} \right] \right\} \qquad (63)$$

The anharmonicity correction factor for the quantum mechanical partition function γ_{qm} is

$$\gamma_{qm} = \frac{Q_{qm}}{Q^{0}_{qm}} = S\, e^{\frac{u\chi}{4}} \left[1-e^{-u_e} \right] \qquad (64)$$

In Figures 7 and 8 we compare γ_{qm} calculated by using Eqs.(63) and (64), which are denoted by $\gamma_{qm}(3)$ with $\gamma_{qm}(3)$ calculated by using Eqs.(64) and (65), which are denoted by $\gamma^{*}_{qm}(3)$:

$$S \simeq \frac{1}{1-e^{-u_e}} + b\,\frac{e^{-u_e}}{(1-e^{-u_e})^2} + \left(b+\frac{b^2}{2}\right)$$

$$\left[\frac{e^{-u_e}}{(1-e^{-u_e})^2} + \frac{2e^{-2u_e}}{(1-e^{-u_e})^3}\right] \qquad (65)$$

Figure 7 is for x = 0.02, and Figure 8 is for x = 0.05. It should be recalled[1] that γ_{qm} depends on the frequency and anharmonicity constant χ individually, whereas the classical anharmonicity depends only on the ratio of frequency and anharmonicity constant, i.e., ρ.

C. THE REDUCED PARTITION FUNCTION FOR A NON-ROTATING DIATOMIC OSCILLATOR IN THE MORSE POTENTIAL

The reduced partition function ratio for a pair of isotopic molecules, $\frac{s}{s'}f$, is a ratio of Q_{qm}/Q_{cl} of the heavier molecule to Q'_{qm}/Q'_{cl} of the lighter one. Using the $\gamma_{cl}0(3)$ approximation for Q_{cl} and Q'_{cl} and Eqs.(63) and (64) for Q_{qm} and Q'_{qm}, I obtain, for the Morse oscillator,

$$\ln\frac{s}{s'} \simeq \sum_i \ln\frac{u_i e^{-u_i/2}(1-e^{-u_i'})}{u_i' e^{-u_i'/2}(1-e^{-u_i})} +$$

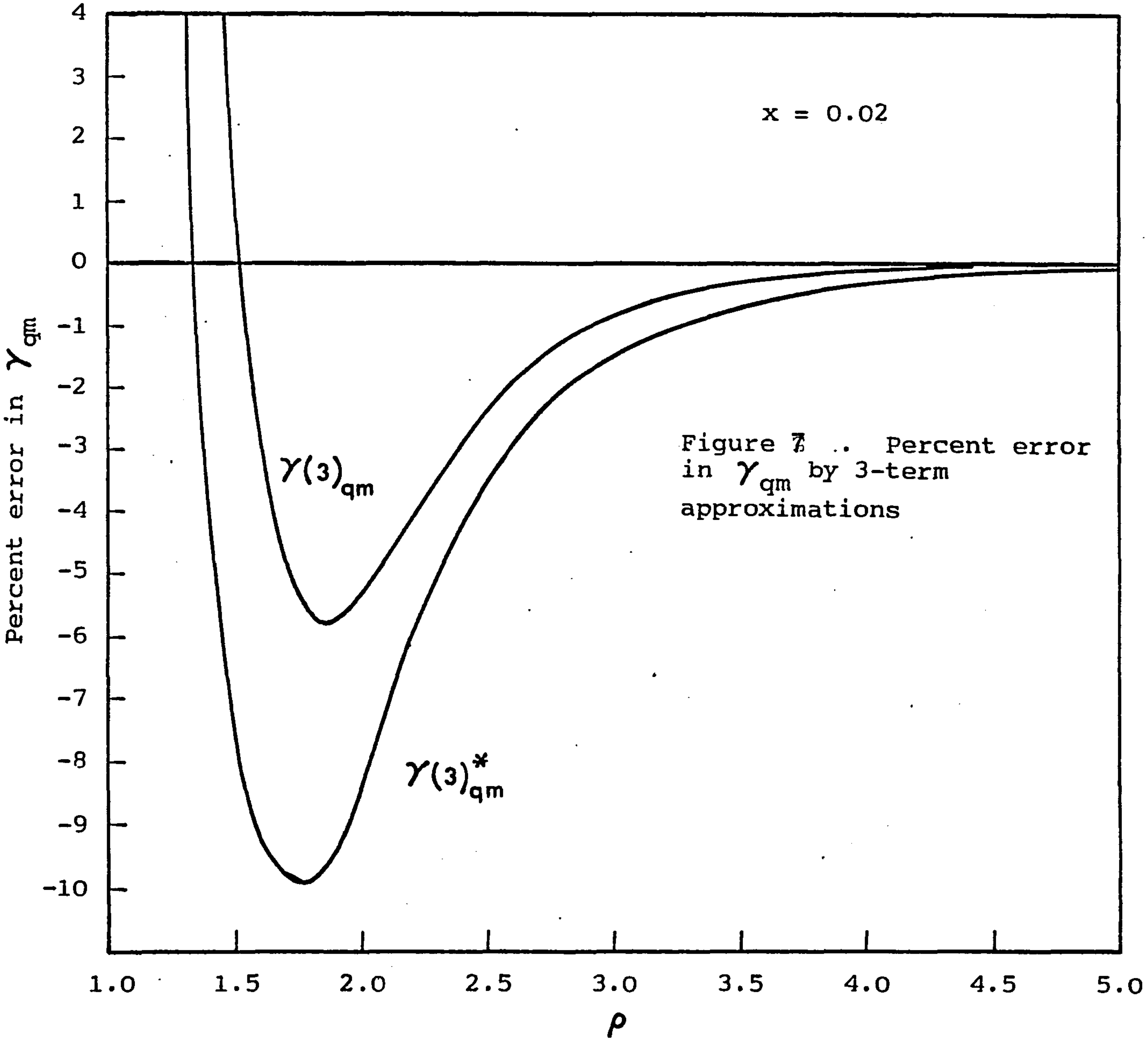


Figure 7 .. Percent error in γ_{qm} by 3-term approximations

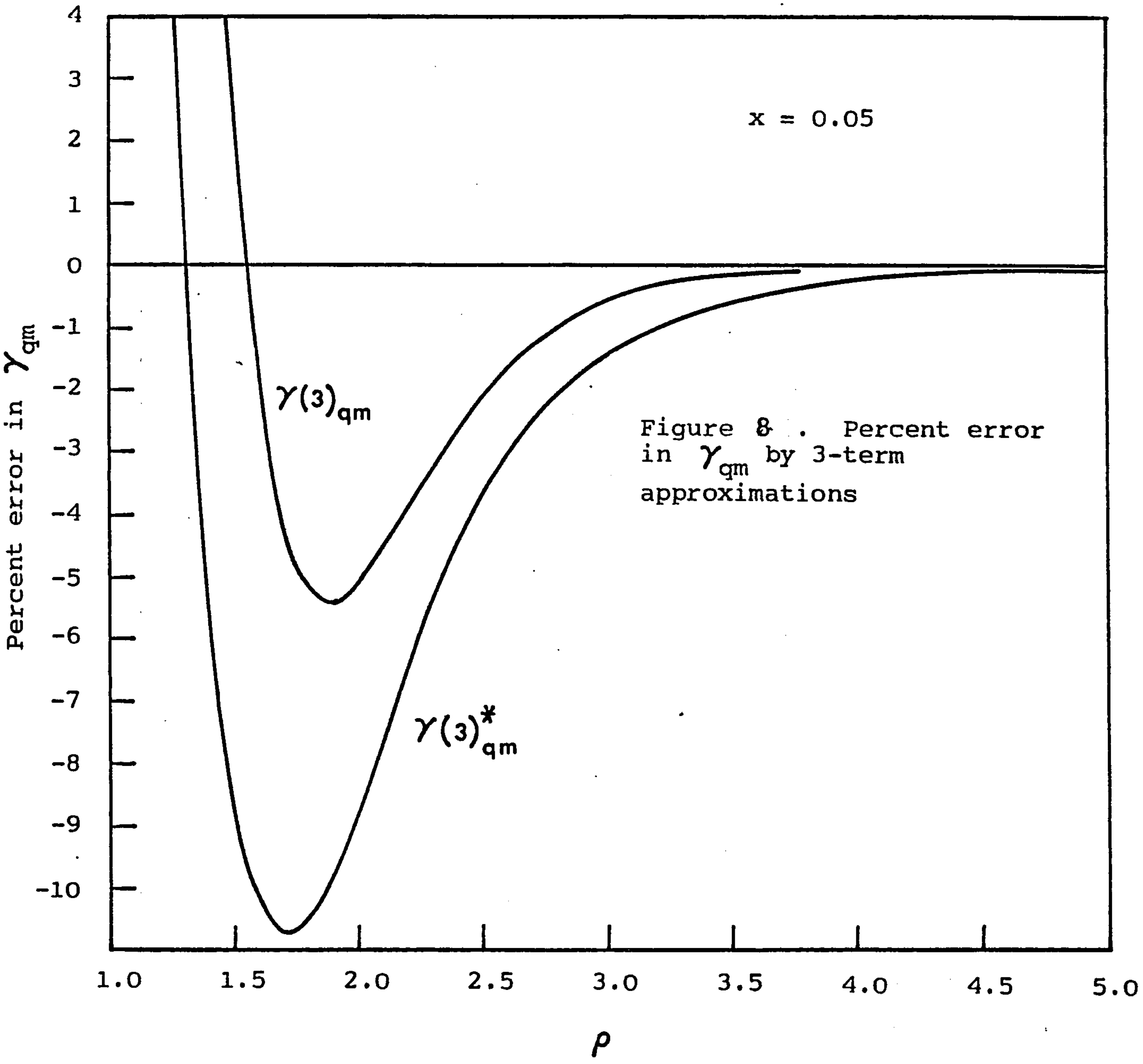


Figure 8 . Percent error in γ_{qm} by 3-term approximations

$$+ \sum_i \ln \frac{e^{u_i \chi_i/4}(1-e^{-u_{ei}})(1-e^{-u_i{}'})(1+1/2\rho'^2)A(u_i)}{e^{u_i{}'\chi_i{}'/4}(1-e^{-u_{e_i}{}'})(1-e^{-u_i})(1+1/2\rho^2)A(u_i{}')} \tag{66}$$

where $b = u\chi$ and

$$A(u) = 1 + \frac{2b}{(e^u-1)^2} + \frac{b^2}{2}\left[\frac{e^{-u}+e^{-2u}}{(1-e^{-u})^2}\right] . \tag{67}$$

The harmonic terms have been studied extensively by Bigeleisen and Ishida[12,13,14]. Here our interest is to examine the anharmonic terms. For a small anharmonicity, $b \ll u$,

$$\ln \frac{s}{s'}f \simeq (\ln \frac{s}{s'}f)_{\text{harmonic}}$$

$$+ \sum_i \left\{ \frac{1}{4}(b_i-b_i{}') + \left[\frac{2b_i}{(e^{u_{e_i}}-1)} - \frac{2b_i{}'}{(e^{u_{e_i}{}'}-1)}\right]\right.$$

$$\left. + \left[\frac{2b_i}{(e^{u_i}-e)^2} - \frac{2b_i{}'}{(e^{u_i{}'}-1)^2}\right] + \left[\frac{1}{2\rho'^2} - \frac{1}{2\rho^2}\right]\right\} \tag{68}$$

The terms under the summation sign in Eq.(68) represent contributions of anharmonicity. Its first term, $\Sigma\, \frac{1}{4}(b_i-b_i{}')$, is the commonly used anharmonicity correction on the zero point energy. The terms inside the bracket after $\sum_i$ in Eq.(68) have been used to account for the anharmonicity in each oscillator of the 2-D and 3-D problems in later chapters.

CHAPTER IV

APPROXIMATIONS FOR THE PARTITION FUNCTIONS OF POLYATOMIC SYSTEMS

As stated earlier, the purpose of this research has been to develop a good approximation method in accounting for anharmonicity in calculations of the molecular vibrational partition functions. The simplest problem, i.e., that of the diatomic molecule with one degree of freedom, has been presented in the preceding chapter. When one attempts to apply an approximation method to a polyatomic molecule, the major problem is in evaluating the exact partition functions, either classical or quantum-mechanical, and in accounting for the off-diagonal terms in the Hamiltonian.

A. MODEL 2-D SYSTEM

Due to the complexity of the general polyatomic problem involved, I first worked with a model 2-D system with two degrees of freedom which simulates the two stretching modes of carbon dioxide and its associated isotopes.

a.i. Exact Solution for the Classical Partition Function of a Model System with Two Degrees of Freedom

The classical partition function Q_{cl}^{anh} of the bound state of the model 2-D anharmonic oscillator in the potential given by

$$U(z_1,z_2) = kT \left[\rho_1(1-e^{-z_1/\rho_1})^2 + \rho_2(1-e^{-z_2/\rho_2})^2 + \gamma_{112}z_1^2z_2 + \gamma_{122}z_1z_2^2\right] \qquad (68)$$

is evaluated by using the following equation:

$$Q_{cl}^{anh} = \frac{1}{u_{e_1}}\frac{1}{u_{e_2}}\left(\frac{2}{\pi}\right)^2 \int_{-\rho_1 \ln 2}^{\infty} e^{-\rho_1^2(1-e^{-z_1/\rho_1})^2} \int_0^{\rho_1\sqrt{2e^{-z_1/\rho_1} - e^{-2z_1/\rho_1}}} e^{-y_1^2} \; X$$

$$\int_{-\rho_2 \ln 2}^{L_2(z_1)} e^{-\rho_2^2(1-e^{-z_2^2/\rho_2^2})^2 - \gamma_{112}z_1^2z_2 - \gamma_{122}z_1z_2^2}$$

$$\int_0^{y_{2+}} dy_2dz_2dy_1dz_1 \qquad (69)$$

where ρ, z, y are defined analogous to those in the 1-D Morse oscillator problem and $\gamma_{112} = \frac{1}{2\sqrt{2}} \frac{1}{\alpha_1^2\alpha_2 kT} \frac{1}{\rho_2\rho_1^2} f_{112}$,

etc. One finds y_{2+}, the upper limit of the variable y_2, appearing in Eq.(69) as

$$y_{2+} = \sqrt{\rho_2^2(1 - (1-e^{-z_2/\rho_2})^2 - \gamma_{122}z_1z_2^2 - \gamma_{133}z_1z_3^2} \quad . \tag{70}$$

Care is taken in the calculations of the upper limits of z , $L_2(z_1)$, to avoid inclusion of contributions from the unstable states corresponding to the repulsive forces that fictitiously arise from the truncation of the polynomial potential function. If the anharmonic term of the highest order of polynomial with respect to z_2 is positive, then $L_2(z_1) \to \infty$.

a.ii. Exact Solution for the Quantum Partition Function of a Model System with Two Degrees of Freedom

The quantum mechanical partition function is exactly expressed as

$$Q_{qm}^{anh} = \sum_{n_2=0}^{V_{D_2}} \sum_{n_1=0}^{V_{D_1}} e^{-\varepsilon(1,2)/kT} \tag{71}$$

where

$$\begin{aligned} G(v_1,v_2) = \frac{\varepsilon(1,2)}{hc} &= \omega_{e_1}(n_1+\tfrac{1}{2}) + \omega_{e_2}(n_2+\tfrac{1}{2}) \\ &- \omega_{e_1}\chi_{e_1}(n_1+\tfrac{1}{2})^2 + - \omega_{e_2}\chi_{e_2}(n_2+\tfrac{1}{2}) \\ &+ \chi_{12}(n_1+\tfrac{1}{2})(n_2+\tfrac{1}{2}) \end{aligned} \tag{72}$$

One observes that there are two upper limits, V_{D1} and V_{D2}, to be solved for. First I chose to define n_2 as the outer loop and n_1 as the inner loop. To obtain the value V_D for the inner loop, set

$$\frac{\partial G(V_1,V_2)}{\partial V_1} = 0 \qquad (73)$$

and we obtain

$$V_{1_D} = \frac{\omega_{e_1} - \omega_{e_1}\chi_{e_1} + \chi_{12}(n_2 + \frac{1}{2})}{2\chi_{e_1}\omega_{e_1}} \qquad (74)$$

For the outer loop, solving

$$\frac{\partial G(V_1=0,V_2)}{\partial V_2} = 0 \qquad (75)$$

will yield V_{D2} for V_2 as

$$V_{D_2} = \frac{\omega_{e_2} - \chi_{e_2}\omega_{e_2}}{2\chi_{e_2}\omega_{e_2}} \qquad (76)$$

Once Q_{cl}^{anh} and Q_{qm}^{anh} have been set up, the exact value of the logarithm of the reduced partition function can be calculated.

b. Approximations for the Partition Functions of the Polyatomic System

In this section I describe an approximation method I developed to account for the off-diagonal terms in the potential energy surface of a polyatomic molecule. Schwinger's perturbation theory is utilized to evaluate the vibrational partition functions. The basis coordinate system chosen was the normal coordinates of the given molecule. The Hamiltonian is, thus,

$$H = \frac{1}{2} \sum_i \lambda_{ii} Q_i^2 + \frac{1}{2} \sum_i \dot{Q}_i^2 + \sum_{ijk} f_{ijk} Q_i Q_j Q_k \ , \qquad (77)$$

with the unperturbed Hamiltonian operator

$$H_0 = \frac{1}{2} \sum_i \lambda_{ii} Q_i^2 + \frac{1}{2} \sum_i \dot{Q}_i^2 + \sum_i f_{iii} Q_i^3 \qquad (78)$$

and the perturbation

$$H_1 = \sum_{i \neq j \neq k} f_{ijk} Q_i Q_j Q_k + \sum_{i \neq j} f_{iij} Q_i Q_i Q_j \qquad (79)$$

where the Q's are normal coordinates. Analytical expression for the perturbation terms of the vibrational partition functions are obtained up to the second order.

In Schwinger's perturbation method for partition functions, the Hamiltonian operator H is divided into an unperturbed H_0 and a perturbation H_1. The diagonal density matrix is taken with respect to the eigenfunctions of H_0. This perturbation method was developed by Schwinger[8,9] to solve problems involving partition functions and exponential expressions in field theory.

From the development of the Schwinger perturbation theory, the final formula for the partition function is

$$
\begin{aligned}
Q = \mathrm{Tr}\ e^{-\beta(H_0+H_1)} &= Q_0 + Q_1 + Q_2 + \ldots + Q_{n+1} + \ldots \\
&= \mathrm{Tr}\ e^{-\beta H_0} - \mathrm{Tr}\ H_1 e^{-\beta H_0} \\
&+ \frac{\beta^2}{2}\ \mathrm{Tr} \int_0^1 dt_1 H_1 e^{-\beta H_0(1-t_1)} H_1 e^{-\beta H_0 t_1} + \ldots \\
&+ \frac{(-1)^{n+1}}{n+1}\ \beta^{n+1}\ \mathrm{Tr} \int_0^1 t_1^{\,n-1}\, dt_1 \int_0^1 t_2^{\,n-2}\, dt_2 \ldots \\
&\int_0^1 dt_n \Big[H_1 e^{-\beta H_0(1-t_1)}\ H_1 e^{-\beta H_0 t_1(1-t_2)} \\
&H_1 e^{-\beta H_0 t_1 t_2 (1-t_3)} \ldots H_1 e^{-\beta H_0 t_1 t_2 \ldots t_n} \Big] + \ldots
\end{aligned}
\tag{80}
$$

The first term in the perturbation formula is just the partition function for the unperturbed Hamiltonian--the zeroeth order harmonic approximation. Successive terms contain higher powers of the perturbation H_1. Employing the second quantization method with the raising and lowering operators $a^{\dagger}$ and a which obey the commutation rules,

$$[a_i, a_i^{\dagger}] = \delta_{ij}$$

and

$$[a_i, a_j] = [a_i^{\dagger}, a_j^{\dagger}] = 0 \tag{81}$$

we can express[15]

$$Q_i = \left(\frac{\hbar}{2\omega_i}\right)^{1/2} (a_i + a_i^{\dagger})$$

$$P_i = i\left(\frac{\hbar\omega_i}{2}\right)^{1/2} (a_i^{\dagger} - a_i) \tag{82}$$

In terms of these operators, one obtains, after casting the conjugated momenta and coordinates in a form suitable for second quantization method,[16,17]

$$H_0 = \frac{\hbar}{2} \Sigma \lambda_i^{1/2} \left\{ \left(\frac{p_i}{\hbar}\right)^2 + q_i \right\} + hc \sum_i f_{iii} q_i^3 , \tag{83a}$$

$$H_1 = hc \sum_i \sum_j f_{ijj} q_i q_j^2 + hc \sum_i \sum_j \sum_k f_{ijk} q_i q_j q_k , \tag{83b}$$

where

$$p_i = \frac{i\hbar}{2} \sqrt{2}\, (a_i^{\dagger} - a_i) , \tag{84a}$$

and

$$q_i = \frac{1}{2}\sqrt{2}\,(a_i^{\dagger}+a_i) \ . \tag{84b}$$

Now

$$Q_0 = \mathrm{Tr}\ e^{-\beta H_0} = \sum_{n_1,n_2\ldots} < | \ e^{-\beta E_{n_1,n_2\ldots}} \ | >$$

$$= \sum_{n_i} e^{-\beta\hbar E^{anh}_{n_1}} \ , \tag{85}$$

where

$$E^{anh}_{n_i} = \omega_{e_i}(n_i+\tfrac{1}{2}) + \omega_{e_i}\chi_{e_i}\,(n_i+\tfrac{1}{2})^2 \ ,$$

$$| > = |n_1 n_2 \ \ldots \ > \ , \tag{86}$$

and for this zeroeth order partition function, eigenfunctions for the Morse oscillator have been utilized.

The previous results that I obtained for the diatomic molecules employ the internal valence coordinates. However, since the internal coordinate and the normal coordinate are identical for diatomic molecules, all the equations derived for the one-dimensional case can be said to be in terms of the normal coordinate. If the normal coordinates for polyatomic molecules were uncoupled under the anharmonic forces, then the partition functions of such polyatomic molecules would have been expressible simply as the products of the diatomic functions. Thus, we make use of Schwinger's perturbation method in the following way. The unperturbed problem consists of an assembly of independent Morse-type potential,

$$U_i = D_i(1 - e^{-\alpha_i Q_i})^2 \tag{87}$$

where Q_i is the i-th normal coordinate. For each such oscillator, the mass is unity, and the force constant is λ_i, the i-th eigenvalue of the corresponding harmonic oscillator problem. The perturbation is represented by the cubic off-diagonal terms, $f_{iij}Q_iQ_iQ_j$ and $f_{ijk}Q_iQ_jQ_k$.

The association of the energy levels of H_0 to that of the Morse potential is based on the assumption that for small anharmonicity,

$$\begin{aligned} U_i &= D_i(1 - e^{-\alpha_i Q_i})^2 \\ &\simeq D_i\alpha_i^2 Q_i^2 - D_i\alpha_i^3 Q_i^3 \\ &= \frac{1}{2}\lambda_{ii}Q_i^2 + \frac{1}{2}f_{iii}Q_i^3 . \end{aligned} \tag{88}$$

The relationship between the Morse potential parameter D_i, α_i and quadratic and cubic coefficients λ_{ii} and f_{iii} will enable one to calculate ω_{e_i} and χ_{e_i} in terms of known λ_{ii} and f_{iii}. Physically this represents the picture in which the eigenfunctions of the unperturbed Hamiltonian are products of uncoupled Morse-type oscillators, corresponding to the various frequencies ω_{e_i} and not to complicate the situation any further, $|n>$ is taken to be the same as in the harmonic case.

Q_1 and Q_2 terms in Eq. (80) are evaluated as follows.

$$Q_1 = -\beta \mathrm{Tr}\left[H_1 e^{-\beta H_0}\right] = 0 \tag{89}$$

$$\begin{aligned}
Q_2 = \frac{1}{2}\beta^2 \mathrm{Tr} \Bigg[& \sum_{i\neq j} \int_0^1 dt\, F^2_{iij}\, [a_k a_i (a_j + a_j^\dagger) \\
& + a_i^\dagger a_i^\dagger (a_j + a_j^\dagger) + 2a_i^\dagger a_i (a_j + a_j^\dagger) + (a_j + a_j^\dagger)] \\
& \quad e^{-\beta H_0} [a_i a_i e^{-2\beta\omega_{e_i}\hbar t} (a_j e^{-\beta\hbar\omega_{e_j} t} + a_j^\dagger e^{\beta\hbar\omega_{e_j} t}) \\
& + a_i^\dagger a_i^\dagger e^{2\beta\hbar\omega_{e_i} t} (a_j e^{-\beta\hbar\omega_{e_i} t} + a_j^\dagger e^{\beta\hbar\omega_{e_j} t}) \\
& + 2a_i^\dagger a_i (a_j e^{-\beta\hbar\omega_{e_j} t} + a_j^\dagger e^{\beta\hbar\omega_{e_j} t}) \\
& + (a_j e^{-\beta\hbar\omega_{e_j} t} + a_j^\dagger e^{\beta\hbar\omega_{e_j} t})] \\
& + \sum_{i\neq j\neq k} \int_0^1 dt\, F^2_{ijk}\, [a_i a_j a_k + a_i a_j a_k^\dagger + a_i a_j^\dagger a_k \\
& + a_i a_j^\dagger a_k^\dagger + a_i^\dagger a_j a_k + a_i^\dagger a_j a_k^\dagger + a_i^\dagger a_j^\dagger a_k + a_i^\dagger a_j^\dagger a_k^\dagger]
\end{aligned}$$

$$
\begin{aligned}
& e^{-\beta H_0} \; [a_i a_j a_k{}^\dagger e^{-\beta\hbar(\omega_{e_i}+\omega_{e_j}+\omega_{e_k})t} \\
& + a_i a_j a_k{}^\dagger \; e^{-\beta\hbar(\omega_{e_j}+\omega_{e_j}-\omega_{e_k})t} \\
& + a_i a_j{}^\dagger a_k \; e^{-\beta\hbar(\omega_{e_i}+\omega_{e_k}-\omega_{e_j})t} \\
& + a_i a_j{}^\dagger a_k{}^\dagger \; e^{-\beta\hbar(\omega_{e_i}-\omega_{e_j}-\omega_{e_k})t} \\
& + a_i{}^\dagger a_j a_k \; e^{-\beta\hbar(\omega_{e_j}+\omega_{e_k}-\omega_{e_i})t} \\
& + a_i{}^\dagger a_j a_k{}^\dagger \; e^{-\beta\hbar(\omega_{e_j}-\omega_{e_k}-\omega_{e_i})t} \\
& + a_i{}^\dagger a_j{}^\dagger a_k \; e^{-\beta\hbar(\omega_{e_k}-\omega_{e_i}-\omega_{e_j})t} \\
& + a_i{}^\dagger a_j{}^\dagger a_k{}^\dagger \; e^{\beta\hbar(\omega_{e_k}+\omega_{e_i}+\omega_{e_j})t} \;]
\end{aligned}
\tag{90}
$$

where

$$F_{ijk} = \left(\frac{1}{\sqrt{2}}\right)^3 f_{ijk}hc \; ,$$

Q_2 can be simplified further. Details of the simplification will be given in Appendix D. The final result is

$$Q_2 = \frac{\beta^2}{2} \left(\sum_{i}^{3N-6} e^{-\beta\hbar\omega_i/2} \right) \prod_{\ell} Z_{0\ell} \sum_i \sum_j \sum_k \Big\{ F_{ijk}{}^2$$

$$(U_{ijk} + U_{i-jk} + U_{ij-k} + U_{-ijk} + U_{i-j-k} + U_{-ijk}$$

$$\left. + U_{-i-jk} + U_{-i-j-k}) \right] \qquad (91)$$

where

$$U_{ijk} = Z_{1i}Z_{1j}Z_{1k} \frac{Y(i+j+k)-1}{\beta\hbar(\omega_{e_i}+\omega_{e_j}+\omega_{e_k})}, \qquad (92a)$$

$$U_{i-jk} = Z_{1i}(Z_{1j}+Z_{0j})Z_{1k} \frac{Y(i-j+k)-1}{\beta\hbar(\omega_{e_i}-\omega_{e_j}+\omega_{e_k})}, \qquad (92b)$$

$$U_{i-j-k} = Z_{1i}(Z_{1j}+Z_{0j})(Z_{1k}+Z_{0k}) \frac{Y(i-j-k)-1}{\beta\hbar(\omega_{e_i}-\omega_{e_j}-\omega_{e_k})}, \qquad (92c)$$

$$U_{-i-j-k} = (Z_{1i}{}^{\dagger}Z_{0i})(Z_{1k}+Z_{0j})(Z_{1k}+Z_{0k}) \frac{1 - Y^{-1}(i+j+k)}{\beta\hbar(\omega_{e_i}+\omega_{e_j}+\omega_{e_k})}. \qquad (92d)$$

with

$$Z_0 = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega_{e_n}} = e^{v_e}(e^{v_e}-1)^{-1}, \qquad (93a)$$

$$Z_1 = \sum_{n=0}^{\infty} n\, e^{-\beta\hbar\omega_{e_n}} = e^{v_e}(e^{v_e}-1)^{-2}, \qquad (93b)$$

$$Z_2 = \sum_{n=0}^{\infty} n^2\, e^{-\beta\hbar\omega_{e_n}} = e^{v_e}(e^{v_e}+1)(e^{v_e}-1)^{-3}, \qquad (93c)$$

$$Y(i\pm j\ \ldots) = e^{\beta\hbar(\omega_{e_i}\pm\omega_{e_j}\pm\ldots)}\ , \tag{94a}$$

$$Y^{-1}\ (i\pm j\pm\ldots) = e^{-\beta\hbar(\omega_{e_i}\pm\omega_{e_j}\pm\ldots)}\ , \tag{94b}$$

in which $v_e = \beta\hbar\omega_e$.

In Eq. (91) the product over ℓ is taken over 1 to 3N-6, excluding i,j,k, and the summations are taken over each of i,j,k from 1 to 3N-6, excluding the cases when i=j=k.

The preceding solution was applied to a model 2-D system with two degrees of freedom. In the expansion of $\frac{s}{s'}f = \frac{Qr}{Qr'}$, the final expression of $\ln \frac{s}{s'}f$ for our model system is

$$\ln \frac{s}{s'}\ f = \left(\ln \frac{s}{s'}\ f\right)_{harm} + \sum_{i}^{2} \ln A_i + (D-D') + (E'-E)\ , \tag{95}$$

where

$$\left(\ln \frac{s}{s'}\ f\right)_{harm} = \ln \prod_{i=1}^{2} \frac{v_{e_i}\, e^{-\frac{v_{e_i}}{2}}\left(1-e^{-v_{e_i}'}\right)}{v_{e_i}'\, e^{-\frac{v_{e_i}'}{2}}\left(1-e^{-v_{e_i}}\right)}\ , \tag{96}$$

and A_i is the same as in Eq. (66) with the proper identification of variables.

$$D = \frac{Q_2^{\text{quant}}}{\sum\limits_{ni} e^{-\beta\hbar E^{\text{anh}}_{n_i}}} \tag{97a}$$

$$E = \frac{Q_2^{\text{class}}}{\prod\limits_{i=1}^{2} \frac{1}{v_{e_i}} \prod\limits_{i=1}^{2} (1 + \frac{1}{2\rho_i^2})} \tag{97b}$$

and D' and E' are D and E of the lighter isotopic molecule.

In Eqs. (97a, 97b),

$$\begin{aligned} Q_2^{\text{quant}} = \frac{\beta^2}{2} e^{-\frac{v_{e_i}}{2}} e^{-\frac{v_{e_2}}{2}} \Big\{ & F_{112}{}^2([(Z_{21}-Z_{11})- \\ & Z_{12}U(2v_{e1}+v_{e2})] + [(4Z_{21}+4Z_{11}+Z_{01})Z_{12}U(v_{e_2})] \\ & + [(Z_{21}-Z_{11})(Z_{12}+Z_{02})U(2v_{e_1}-v_{e_2})] \\ & + [(Z_{21}+3Z_{11}+2Z_{12})(Z_{12}+Z_{02})U(-2v_{e_1}+v_{e_2})] \\ & + [(4Z_{21}+4Z_{11}+Z_{01})(Z_{12}+Z_{02})U(-v_{e_1})] \\ & + [(Z_{21}+2Z_{11}+Z_{01})(Z_{12}+Z_{02})U(-2v_{e_1}-v_{e_2})]) \\ & + F_{122}^2([\text{ with 1 \& 2 interchanged}])\Big\} , \end{aligned} \tag{98}$$

with

$$U(v_{e_i}+v_{e_i}-v_{e_j}) = \frac{e^{v_{e_i}+v_{e_i}-v_{e_j}}-1}{v_{e_i}+v_{e_j}-v_{e_j}}, \qquad (99a)$$

$$U(-v_{e_i}) = \frac{e^{-v_{e_i}}-1}{-v_{e_j}}, \qquad (99b)$$

$$Q_2^{\text{class}} = \frac{\beta^2}{2} \sum_{i,j=1}^{2} 24F_{iij}{}^2 \frac{1}{v_{e_i}{}^2 \, v_{e_j}{}^2} . \qquad (100)$$

The expression of Eq.(100) for the classical vibrational partition function Q_2^{class} was obtained in the limit of T→∞ from Q_2^{quant} for the 2-D system.

c. Numerical Results for the Model System

Numerical results of the 2-D cases are first presented with a discussion following right after this section. Equation(94) is used to calculate the $\ln \frac{s}{s'} f$ (anharm). Equation(95) is used to calculate $\ln \frac{s}{s'} f$ (harm). To calculate $\ln \frac{s}{s'} f$ (exact), the numerical integration method is employed for the classical partition function and numerical summation is used for the quantum partition function of the model system. The program for the actual calculation of the 2-D case is listed in the appendix.

Inputs for the program are the temperature, the symmetric stretching frequency ω_1, the antisymmetric stretching frequency ω_2, anharmonicity constants χ_1, χ_2. From Nielsen's result of the relationship between anharmonicity constants χ_i and cubic coefficients F_{ijk}, one can calculate F_{122}, F_{111} by knowing the values of F_{112}, F_{222} (which equal zero in this model case due to symmetry), χ_i, and ω_i.

In the following tables, first values of χ_1, χ_2 are tabulated. The values of the exact, harmonic, anharmonic $\ln \frac{s}{s'} f$ are presented in columns 3,4,5. Columns 6,7 yield the percent error of the harmonic $\ln \frac{s}{s'} f$ vs exact and that of the anharmonic $\ln \frac{s}{s'} f$ vs exact respectively. In columns 8,9,10, A stands for $\sum_{i=1}^{2} \ln A_i$; E stands for E'-E; D stands for D-D'. The last two entries are the calculated values of F_{122}, F_{122}', F_{111} and F_{111}'.

Table 2 . Ln(s/s')f for model 2-D system #1 at 100° K

```
T = 100.000          WE'(1) =    500.00          WE(1) =    475.00          WE'(2) =    800.00          WE(2) =    760.00
```

```
                         LN(S/S')F                % ERROR
                 ---------------------------   -------------
   X1     X2      EXACT      HARM.    ANHARM.  HARM. ANHARM.     A          E          D        (F122,F122')  (F111,F111')
  ----   -----   --------   --------   --------  ----- ------- ---------  ---------  ---------  ------------  ------------
 0.002   0.002   0.364130   0.365352   0.364511  0.336  0.105  -0.000507  -0.000028  -0.000307 ( -39.1, -41.1)( -11.0, -11.5)
         0.005   0.363064   0.365352   0.363571  0.630  0.140  -0.000965  -0.000068  -0.000747 ( -61.8, -65.0)( -11.0, -11.5)
         0.010   0.361446   0.365352   0.362057  1.081  0.169  -0.001729  -0.000135  -0.001431 ( -87.4, -92.0)( -11.0, -11.5)

 0.005   0.002   0.363533   0.365352   0.364213  0.500  0.187  -0.000808  -0.000027  -0.000304 ( -39.1, -41.1)( -17.3, -18.3)
         0.005   0.362297   0.365352   0.363279  0.843  0.271  -0.001267  -0.000067  -0.000739 ( -61.8, -65.0)( -17.3, -18.3)
         0.010   0.360487   0.365352   0.361772  1.350  0.356  -0.002031  -0.000133  -0.001416 ( -87.4, -92.0)( -17.3, -18.3)

 0.010   0.002   0.362699   0.365352   0.363718  0.731  0.281  -0.001309  -0.000027  -0.000298 ( -39.1, -41.1)( -24.5, -25.8)
         0.005   0.361271   0.365352   0.362792  1.130  0.421  -0.001767  -0.000066  -0.000727 ( -61.8, -65.0)( -24.5, -25.8)
         0.010   0.359245   0.365352   0.361298  1.700  0.572  -0.002531  -0.000131  -0.001392 ( -87.4, -92.0)( -24.5, -25.8)
```

```
T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 3. Ln(s/s')f for model 2-D system #2 at 100° K

```
 T = 100.000           WE'(1) =   500.00          WE(1) =   475.00          WE'(2) =  1600.00          WE(2) =  1520.00


                                LN(S/S')F                 % ERROR
                    ----------------------------   -------------
   X1       X2      EXACT       HARM.     ANHARM.  HARM. ANHARM.      A           E           D       (F122,F122')  (F111,F111')
  ----     -----   --------   --------   --------  ----- ------- ----------  ----------  ----------  ------------- -------------
  0.002    0.002   0.651429   0.653102   0.651808  0.257  0.058  -0.000786   -0.000013   -0.000494 ( -54.1, -56.9)( -11.0, -11.5)
           0.005   0.649868   0.653102   0.650228  0.498  0.055  -0.001663   -0.000033   -0.001178 ( -85.5, -90.0)( -11.0, -11.5)
           0.010   0.647485   0.653102   0.647737  0.867  0.039  -0.003124   -0.000066   -0.002175 (-120.9,-127.3)( -11.0, -11.5)

  0.005    0.002   0.650720   0.653102   0.651512  0.366  0.122  -0.001087   -0.000013   -0.000489 ( -54.1, -56.9)( -17.3, -18.3)
           0.005   0.648922   0.653102   0.649940  0.644  0.157  -0.001964   -0.000033   -0.001166 ( -85.5, -90.0)( -17.3, -18.3)
           0.010   0.646274   0.653102   0.647459  1.057  0.183  -0.003426   -0.000065   -0.002152 (-120.9,-127.3)( -17.3, -18.3)

  0.010    0.002   0.649759   0.653102   0.651020  0.514  0.194  -0.001588   -0.000013   -0.000481 ( -54.1, -56.9)( -24.5, -25.8)
           0.005   0.647696   0.653102   0.649460  0.835  0.272  -0.002465   -0.000032   -0.001145 ( -85.5, -90.0)( -24.5, -25.8)
           0.010   0.644748   0.653102   0.646997  1.296  0.349  -0.003926   -0.000064   -0.002115 (-120.9,-127.3)( -24.5, -25.8)


 T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 4. Ln(s/s')f for model 2-D system at 100° K #3

```
 T = 100.000          WE'(1) =    500.00          WE(1) =    475.00          WE'(2) =  2400.00          WE(2) =  2280.00


                                LN(S/S')F                 % ERROR
                      ----------------------------- -------------
   X1       X2      EXACT      HARM.     ANHARM.   HARM. ANHARM.       A           E           D       (F122,F122')  (F111,F111')
  ----     -----   --------   --------   --------  ----- ------- ---------   ---------   ---------  ------------- -------------
  0.002    0.002   0.938751   0.940859   0.939143  0.225   0.042  -0.001071   -0.000009   -0.000637 ( -66.0, -69.5)( -11.0, -11.5)
           0.005   0.936679   0.940859   0.936982  0.446   0.032  -0.002375   -0.000022   -0.001481 (-104.4,-109.8)( -11.0, -11.5)
           0.010   0.933493   0.940859   0.933639  0.789   0.016  -0.004548   -0.000044   -0.002628 (-147.6,-155.3)( -11.0, -11.5)

  0.005    0.002   0.937953   0.940859   0.938849  0.310   0.096  -0.001372   -0.000009   -0.000630 ( -66.0, -69.5)( -17.3, -18.3)
           0.005   0.935592   0.940859   0.936697  0.563   0.118  -0.002676   -0.000022   -0.001465 (-104.4,-109.8)( -17.3, -18.3)
           0.010   0.932082   0.940859   0.933367  0.942   0.138  -0.004849   -0.000043   -0.002600 (-147.6,-155.3)( -17.3, -18.3)

  0.010    0.002   0.937199   0.940859   0.938359  0.390   0.124  -0.001872   -0.000009   -0.000619 ( -66.0, -69.5)( -24.5, -25.8)
           0.005   0.934206   0.940859   0.936223  0.712   0.216  -0.003176   -0.000021   -0.001439 (-104.4,-109.8)( -24.5, -25.8)
           0.010   0.930331   0.940859   0.932914  1.132   0.278  -0.005350   -0.000042   -0.002553 (-147.6,-155.3)( -24.5, -25.8)


 T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 5. Ln(s/s')f for model 2-D system #4 at 100° K

```
 T = 100.000          WE'(1) =    500.00          WE(1) =    475.00          WE'(2) =  3200.00          WE(2) =  3140.00



                               LN(S/S')F                 % ERROR
                   ----------------------------  -------------
   X1      X2       EXACT      HARM.     ANHARM.  HARM. ANHARM.      A            E            D        (F122,F122')   (F111,F111')
  ----    -----   --------   --------   --------  ----- -------  ----------   ----------   ----------   ------------- -------------
 0.002    0.002   0.540094   0.541588   0.540638  0.277   0.101  -0.000634    -0.000002    -0.000314 ( -77.4, -80.1)( -11.0, -11.5)
          0.005   0.538777   0.541588   0.539581  0.522   0.149  -0.001284    -0.000006    -0.000717 (-122.3,-126.7)( -11.0, -11.5)
          0.010   0.536796   0.541588   0.537971  0.893   0.219  -0.002368    -0.000012    -0.001238 (-173.0,-179.2)( -11.0, -11.5)

 0.005    0.002   0.539246   0.541588   0.540342  0.434   0.203  -0.000936    -0.000002    -0.000308 ( -77.4, -80.1)( -17.3, -18.3)
          0.005   0.537853   0.541588   0.539293  0.694   0.268  -0.001586    -0.000006    -0.000704 (-122.3,-126.7)( -17.3, -18.3)
          0.010   0.535616   0.541588   0.537694  1.115   0.388  -0.002669    -0.000011    -0.001214 (-173.0,-179.2)( -17.3, -18.3)

 0.010    0.002   0.531178   0.541588   0.539851  1.960   1.633  -0.001436    -0.000002    -0.000299 ( -77.4, -80.1)( -24.5, -25.8)
          0.005   0.536652   0.541588   0.538814  0.929   0.403  -0.002086    -0.000006    -0.000682 (-122.3,-126.7)( -24.5, -25.8)
          0.010   0.534127   0.541588   0.537232  1.397   0.581  -0.003169    -0.000011    -0.001176 (-173.0,-179.2)( -24.5, -25.8)



 T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 6 . Ln(s/s')f for model 2-D system #5 at 100° K

```
T = 100.000          WE'(1) =  1000.00        WE(1) =   950.00        WE'(2) =   800.00        WE(2) =   760.00



                              LN(S/S')F                 % ERROR
                   ---------------------------     -------------
   X1      X2      EXACT      HARM.     ANHARM.   HARM. ANHARM.      A          E          D       (F122,F122')  (F111,F111')
  ----    -----  --------   --------   --------   ----- -------  ---------  ---------  ---------  ------------- -------------
  0.002   0.002  0.542472   0.544876   0.543642   0.443  0.216   -0.000680  -0.000039  -0.000515 ( -65.2, -68.6)( -21.9, -23.1)
          0.005  0.540213   0.544876   0.542394   0.863  0.404   -0.001139  -0.000096  -0.001247 (-103.1,-108.5)( -21.9, -23.1)
          0.010  0.536717   0.544876   0.540416   1.520  0.689   -0.001903  -0.000189  -0.002368 (-145.8,-153.5)( -21.9, -23.1)

  0.005   0.002  0.541413   0.544876   0.543091   0.640  0.310   -0.001241  -0.000038  -0.000504 ( -65.2, -68.6)( -34.7, -36.5)
          0.005  0.538866   0.544876   0.541859   1.115  0.556   -0.001700  -0.000095  -0.001221 (-103.1,-108.5)( -34.7, -36.5)
          0.010  0.535044   0.544876   0.539906   1.837  0.909   -0.002464  -0.000187  -0.002319 (-145.8,-153.5)( -34.7, -36.5)

  0.010   0.002  0.539917   0.544876   0.542174   0.918  0.418   -0.002177  -0.000038  -0.000487 ( -65.2, -68.6)( -49.1, -51.6)
          0.005  0.537044   0.544876   0.540967   1.458  0.731   -0.002636  -0.000094  -0.001179 (-103.1,-108.5)( -49.1, -51.6)
          0.010  0.532856   0.544876   0.539053   2.256  1.163   -0.003400  -0.000185  -0.002238 (-145.3,-153.5)( -49.1, -51.6)



T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 7 . Ln(s/s')f for model 2-D system #6 at 100^{o} K

```
 T = 100.000          WE'(1) =  1000.00          WE(1) =   950.00          WE'(2) =  1600.00          WE(2) =  1520.00


                          LN(S/S')F                  % ERROR
                    ----------------------------  -----------
    X1      X2      EXACT       HARM.     ANHARM.   HARM. ANHARM.       A           E           D        (F122,F122')  (F111,F111')
   ----   -----   --------   --------   --------   ----- -------  ---------   ---------   ---------   -------------  -------------
  0.002   0.002   0.830219   0.832625   0.831049   0.290   0.100  -0.000959   -0.000014   -0.000603 ( -78.1, -82.3)( -21.9, -23.1)
          0.005   0.828114   0.832625   0.829322   0.545   0.146  -0.001836   -0.000035   -0.001433 (-123.6,-130.1)( -21.9, -23.1)
          0.010   0.824928   0.832625   0.826626   0.933   0.206  -0.003298   -0.000069   -0.002633 (-174.7,-183.9)( -21.9, -23.1)

  0.005   0.002   0.829062   0.832625   0.830500   0.430   0.173  -0.001520   -0.000014   -0.000591 ( -78.1, -82.3)( -34.7, -36.5)
          0.005   0.826611   0.832625   0.828791   0.728   0.264  -0.002397   -0.000034   -0.001403 (-123.6,-130.1)( -34.7, -36.5)
          0.010   0.823034   0.832625   0.826120   1.165   0.375  -0.003859   -0.000068   -0.002578 (-174.7,-183.9)( -34.7, -36.5)

  0.010   0.002   0.827454   0.832625   0.829595   0.625   0.258  -0.002456   -0.000014   -0.000570 ( -78.1, -82.3)( -49.1, -51.6)
          0.005   0.824613   0.832625   0.827905   0.972   0.399  -0.003333   -0.000034   -0.001354 (-123.6,-130.1)( -49.1, -51.6)
          0.010   0.820596   0.832625   0.825276   1.466   0.570  -0.004795   -0.000067   -0.002487 (-174.7,-183.9)( -49.1, -51.6)


 T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 8 . Ln(s/s')f for model 2-D system #7 at 100^{o} K

```
T = 100.000          WE'(1) =  1000.00          WE(1) =    950.00          WE'(2) =  2400.00          WE(2) =  2280.00


                         LN(S/S')F                  % ERROR
                 --------------------------   -------------
   X1       X2     EXACT      HARM.     ANHARM.   HARM. ANHARM.      A           E           D        (F122,F122')  (F111,F111')
  ----    -----  --------   --------   --------   ----- ------- ---------   ---------   ---------   ------------- -------------
  0.002   0.002  1.117519   1.120382   1.118421   0.256   0.081  -0.001244   -0.000009   -0.000708 ( -94.2, -99.1)( -21.9, -23.1)
          0.005  1.114920   1.120382   1.116171   0.490   0.112  -0.002548   -0.000023   -0.001641 (-148.9,-156.7)( -21.9, -23.1)
          0.010  1.110975   1.120382   1.112722   0.847   0.157  -0.004721   -0.000045   -0.002895 (-210.5,-221.6)( -21.9, -23.1)

  0.005   0.002  1.116239   1.120382   1.117876   0.371   0.147  -0.001805   -0.000009   -0.000693 ( -94.2, -99.1)( -34.7, -36.5)
          0.005  1.113223   1.120382   1.115646   0.643   0.218  -0.003109   -0.000022   -0.001605 (-148.9,-156.7)( -34.7, -36.5)
          0.010  1.108809   1.120382   1.112226   1.044   0.308  -0.005283   -0.000044   -0.002830 (-210.5,-221.6)( -34.7, -36.5)

  0.010   0.002  1.114494   1.120382   1.116965   0.528   0.222  -0.002741   -0.000009   -0.000667 ( -94.2, -99.1)( -49.1, -51.6)
          0.005  1.111008   1.120382   1.114770   0.844   0.339  -0.004045   -0.000022   -0.001545 (-148.9,-156.7)( -49.1, -51.6)
          0.010  1.106064   1.120382   1.111397   1.295   0.482  -0.006218   -0.000044   -0.002724 (-210.5,-221.6)( -49.1, -51.6)


T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 9 . Ln(s/s')f for model 2-D system #8 at 100° K

```
T = 100.000          WE'(1) =  1000.00          WE(1) =   950.00          WE'(2) =  3200.00          WE(2) =  3140.00


                       LN(S/S')F                      % ERROR
             ---------------------------------   -------------
  X1     X2      EXACT     HARM.    ANHARM.   HARM. ANHARM.      A          E          D        (F122,F122')  (F111,F111')
 ----   -----  --------  --------  --------   -----  -------  ---------  ---------  ---------  ------------  -------------
 0.002  0.002  0.718931  0.721112  0.719947   0.303  0.141  -0.000608  -0.000002  -0.000355 (-109.9,-113.9)( -21.9, -23.1)
        0.005  0.717113  0.721112  0.718837   0.558  0.240  -0.001458  -0.000006  -0.000812 (-173.7,-180.0)( -21.9, -23.1)
        0.010  0.714406  0.721112  0.717154   0.939  0.385  -0.002541  -0.000011  -0.001405 (-245.7,-254.6)( -21.9, -23.1)

 0.005  0.002  0.717787  0.721112  0.719398   0.463  0.225  -0.001369  -0.000002  -0.000342 (-109.9,-113.9)( -34.7, -36.5)
        0.005  0.715642  0.721112  0.718304   0.764  0.372  -0.002019  -0.000006  -0.000783 (-173.7,-180.0)( -34.7, -36.5)
        0.010  0.712558  0.721112  0.716645   1.200  0.574  -0.003102  -0.000011  -0.001353 (-245.7,-254.6)( -34.7, -36.5)

 0.010  0.002  0.716009  0.721112  0.718483   0.713  0.346  -0.002305  -0.000002  -0.000322 (-109.9,-113.9)( -49.1, -51.6)
        0.005  0.713680  0.721112  0.717416   1.041  0.523  -0.002955  -0.000006  -0.000735 (-173.7,-180.0)( -49.1, -51.6)
        0.010  0.710171  0.721112  0.715794   1.541  0.792  -0.004038  -0.000011  -0.001269 (-245.7,-254.6)( -49.1, -51.6)


 T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 10 . Ln(s/s')f for model 2-D system #9 at 100^0 K

```
T = 100.000          WE'(1) =  1500.00          WE(1) =  1425.00          WE'(2) =  1600.00          WE(2) =  1520.00

                         LN(S/S')F                  % ERROR
                 ----------------------------   -------------
 X1     X2      EXACT       HARM.     ANHARM.   HARM. ANHARM.      A          E          D        (F122,F122')  (F111,F111')
----   -----   --------   --------   --------   ----- -------  ---------  ---------  ---------  ------------- -------------
0.002  0.002  1.009217   1.012473   1.010589   0.323   0.136  -0.001134  -0.000016  -0.000735 (-100.4,-105.7)( -32.9, -34.6)
       0.005  1.006367   1.012473   1.008686   0.607   0.230  -0.002011  -0.000038  -0.001738 (-158.8,-167.1)( -32.9, -34.6)
       0.010  1.002030   1.012473   1.005750   1.042   0.371  -0.003473  -0.000076  -0.003175 (-224.5,-236.4)( -32.9, -34.6)

0.005  0.002  1.007627   1.012473   1.009788   0.481   0.214  -0.001958  -0.000015  -0.000712 (-100.4,-105.7)( -52.0, -54.8)
       0.005  1.004332   1.012473   1.007917   0.811   0.357  -0.002835  -0.000038  -0.001683 (-158.8,-167.1)( -52.0, -54.8)
       0.010  0.999494   1.012473   1.005026   1.299   0.553  -0.004296  -0.000075  -0.003075 (-224.5,-236.4)( -52.0, -54.8)

0.010  0.002  1.005391   1.012473   1.008452   0.704   0.304  -0.003331  -0.000015  -0.000674 (-100.4,-105.7)( -73.6, -77.5)
       0.005  1.001595   1.012473   1.006632   1.086   0.503  -0.004208  -0.000038  -0.001595 (-158.8,-167.1)( -73.6, -77.5)
       0.010  0.996191   1.012473   1.003814   1.634   0.765  -0.005670  -0.000075  -0.002915 (-224.5,-236.4)( -73.6, -77.5)

T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 11 . Ln(s/s')f for model 2-D system #10 at 100° K

```
 T = 100.000          WE'(1) =  1500.00          WE(1) =  1425.00          WE'(2) =  2400.00          WE(2) =  2280.00




                            LN(S/S')F              % ERROR
                     ---------------------------  -------------
   X1      X2      EXACT      HARM.     ANHARM.  HARM. ANHARM.      A          E          D      (F122,F122')  (F111,F111')
  ----   -----   --------   --------   --------  ----- -------  ---------  ---------  ---------  ------------- -------------
 0.002   0.002   1.296642   1.300230   1.298022  0.277  0.106   -0.001419  -0.000009  -0.000780 (-117.2,-123.4)( -32.9, -34.6)
         0.005   1.293496   1.300230   1.295684  0.521  0.169   -0.002723  -0.000023  -0.001800 (-185.3,-195.1)( -32.9, -34.6)
         0.010   1.288735   1.300230   1.292130  0.892  0.263   -0.004896  -0.000046  -0.003157 (-262.1,-275.9)( -32.9, -34.6)

 0.005   0.002   1.294924   1.300230   1.297224  0.410  0.178   -0.002243  -0.000009  -0.000754 (-117.2,-123.4)( -52.0, -54.8)
         0.005   1.291259   1.300230   1.294920  0.695  0.284   -0.003547  -0.000023  -0.001740 (-185.3,-195.1)( -52.0, -54.8)
         0.010   1.285913   1.300230   1.291414  1.113  0.428   -0.005720  -0.000046  -0.003050 (-262.1,-275.9)( -52.0, -54.8)

 0.010   0.002   1.292544   1.300230   1.295893  0.595  0.259   -0.003616  -0.000009  -0.000712 (-117.2,-123.4)( -73.6, -77.5)
         0.005   1.288293   1.300230   1.293645  0.927  0.415   -0.004920  -0.000023  -0.001642 (-185.3,-195.1)( -73.6, -77.5)
         0.010   1.282287   1.300230   1.290215  1.399  0.618   -0.007093  -0.000046  -0.002876 (-262.1,-275.9)( -73.6, -77.5)




 T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 12 . Ln(s/s')f for model 2-D system #11 at 100° K

```
 T = 100.000          WE'(1) =  1500.00          WE(1) =  1425.00          WE'(2) =  3200.00          WE(2) =  3140.00



                           LN(S/S')F                 % ERROR
                   ---------------------------   ------------
   X1      X2      EXACT      HARM.     ANHARM.  HARM. ANHARM.     A           E            D        (F122,F122')  (F111,F111')
  ----   -----   --------   --------   --------  ----- -------  ---------   ---------   ---------   ------------- -------------
 0.002   0.002   0.898085   0.900960   0.899574  0.329  0.166  -0.000983   -0.000002   -0.000401 (-135.6,-140.6)( -32.9, -34.6)
         0.005   0.895736   0.900960   0.898403  0.583  0.298  -0.001633   -0.000006   -0.000918 (-214.5,-222.3)( -32.9, -34.6)
         0.010   0.892212   0.900960   0.896639  0.980  0.496  -0.002716   -0.000011   -0.001593 (-303.3,-314.4)( -32.9, -34.6)

 0.005   0.002   0.896538   0.900960   0.898770  0.493  0.249  -0.001807   -0.000002   -0.000381 (-135.6,-140.6)( -52.0, -54.8)
         0.005   0.893770   0.900960   0.897626  0.804  0.431  -0.002456   -0.000005   -0.000872 (-214.5,-222.3)( -52.0, -54.8)
         0.010   0.889774   0.900960   0.895898  1.257  0.688  -0.003540   -0.000011   -0.001511 (-303.3,-314.4)( -52.0, -54.8)

 0.010   0.002   0.894350   0.900960   0.897429  0.739  0.344  -0.003180   -0.000002   -0.000348 (-135.6,-140.6)( -73.6, -77.5)
         0.005   0.891110   0.900960   0.896327  1.105  0.586  -0.003830   -0.000005   -0.000797 (-214.5,-222.3)( -73.6, -77.5)
         0.010   0.886581   0.900960   0.894658  1.622  0.911  -0.004913   -0.000011   -0.001378 (-303.3,-314.4)( -73.6, -77.5)



 T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARF DIMENSIONLESS
```

Table 13 . Ln(s/s')f for model 2-D system #1 at 300° K

```
 T = 300.000          WE'(1) =    500.00          WE(1) =    475.00          WE'(2) =    800.00          WE(2) =    760.00



                              LN(S/S')F              % ERROR
                    -----------------------------  -------------
   X1      X2      EXACT      HARM.     ANHARM.   HARM. ANHARM.      A          E          D       (F122,F122')  (F111,F111')
  ----    -----   --------   --------   --------  ----- -------  ---------  ---------  ---------  ------------- -------------
  0.002   0.002   0.070522   0.070772   0.070487  0.356 -0.049   -0.000144  -0.000080  -0.000061 ( -39.1, -41.1)( -11.0, -11.5)
          0.005   0.070287   0.070772   0.070141  0.690 -0.209   -0.000284  -0.000197  -0.000151 ( -61.8, -65.0)( -11.0, -11.5)
          0.010   0.069928   0.070772   0.069579  1.207 -0.499   -0.000513  -0.000383  -0.000297 ( -87.4, -92.0)( -11.0, -11.5)

  0.005   0.002   0.070412   0.070772   0.070418  0.511  0.007   -0.000215  -0.000078  -0.000061 ( -39.1, -41.1)( -17.3, -18.3)
          0.005   0.070155   0.070772   0.070074  0.880 -0.115   -0.000355  -0.000192  -0.000151 ( -61.8, -65.0)( -17.3, -18.3)
          0.010   0.069772   0.070772   0.069517  1.434 -0.365   -0.000584  -0.000374  -0.000297 ( -87.4, -92.0)( -17.3, -18.3)

  0.010   0.002   0.070259   0.070772   0.070308  0.731  0.069   -0.000328  -0.000076  -0.000061 ( -39.1, -41.1)( -24.5, -25.8)
          0.005   0.069977   0.070772   0.069967  1.136 -0.014   -0.000468  -0.000187  -0.000151 ( -61.8, -65.0)( -24.5, -25.8)
          0.010   0.069572   0.070772   0.069415  1.726 -0.225   -0.000696  -0.000364  -0.000297 ( -87.4, -92.0)( -24.5, -25.8)



 T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 14 . Ln(s/s')f for model 2-D system #2 at 300° K

```
T = 300.000          WE'(1) =    500.00          WE(1) =    475.00          WE'(2) =  1600.00          WE(2) =  1520.00


                              LN(S/S')F                 % ERROR
                    -----------------------------  -------------
  X1      X2      EXACT      HARM.     ANHARM.   HARM. ANHARM.      A          E          D       (F122,F122')  (F111,F111')
 ----    -----  ---------  ---------  ---------  ----- -------  ---------  ---------  ---------  ------------- -------------
0.002    0.002  0.161786   0.162238   0.161792   0.279  0.004  -0.000263  -0.000039  -0.000144 ( -54.1, -56.9)( -11.0, -11.5)
         0.005  0.161316   0.162238   0.161205   0.571 -0.069  -0.000583  -0.000096  -0.000354 ( -85.5, -90.0)( -11.0, -11.5)
         0.010  0.160582   0.162238   0.160248   1.031 -0.208  -0.001115  -0.000188  -0.000686 (-120.9,-127.3)( -11.0, -11.5)

0.005    0.002  0.161634   0.162238   0.161722   0.374  0.054  -0.000334  -0.000038  -0.000144 ( -54.1, -56.9)( -17.3, -18.3)
         0.005  0.161114   0.162238   0.161137   0.697  0.014  -0.000654  -0.000094  -0.000353 ( -85.5, -90.0)( -17.3, -18.3)
         0.010  0.160326   0.162238   0.160183   1.193 -0.089  -0.001186  -0.000184  -0.000685 (-120.9,-127.3)( -17.3, -18.3)

0.010    0.002  0.161432   0.162238   0.161611   0.499  0.111  -0.000447  -0.000037  -0.000143 ( -54.1, -56.9)( -24.5, -25.8)
         0.005  0.160859   0.162238   0.161028   0.857  0.105  -0.000766  -0.000091  -0.000352 ( -85.5, -90.0)( -24.5, -25.8)
         0.010  0.160013   0.162238   0.160077   1.391  0.040  -0.001298  -0.000179  -0.000683 (-120.9,-127.3)( -24.5, -25.8)


T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 15 . Ln(s/s')f for model 2-D system #3 at 300° K

```
 T = 300.000           WE'(1) =   500.00          WE(1) =   475.00          WE'(2) =  2400.00          WE(2) =  2280.00



                              LN(S/S')F                % ERROR
                    ----------------------------  -------------
   X1      X2      EXACT      HARM.     ANHARM.  HARM. ANHARM.      A           E           D        (F122,F122')  (F111,F111')
  ----   -----   --------   --------   --------  ----- -------  ---------   ---------   ---------   -------------- --------------
 0.002   0.002   0.257367   0.257947   0.257359  0.225  -0.003  -0.000355   -0.000026   -0.000207 ( -66.0, -69.5)( -11.0, -11.5)
         0.005   0.256738   0.257947   0.256564  0.471  -0.068  -0.000814   -0.000064   -0.000505 (-104.4,-109.8)( -11.0, -11.5)
         0.010   0.255751   0.257947   0.255275  0.859  -0.186  -0.001578   -0.000126   -0.000968 (-147.6,-155.3)( -11.0, -11.5)

 0.005   0.002   0.257195   0.257947   0.257288  0.292   0.036  -0.000426   -0.000025   -0.000207 ( -66.0, -69.5)( -17.3, -18.3)
         0.005   0.256505   0.257947   0.256495  0.562  -0.004  -0.000885   -0.000062   -0.000504 (-104.4,-109.8)( -17.3, -18.3)
         0.010   0.255448   0.257947   0.255209  0.978  -0.094  -0.001649   -0.000123   -0.000966 (-147.6,-155.3)( -17.3, -18.3)

 0.010   0.002   0.256971   0.257947   0.257177  0.380   0.080  -0.000539   -0.000025   -0.000206 ( -66.0, -69.5)( -24.5, -25.8)
         0.005   0.256215   0.257947   0.256386  0.676   0.067  -0.000997   -0.000061   -0.000503 (-104.4,-109.8)( -24.5, -25.8)
         0.010   0.255086   0.257947   0.255103  1.121   0.006  -0.001761   -0.000120   -0.000963 (-147.6,-155.3)( -24.5, -25.8)



 T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 16 . Ln(s/s')f for model 2-D system #4 at 300° K

```
T = 300.000          WE'(1) =    500.00          WE(1) =    475.00          WE'(2) =  3200.00          WE(2) =  3140.00



                               LN(S/S')F                 % ERROR
                     ---------------------------    -------------
  X1     X2      EXACT     HARM.    ANHARM.   HARM. ANHARM.      A          E          D       (F122,F122')  (F111,F111')
 ----   -----  --------  --------  --------   ----- -------  ---------  ---------  ---------  ------------- -------------
 0.002  0.002  0.146101  0.146426  0.146118   0.223  0.012  -0.000198  -0.000007  -0.000103 ( -77.4, -80.1)( -11.0, -11.5)
        0.005  0.145764  0.146426  0.145740   0.454 -0.017  -0.000421  -0.000017  -0.000248 (-122.3,-126.7)( -11.0, -11.5)
        0.010  0.145233  0.146426  0.145131   0.821 -0.071  -0.000794  -0.000033  -0.000468 (-173.0,-179.2)( -11.0, -11.5)

 0.005  0.002  0.145987  0.146426  0.146047   0.301  0.041  -0.000270  -0.000007  -0.000103 ( -77.4, -80.1)( -17.3, -18.3)
        0.005  0.145624  0.146426  0.145669   0.551  0.031  -0.000493  -0.000016  -0.000248 (-122.3,-126.7)( -17.3, -18.3)
        0.010  0.145064  0.146426  0.145060   0.939 -0.003  -0.000865  -0.000032  -0.000469 (-173.0,-179.2)( -17.3, -18.3)

 0.010  0.002  0.145831  0.146426  0.145935   0.409  0.071  -0.000382  -0.000006  -0.000103 ( -77.4, -80.1)( -24.5, -25.8)
        0.005  0.145444  0.146426  0.145557   0.675  0.078  -0.000605  -0.000015  -0.000248 (-122.3,-126.7)( -24.5, -25.8)
        0.010  0.144860  0.146426  0.144949   1.081  0.061  -0.000977  -0.000031  -0.000469 (-173.0,-179.2)( -24.5, -25.8)



T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 17 . Ln(s/s')f for model 2-D system #5 at 300° K

```
T = 300.000          WE'(1) =  1000.00          WE(1) =   950.00          WE'(2) =   800.00          WE(2) =   760.00



                          LN(S/S')F                   % ERROR
                ----------------------------   -------------
  X1      X2      EXACT     HARM.     ANHARM.   HARM. ANHARM.     A          E          D       (F122,F122')  (F111,F111')
 ----    -----  --------  --------   --------  ----- -------  ---------  ---------  ---------  ------------- -------------
 0.002   0.002  0.119489  0.120163   0.119695  0.565  0.172  -0.000224  -0.000113  -0.000132 ( -65.2, -68.6)( -21.9, -23.1)
         0.005  0.118883  0.120163   0.119197  1.077  0.264  -0.000364  -0.000277  -0.000326 (-103.1,-108.5)( -21.9, -23.1)
         0.010  0.117958  0.120163   0.118392  1.870  0.368  -0.000592  -0.000539  -0.000640 (-145.8,-153.5)( -21.9, -23.1)

 0.005   0.002  0.119166  0.120163   0.119505  0.837  0.284  -0.000416  -0.000111  -0.000131 ( -65.2, -68.6)( -34.7, -36.5)
         0.005  0.118489  0.120163   0.119012  1.413  0.442  -0.000556  -0.000272  -0.000323 (-103.1,-108.5)( -34.7, -36.5)
         0.010  0.117486  0.120163   0.118214  2.279  0.620  -0.000785  -0.000529  -0.000635 (-145.8,-153.5)( -34.7, -36.5)

 0.010   0.002  0.118701  0.120163   0.119192  1.232  0.414  -0.000733  -0.000109  -0.000129 ( -65.2, -68.6)( -49.1, -51.6)
         0.005  0.117944  0.120163   0.118704  1.882  0.645  -0.000873  -0.000267  -0.000319 (-103.1,-108.5)( -49.1, -51.6)
         0.010  0.116856  0.120163   0.117915  2.830  0.906  -0.001102  -0.000519  -0.000628 (-145.8,-153.5)( -49.1, -51.6)



T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 18 . Ln(s/s')f for model 2-D system #6 at 300° K

T = 300.000   WE'(1) = 1000.00   WE(1) = 950.00   WE'(2) = 1600.00   WE(2) = 1520.00

		LN(S/S')F			% ERROR						
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')
0.002	0.002	0.210840	0.211628	0.211048	0.374	0.099	-0.000343	-0.000041	-0.000196	(-78.1, -82.3)	(-21.9, -23.1)
	0.005	0.210143	0.211628	0.210383	0.707	0.114	-0.000663	-0.000101	-0.000482	(-123.6,-130.1)	(-21.9, -23.1)
	0.010	0.209081	0.211628	0.209298	1.218	0.104	-0.001195	-0.000199	-0.000936	(-174.7,-183.9)	(-21.9, -23.1)
0.005	0.002	0.210464	0.211628	0.210858	0.553	0.187	-0.000535	-0.000040	-0.000195	(-78.1, -82.3)	(-34.7, -36.5)
	0.005	0.209662	0.211628	0.210195	0.938	0.254	-0.000855	-0.000100	-0.000479	(-123.6,-130.1)	(-34.7, -36.5)
	0.010	0.208482	0.211628	0.209116	1.509	0.304	-0.001387	-0.000196	-0.000930	(-174.7,-183.9)	(-34.7, -36.5)
0.010	0.002	0.209939	0.211628	0.210544	0.805	0.288	-0.000852	-0.000040	-0.000193	(-78.1, -82.3)	(-49.1, -51.6)
	0.005	0.209019	0.211628	0.209885	1.249	0.415	-0.001172	-0.000098	-0.000474	(-123.6,-130.1)	(-49.1, -51.6)
	0.010	0.207708	0.211628	0.208812	1.888	0.532	-0.001704	-0.000192	-0.000920	(-174.7,-183.9)	(-49.1, -51.6)

T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS

Table 19 . Ln(s/s')f for model 2-D system #7 at 300° K

```
 T = 300.000          WE'(1) =  1000.00          WE(1) =    950.00          WE'(2) =  2400.00          WE(2) =  2280.00

                                 LN(S/S')F                  % ERROR
                        ----------------------------   -------------
     X1      X2      EXACT       HARM.      ANHARM.   HARM. ANHARM.       A           E           D      (F122,F122')  (F111,F111')
    ----    -----  --------    --------    --------   ----- -------  ---------   ---------   ---------  ------------- -------------
   0.002    0.002  0.306401    0.307338    0.306614   0.306  0.070   -0.000435   -0.000027   -0.000262 ( -94.2, -99.1)( -21.9, -23.1)
            0.005  0.305541    0.307338    0.305740   0.589  0.065   -0.000893   -0.000066   -0.000638 (-148.9,-156.7)( -21.9, -23.1)
            0.010  0.304229    0.307338    0.304326   1.022  0.032   -0.001657   -0.000130   -0.001224 (-210.5,-221.6)( -21.9, -23.1)

   0.005    0.002  0.305986    0.307338    0.306424   0.442  0.143   -0.000627   -0.000026   -0.000260 ( -94.2, -99.1)( -34.7, -36.5)
            0.005  0.304998    0.307338    0.305553   0.767  0.182   -0.001086   -0.000065   -0.000634 (-148.9,-156.7)( -34.7, -36.5)
            0.010  0.303543    0.307338    0.304144   1.250  0.198   -0.001850   -0.000128   -0.001217 (-210.5,-221.6)( -34.7, -36.5)

   0.010    0.002  0.305416    0.307338    0.306111   0.629  0.227   -0.000944   -0.000026   -0.000257 ( -94.2, -99.1)( -49.1, -51.6)
            0.005  0.304286    0.307338    0.305244   1.003  0.315   -0.001403   -0.000063   -0.000628 (-148.9,-156.7)( -49.1, -51.6)
            0.010  0.302671    0.307338    0.303842   1.542  0.387   -0.002167   -0.000125   -0.001204 (-210.5,-221.6)( -49.1, -51.6)

 T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 20 . Ln(s/s')f for model 2-D system #8 at 300^{o} K

```
T = 300.000          WE'(1) =  1000.00          WE(1) =    950.00          WE'(2) =  3200.00          WE(2) =  3140.00


                           LN(S/S')F                 % ERROR
                 ---------------------------  -------------
  X1     X2      EXACT     HARM.     ANHARM.  HARM. ANHARM.      A          E          D      (F122,F122')  (F111,F111')
 ----  -----  --------  --------  --------  ----- -------  ---------  ---------  ---------  -------------- --------------
 0.002  0.002  0.195124  0.195817  0.195370  0.355  0.126  -0.000278  -0.000007  -0.000162 (-109.9,-113.9)( -21.9, -23.1)
        0.005  0.194548  0.195817  0.194905  0.652  0.183  -0.000501  -0.000017  -0.000394 (-173.7,-180.0)( -21.9, -23.1)
        0.010  0.193682  0.195817  0.194161  1.102  0.247  -0.000873  -0.000033  -0.000750 (-245.7,-254.6)( -21.9, -23.1)

 0.005  0.002  0.194761  0.195817  0.195179  0.543  0.214  -0.000470  -0.000007  -0.000161 (-109.9,-113.9)( -34.7, -36.5)
        0.005  0.194089  0.195817  0.194716  0.890  0.323  -0.000694  -0.000016  -0.000390 (-173.7,-180.0)( -34.7, -36.5)
        0.010  0.193114  0.195817  0.193976  1.400  0.446  -0.001066  -0.000032  -0.000743 (-245.7,-254.6)( -34.7, -36.5)

 0.010  0.002  0.194252  0.195817  0.194865  0.806  0.316  -0.000787  -0.000006  -0.000159 (-109.9,-113.9)( -49.1, -51.6)
        0.005  0.193472  0.195817  0.194406  1.212  0.483  -0.001010  -0.000016  -0.000385 (-173.7,-180.0)( -49.1, -51.6)
        0.010  0.192377  0.195817  0.193671  1.788  0.673  -0.001383  -0.000031  -0.000732 (-245.7,-254.6)( -49.1, -51.6)


T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 21 . Ln(s/s')f for model 2-D system #9 at 300° K

```
T = 300.000          WE'(1) =  1500.00        WE(1) =  1425.00        WE'(2) =  1600.00        WE(2) =  1520.00


                        LN(S/S')F                   % ERROR
               -----------------------------   -------------
  X1     X2      EXACT     HARM.    ANHARM.   HARM. ANHARM.      A          E           D       (F122,F122')   (F111,F111')
 ----   -----  --------  --------  --------   ----- -------  ---------  ---------  ---------  -------------  -------------
 0.002  0.002  0.268533  0.269643  0.268933   0.413  0.149  -0.000415  -0.000046  -0.000250 (-100.4,-105.7)( -32.9, -34.6)
        0.005  0.267568  0.269643  0.268183   0.776  0.230  -0.000735  -0.000112  -0.000613 (-158.8,-167.1)( -32.9, -34.6)
        0.010  0.266095  0.269643  0.266966   1.333  0.327  -0.001267  -0.000220  -0.001190 (-224.5,-236.4)( -32.9, -34.6)

 0.005  0.002  0.267981  0.269643  0.268635   0.620  0.244  -0.000716  -0.000045  -0.000247 (-100.4,-105.7)( -52.0, -54.8)
        0.005  0.266870  0.269643  0.267890   1.039  0.382  -0.001036  -0.000111  -0.000607 (-158.8,-167.1)( -52.0, -54.8)
        0.010  0.265235  0.269643  0.266681   1.662  0.545  -0.001568  -0.000217  -0.001177 (-224.5,-236.4)( -52.0, -54.8)

 0.010  0.002  0.267196  0.269643  0.268139   0.916  0.353  -0.001216  -0.000044  -0.000243 (-100.4,-105.7)( -73.6, -77.5)
        0.005  0.265922  0.269643  0.267401   1.399  0.556  -0.001536  -0.000109  -0.000597 (-158.8,-167.1)( -73.6, -77.5)
        0.010  0.264104  0.269643  0.266204   2.097  0.795  -0.002068  -0.000214  -0.001157 (-224.5,-236.4)( -73.6, -77.5)


T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

Table 22 . Ln(s/s')f for model 2-D system #10 at 300^{o} K

T = 300.000 WE'(1) = 1500.00 WE(1) = 1425.00 WE'(2) = 2400.00 WE(2) = 2280.00

		LN(S/S')F			% ERROR						
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')
0.002	0.002	0.364130	0.365352	0.364511	0.336	0.105	-0.000507	-0.000028	-0.000307	(-117.2,-123.4)	(-32.9, -34.6)
	0.005	0.363064	0.365352	0.363571	0.630	0.140	-0.000965	-0.000068	-0.000747	(-185.3,-195.1)	(-32.9, -34.6)
	0.010	0.361446	0.365352	0.362057	1.081	0.169	-0.001729	-0.000135	-0.001431	(-262.1,-275.9)	(-32.9, -34.6)
0.005	0.002	0.363533	0.365352	0.364213	0.500	0.187	-0.000808	-0.000027	-0.000304	(-117.2,-123.4)	(-52.0, -54.8)
	0.005	0.362297	0.365352	0.363279	0.843	0.271	-0.001267	-0.000067	-0.000739	(-185.3,-195.1)	(-52.0, -54.8)
	0.010	0.360487	0.365352	0.361772	1.350	0.356	-0.002031	-0.000133	-0.001416	(-262.1,-275.9)	(-52.0, -54.8)
0.010	0.002	0.362699	0.365352	0.363718	0.731	0.281	-0.001309	-0.000027	-0.000298	(-117.2,-123.4)	(-73.6, -77.5)
	0.005	0.361271	0.365352	0.362792	1.130	0.421	-0.001767	-0.000066	-0.000727	(-185.3,-195.1)	(-73.6, -77.5)
	0.010	0.359245	0.365352	0.361298	1.700	0.572	-0.002531	-0.000131	-0.001392	(-262.1,-275.9)	(-73.6, -77.5)

T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS

Table 23 . Ln(s/s')f for model 2-D system #11 at 300° K

```
 T = 300.000          WE'(1) =  1500.00         WE(1) =  1425.00          WE'(2) =  3200.00          WE(2) =  3140.00


                                 LN(S/S')F                   % ERROR
                         ----------------------------  -------------
   X1      X2      EXACT      HARM.      ANHARM.   HARM. ANHARM.      A           E           D        (F122,F122')   (F111,F111')
  ----    -----   --------   --------   --------   ----- -------  ---------   ---------   ---------   ------------- -------------
  0.002   0.002   0.252859   0.253831   0.253268   0.385  0.162   -0.000350   -0.000006   -0.000207 (-135.6,-140.6)( -32.9, -34.6)
          0.005   0.252077   0.253831   0.252740   0.696  0.263   -0.000573   -0.000016   -0.000502 (-214.5,-222.3)( -32.9, -34.6)
          0.010   0.250901   0.253831   0.251898   1.168  0.397   -0.000945   -0.000032   -0.000956 (-303.3,-314.4)( -32.9, -34.6)

  0.005   0.002   0.252321   0.253831   0.252970   0.599  0.257   -0.000651   -0.000006   -0.000204 (-135.6,-140.6)( -52.0, -54.8)
          0.005   0.251401   0.253831   0.252446   0.967  0.416   -0.000874   -0.000016   -0.000495 (-214.5,-222.3)( -52.0, -54.8)
          0.010   0.250072   0.253831   0.251611   1.503  0.616   -0.001247   -0.000031   -0.000942 (-303.3,-314.4)( -52.0, -54.8)

  0.010   0.002   0.251552   0.253831   0.252474   0.906  0.367   -0.001152   -0.000006   -0.000199 (-135.6,-140.6)( -73.6, -77.5)
          0.005   0.250479   0.253831   0.251958   1.338  0.590   -0.001375   -0.000015   -0.000483 (-214.5,-222.3)( -73.6, -77.5)
          0.010   0.248976   0.253831   0.251135   1.950  0.867   -0.001747   -0.000030   -0.000919 (-303.3,-314.4)( -73.6, -77.5)


 T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS
```

d. Discussion

The numerical results in the previous section were obtained by my investigation of a model 2-D system that simulates the two stretching modes of a representative linear triatomic molecule. I chose to model the 2-D cases after CO_2 because this is one of the few triatomic molecules that have readily available data on anharmonicity constants and cubic coefficients.[18] As can be seen from the previous section I varied the symmetric stretching frequency ω_1 from 500 cm^{-1} to 1500 cm^{-1} while the symmetric stretching frequency of $^{12}C^{16}O_2$ is 1349.97 cm^{-1}. The other stretching mode ω_2 is set to values ranging from 800 cm^{-1} to 3200 cm^{-1} while the antisymmetric stretching frequency of CO_2 is 2395.89 cm^{-1}.[18] For the heavier isotopic pair I investigated, I decreased the corresponding ω_1 and ω_2 by 5%. Generally the values of ω_1 and ω_2 were selected to avoid resonance.

Under all circumstances, the new approximation gives substantially improved results over the harmonic oscillator treatment. It shows clearly the dominance of the diagonal Morse potential correction term when the anharmonicity constants χ_i are small but when χ_i values become larger, the off-diagonal quantum-mechanical perturbation terms, D and D', then play a more important role. The classical off-diagonal cubic correction terms, E and E', are generally much smaller in magnitude compared with the Morse potential correction terms and off-diagonal cubic quantum-mechanical perturbation terms. Approximation results are represented for temperatures of both 100°K and 300°K.

One big contrast between the exact result and the approximation result is in the utilized computer time. The former takes about 200 seconds CPU time in the CUNY-UCC IBM 370/168 to execute while the approximate method program takes less than one second CPU time in execution. The more important advantage of the approximation over the exact calculation lies in the physical insight gained by observing the interplay of various factors that make up the reduced partition function so we know under what circumstances we can omit the off-diagonal contribution terms and still have a result within tolerable percentage error.

With the encouraging numerical results that we have obtained this far it was logical to look into the quasi-3-dimensional problem of the total CO_2 vibration.

B. APPROXIMATION FOR 3-D SYSTEM

a. Exact Calculation

i. Numerical Solution for the Phase Integral

The expression for the total energy E becomes quite involved in CO_2 for now we have two stretching modes and a degenerate bending mode to work with. With the designation of q_1 standing for symmetric stretching coordinate, q_2 for antisymmetric stretching coordinate, and q_3 and q_3' for the degenerate bending coordinate, the total energy E then becomes

$$E = \frac{p_1^{\,2}}{2} + D_1(1-e^{-\alpha_1 q_1})^2 + \frac{p_2^{\,2}}{2} + D_2(1-e^{-\alpha_2 q_2})^2$$
$$+ \frac{p_3^{\,2}}{2} + D_3(1-e^{-\alpha_3 q_3})^2 + \frac{p_3'^{\,2}}{2} + D_3'(1-e^{-\alpha_3 q_3'})^2$$
$$+ \gamma_{122} q_1 q_2^{\,2} + \gamma_{133} q_1 q_3^{\,2} + \gamma_{133} q_1 q_3'^{\,2} \qquad (101)$$

The classical partition function Q_{cl} is:

$$Q_{cl} = \int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int e^{-H/kT}\, dpdq$$

$$= \int_{-\frac{\ln 2}{\alpha_1}}^{\infty} \Bigg\{ \int_{p_1^-}^{p_1^+} \int_{-\frac{\ln 2}{\alpha_1}}^{L_2(q_1)} \Bigg[\int_{p_2^-}^{p_2^+} \Bigg(\int_{-\frac{\ln 2}{\alpha_3}}^{L_3(q_1,q_2)}$$
$$\int_{p_3^-}^{p_3^+} e^{-H(q_1,p_1,q_2,p_2,q_3,p_3)/kT}\, dp_3$$
$$dq_3 \Bigg) dp_2 \Bigg] dq_2 \quad dp_1 \Bigg\} dq_1 \, , \qquad (102)$$

whereas degeneracy q_3' is not explicitly included in the above equation for the sake of clarity but will be later on included in the actual computer calculation.

Since it is impossible to find all the integration limits by analytical methods, one has to utilize a numerical technique. By extending the formulation used in dealing with the model 2-D system, recalling that one should recover the classical anharmonic partition function Q_{cl}^{anh} with no interaction as $\gamma_{ijj}\to 0$, we have

$$\begin{aligned}
Q_{cl}^{anh} = {} & \frac{1}{u_{e_1}} \frac{1}{u_{e_2}} \frac{1}{u_{e_3}} \left(\frac{2}{\pi}\right)^3 \int_{-\rho_1 \ln 2}^{\infty} dz_1 \\
& \int_0^{\rho_1 \sqrt{e^{-\frac{z_1}{\rho_1}} \left(2-e^{-\frac{z_1}{\rho_1}}\right)^2}} e^{-y_1^2}\, dy_1 \quad \times \\
& \int_{-\rho_2 \ln 2}^{\infty} dz_2 \int_0^{\rho_2 \sqrt{e^{-\frac{z_2}{\rho_2}} \left(2-e^{-\frac{z_2}{\rho_2}}\right)^2}} e^{-y_2^2}\, dy_2 \\
& \int_{-\rho_3 \ln 2}^{\infty} e^{-\rho_1^2 \left(1-e^{-\frac{z_1}{\rho_1}}\right)^2 - \rho_2^2 \left(1-e^{-\frac{z_2}{\rho_2}}\right)^2} \\
& \quad {}^{-\rho_3^2 \left(1-e^{-\frac{z_3}{\rho_3}}\right)^2 - \gamma_{122} z_1 z_2^2 - \gamma_{133} z_1 z_3^2}\, dz_3 \quad \times \\
& \int_0^{\rho_3 \sqrt{e^{-\frac{z_3}{\rho_3}} \left(2-e^{-\frac{z_3}{\rho_3}}\right)^2}} e^{-y_3^2}\, dy_3 \, , \qquad (103)
\end{aligned}$$

with the usual transformations

$$z_1 = \frac{\alpha_1 q_1}{2}\sqrt{\frac{u_{e_1}}{\chi_{e_1}}} \ , \tag{104a}$$

$$\rho_1 = \frac{1}{2}\sqrt{\frac{u_{e_1}}{\chi_{e_1}}} \ , \tag{104b}$$

and

$$y_1 = \frac{p_1{}^2}{2kT} \ . \tag{104c}$$

Thus, with intercoordinate interactions,

$$Q_{cl}^{anh} = \frac{1}{u_{e_1}}\,\frac{1}{u_{e_2}}\,\frac{1}{u_{e_3}}\left(\frac{2}{\pi}\right)^3 \int_{-\rho_1 \ln 2}^{\infty} dz_1 \int_0^{\rho_1\sqrt{e^{-\frac{z_1}{\rho_1}}\left(2-e^{-\frac{z_1}{\rho_1}}\right)^2}}$$

$$e^{-y_1{}^2}\,dy_1 \qquad \int_{-\rho_2 \ln 2}^{L_2(q_1)} dz_2$$

$$\int_0^{\rho_2\sqrt{1-\left(1-e^{-\frac{z_2}{\rho_2}}\right)^2 - \gamma_{122} z_1 z_2{}^2}} \quad \times$$

$$\int_{-\rho\ln 2}^{L_3(z_1,z_2)} dz_3 \; e^{-\rho_1^2\left(1-e^{-\frac{z_1}{\rho_1}}\right)^2 - \rho_2^2\left(1-e^{-\frac{z_2}{\rho}}\right)^2} \quad \mathrm{x}$$

$$e^{-\rho_3^2\left(1-e^{-\frac{z_3}{\rho_3}}\right)^2 - \gamma_{122}z_1z_2^2 - \gamma_{133}z_1z_3^2} \quad \mathrm{x}$$

$$\int_0^{\rho_3\sqrt{1-\left(1-e^{-\frac{z_3}{\rho_3}}\right)^2 - \gamma_{133}z_1z_3^2}} d^{-y_3^2}\, dy_3 \qquad (105)$$

Care must be taken in the calculations of the upper limits z, L_2, L_3 to avoid inclusion of contributions from the unstable states corresponding to the repulsive forces that fictitiously arise from the truncation of the polynomial potential functions, as in the 2-D model case.

ii. Numerical Solution fro the Quantum Partition Function

The quantum mechanical partition function is exactly expressed as

$$Q_{qm}^{anh} = \sum_{n_1=0}^{v_{D_1}} \sum_{n_2=0}^{v_{D_2}} \sum_{n_3=0}^{v_{D_3}} \sum_{n_4=0}^{v_{D_4}} e^{-\varepsilon(1,2,3,4)/kT} , \qquad (106)$$

where

$$\begin{aligned}
G(n_1,n_2,n_3,n_4) &= \frac{\varepsilon(1,2,3,4)}{hc} \\
&= [\omega_{e_1}(n_1+\tfrac{1}{2}) - \omega_{e_1}\chi_{e_1}(n_1+\tfrac{1}{2})^2] \\
&+ [\omega_{e_2}(n_2+\tfrac{1}{2}) - \omega_{e_2}\chi_{e_2}(n_2+\tfrac{1}{2})^2 + \\
&\chi_{12}(n_1+\tfrac{1}{2})(n_2+\tfrac{1}{2})] + [\omega_{e_3}(n_3+\tfrac{1}{2}) - \\
&\omega_{e_3}\chi_{e_3}(n_3+\tfrac{1}{2})^2 + \chi_{13}(n_1+\tfrac{1}{2})(n_3+\tfrac{1}{2}) + \\
&\chi_{23}(n_2+\tfrac{1}{2})(n_3+\tfrac{1}{2})] + [\omega_{e_3}(n_4+\tfrac{1}{2}) - \\
&\omega_{e_3}\chi_{e_3}(n_4+\tfrac{1}{2})^2 + \chi_{13}(n_1+\tfrac{1}{2})(n_4+\tfrac{1}{2}) + \\
&\chi_{23}(n_2+\tfrac{1}{2})(n_4+\tfrac{1}{2})] \; . \qquad (107)
\end{aligned}$$

Note that the bending vibrational frequency ω_{e_3} is degenerate. By regarding n_1 as the variable for the outer summation, n_2 for the intermediate loop and n_3 and n_4 as the inner loops, one follows a similar approach as in solving Q_{qm}^{anh} in the 2-D numerically.

b. Numerical Results and Discussion

With all the above formulations, it is time now to put them to work. I now try to compare the results of the harmonic reduced partition function $\ln \frac{s}{s'} f(\text{harm})$, and

$\ln \frac{s}{s'} f(\text{harm})$ with the usual anharmonicity correction terms, i.e., $\sum_i \frac{u_{e_i}\chi_{e_i} - u_{e_i}'\chi_{e_i}'}{4}$, and the newly developed approximation $\ln \frac{s}{s'} f$ (anharmonic) and the exact $\ln \frac{s}{s'} f$ numerically evaluated by the methods described in the preceding section.

Evaluation of the sextruple integrals and four-fold summations turns out to be very time consuming. In particular, retention of the small χ_e value for the bending mode of CO_2 in the summation in Eq.(106) requires more computer CPU time than we can handle. For instance, a calculation of one value of Q_{qm}^{anh} with χ_e (bending) = -0.23 at T = 300°K would have taken 200 minutes of the IBM 370-168 CPU time.

Since the purpose of this phase of calculation is merely to show the precision of the newly developed approximation, I chose to use a value of the anharmonicity constants for the degenerate bending mode which is ten times larger than the reported real value, while I retained the real values for the anharmonicity constants of the symmetric and antisymmetric modes. For the temperature of 300°K, I obtain the results reported in Table 24.

The percentage error for anharmonic $\ln \frac{s}{s'} f$ has been halved from 1.3%, the value obtained by the ordinary ZPE correction, to 0.6%, the value achieved by the present method. The value of 0.1751 consists of the contribution of the harmonic approximation = 0.1773, the Morse potential

TABLE 24. Ln $\frac{s}{s'}f$ for a model 3-D system.

Exact	Harmonic	Anharmonic	Anharmonic with ordinary ZPE correction
0.1741	0.1773	0.1751	0.1763

Inputs:

$\omega_1' = 1349.97$, $\chi_{11}' = -2.38$ $\quad$ $\omega_1 = 1349.97$, $\chi_{11} = -2.38$

$\omega_2' = 2395.89$, $\chi_{22}' = -12.4$ $\quad$ $\omega_2 = 2327.41$, $\chi_{22} = -11.64$

$\omega_3' = 674.85$, $\chi_{33}' = -2.3$ $\quad$ $\omega_3 = 655.65$, $\chi_{33} = -2.2$

$F_{133}' = 69.84$ $\quad$ $F_{133} = 67.86$

$F_{122}' = -245.53$ $\quad$ $F_{122} = -238.54$

$\chi_{12}' = -18.5$ $\quad$ $\chi_{12} = -18.05$

$\chi_{13}' = 1.01$ $\quad$ $\chi_{13} = 0.99$

$\chi_{23}' = -12.61$ $\quad$ $\chi_{23} = -11.82$

All above units for inputs are in cm^{-1}.

correction terms = -0.0011, the quantum off-diagonal cubic terms = -0.0015, and the classical off-diagonal cubic terms = 0.0004. The ordinary anharmonicity correction is similar in magnitude to the Morse potential correction and it is -0.0010 in this case. The marked improvement of ln $\frac{s}{s'}$ (anharmonic) over ln $\frac{s}{s'}$ (harmonic) and ln $\frac{s}{s'}$ f (ordinary correction) is the consequence of the inclusion of off-diagonal cubic terms that are not always negligible.

CHAPTER V

POSSIBLE FURTHER STUDIES

My goal of obtaining a better approximation for the reduced partition function of polyatomic systems has been accomplished. As one can readily observe, to arrive at the exact $\ln \frac{s}{s'} f$ requires lengthy computer calculation whereas to obtain the approximate $\ln \frac{s}{s'} f$ takes much less CPU time. More important is the physical insight that one can obtain by using the approximation method. One can investigate the interplay of contributions of terms in $\ln \frac{s}{s'} f$ derived from quadratic and cubic force constants. The extent to which the diagonal approximation is valid will be an interesting problem that one can investigate. Another area that deserves further studies is the relative importance of the off-diagonal cubic terms in contributing to $\ln \frac{s}{s'} f$, which would pinpoint the important sources of anharmonicity correction for the thermodynamic functions.

Another important step forward is to re-examine the potential function of the anharmonic polyatomic systems and include the quartic terms in the framework of the perturbation theory. But this will be a big challenge due to the complexity of the calculation involved.

I am impressed by the interests of physicists in the investigation of the anharmonic oscillator[19,20] because the anharmonic oscillator is a simple model field theory in one-dimensional space-time and the properties exhibited by this model may give some indication of the analytic structure of a more realistic field theory. The same importance can be ascribed to a model anharmonic oscillator in understanding isotopic related studies.

VI APPENDIX

FOREWORD

In the course of doing this research I have looked into the possibilities of using the Padé Approximant and orthogonal series as the approximation methods. In the Appendix, Sections A and B, some results are reported. In Section C I present some key formulae from Nielsen's paper. In Section D the essential details for simplification of the second order perturbation terms are presented. Section E contains listings of computer programs. These programs take ω_i's, χ_{ij}'s, F_{ijk}, °K as input and calculate $\ln \frac{s}{s'} f$ (exact), $\ln \frac{s}{s'} f$ (anh), $\ln \frac{s}{s'} f$ (harm) by using methods developed in the preceding chapters.

A. PADE APPROXIMANT

The classical partition function of a Morse oscillator, Q_{cl}^{anh}, is given by Eq.(7). Substitution of Eq.(41) into Eq.(7) yields

$$Q_{cl}^{anh} = \frac{2}{u_e} e^{-\rho^2} \sum_{k=0}^{\infty} \frac{\rho^{2k+2}}{(2k+1)k!} \tag{108}$$

It can be shown that this Q_{cl}^{anh} tends to Q_{cl}^{harm} as $\rho \to \infty$, as expected. A computer program is written to compare the series obtained in Eq.(107) with the exact value and Eq.(108)

converges to the exact values as expected.

The Padé approximant is originally intended to be used to effect a more rapid convergence. A function may be evaluated from a sequence of rational fractions, called the Padé approximant.[21] This method often evaluates functions beyond the radius of convergence of the corresponding infinite series (if divergent).

Let

$$f(x) = \sum_{n=0}^{\infty} a_n x^n \qquad [a_0 \neq 0] \tag{109}$$

Then, the Padé approximant is expressed as

$$f(x) = \frac{\sum_{n=0}^{j} \alpha_n x^n}{\sum_{n=0}^{k} \beta_n \chi^n} + 0\ (x^{j+k+1})\ , \tag{110}$$

where the coefficients α_n and β_n can be defined by solving

$$f(x) \cdot \sum_{n=0}^{k} \beta_n x^n - \sum_{n=0}^{j} \alpha_n x^n = 0\ (x^{j+k+1})\ , \tag{111}$$

in which the higher order terms have been neglected.

To generalize this process, a function may be evaluated as the root of a quadratic equation

$$f^2(x) \sum_{n=0}^{\ell} \gamma_n x^n + f(x) \sum_{n=0}^{k} \beta_n x^n + \sum_{n=0}^{j} \alpha_n x^n$$

$$= 0 \; (x^{j+k+\ell+2}) \qquad (112)$$

where I again neglect the higher order terms. According to R. Shafer,[22] the "quadratic" approximation is an attractive alternative to the Padé approximant if convergence of the Padé approximation is not rapid.

By applying the Padé approximant to our expansion of Eq.(108) with the objective of effecting a more rapid convergence, I have found that the Padé approximant outperforms the corresponding truncated series, Eq.(108), by a little, but not as fast as I would like it to be: Figures 9,10,11 show plots of the percent errors that the three-five-, and nine-term expansion of Eq.(108) will respectively yield as a function of ρ. Those figures also show plots of percent errors that the Padé approximants P[1,1], P[2,2], and P[4,4] would respectively yield. A Padé approximant P[n,n], which contains 2n+1 adjustable parameters, should be compared to the (2n+1)-term expansion of the type of Eq.(108). For a less than 0.01% accuracy, Padé P[5,5] holds on until ρ = 2.1, while the corresponding eleven term series holds on until ρ = 1.8. Padé [10,10] holds on until ρ = 3.2 as compared with ρ = 2.9 for the 21-term series. I also notice that the roll-off characteristic of Padé for this case is

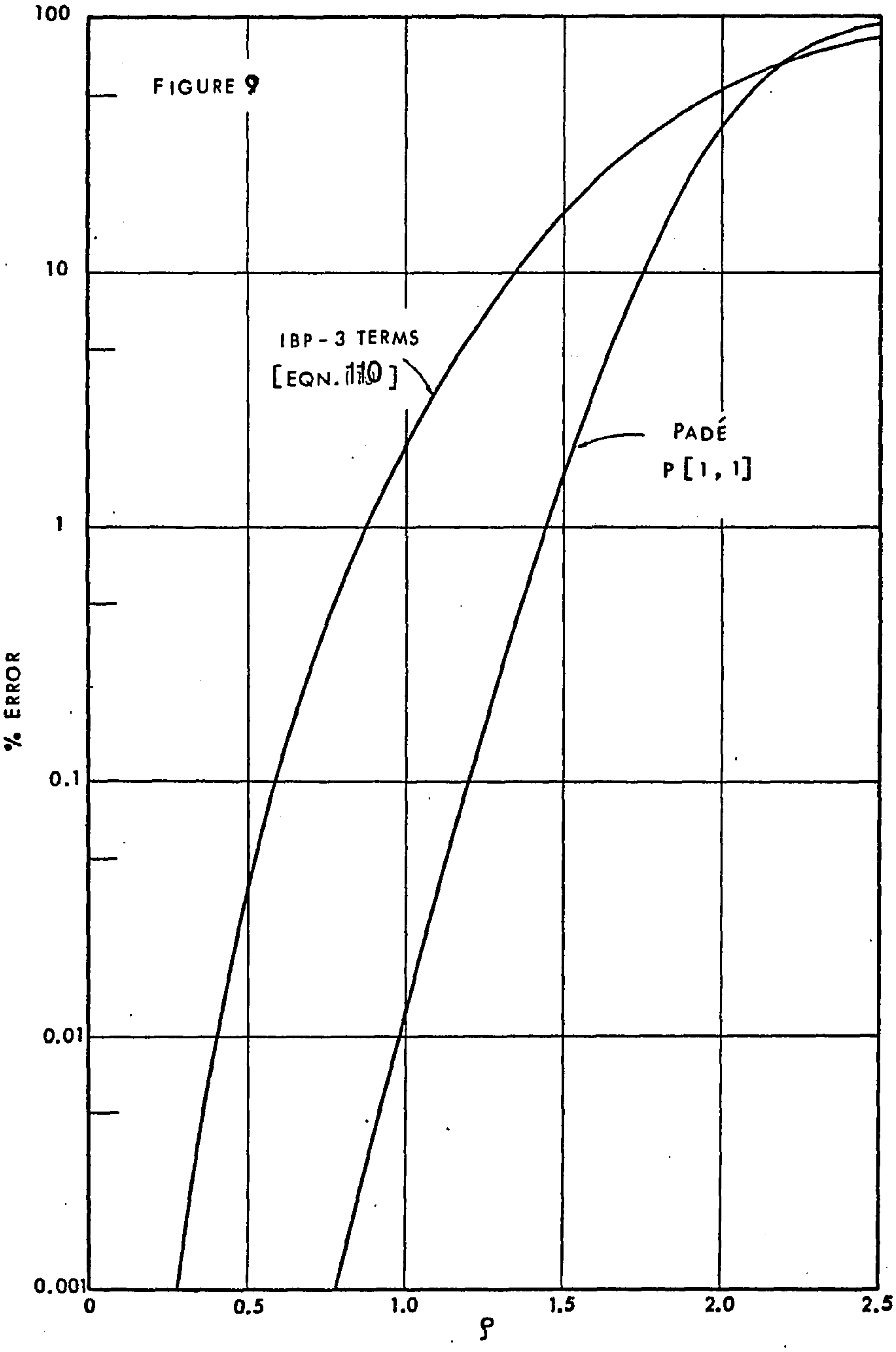


FIGURE 9

100
10
1
0.1
0.01
0.001
% ERROR
0
0.5
1.0
1.5
2.0
2.5
ρ
IBP - 3 TERMS
[EQN. 110]
PADÉ
P [1, 1]

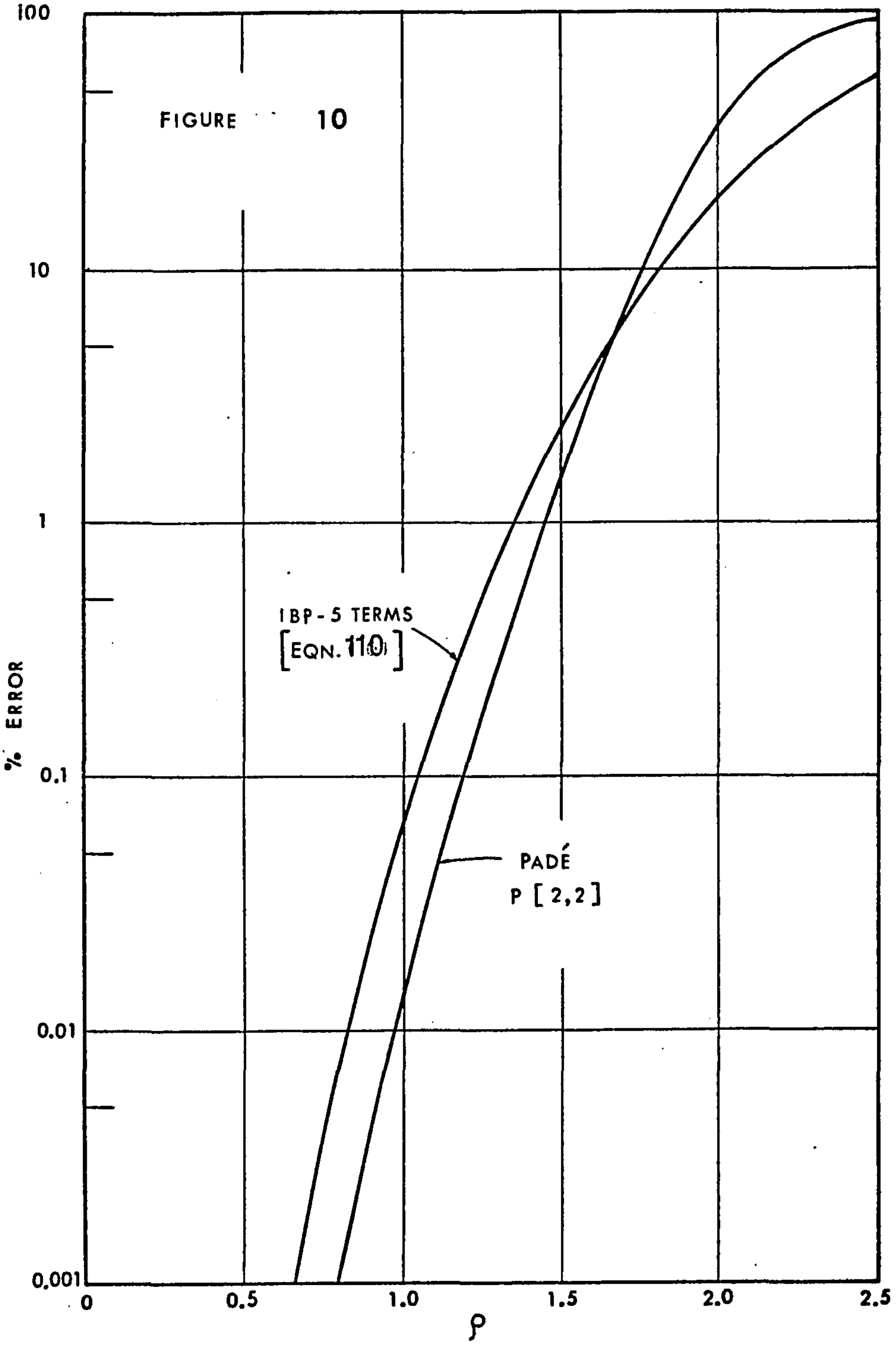


FIGURE 10

100
10
1
0.1
0.01
0,001
% ERROR
0
0.5
1.0
1.5
2.0
2.5
ρ
IBP-5 TERMS
[EQN. 110]
PADÉ
P [2,2]

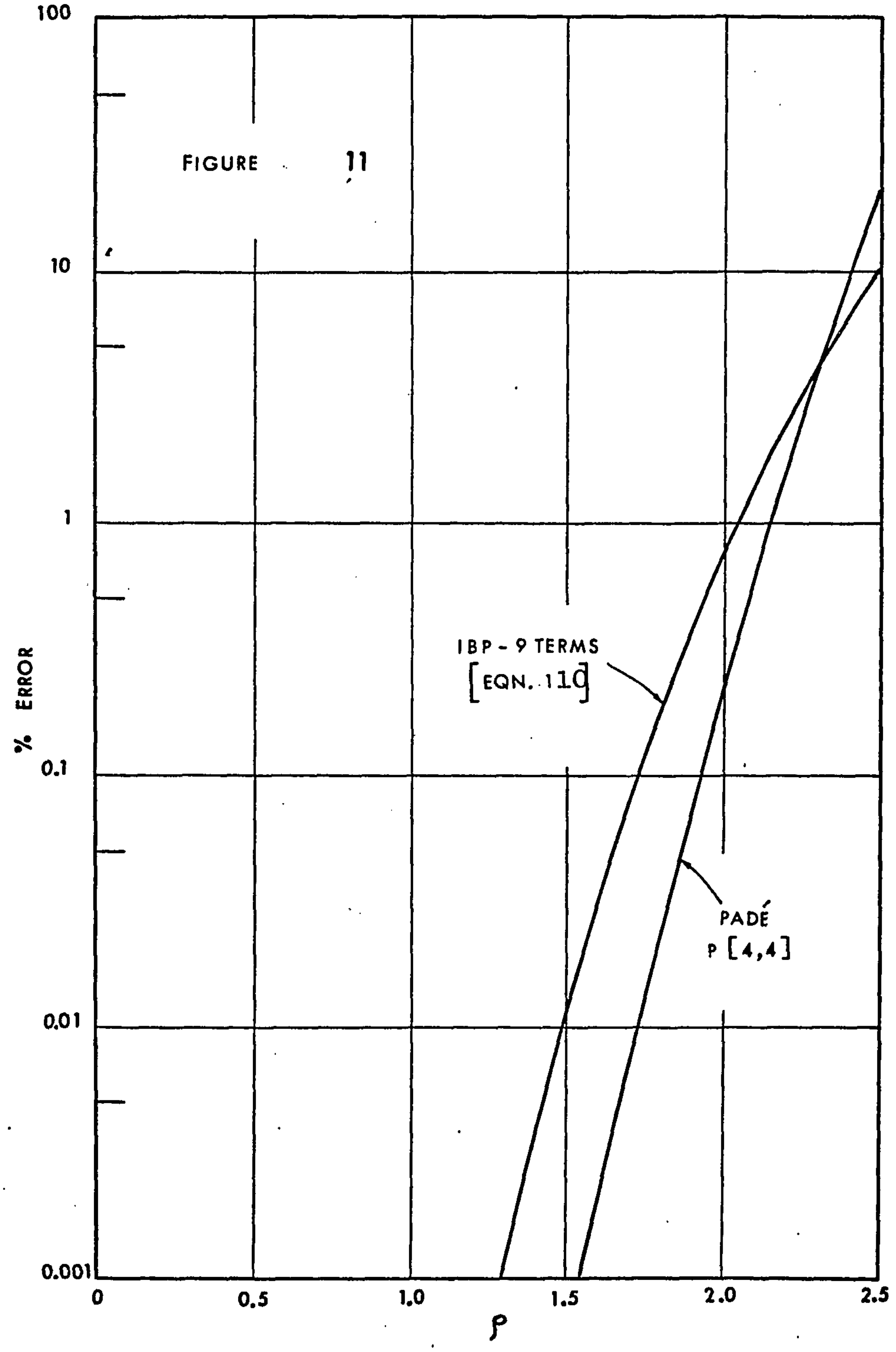


FIGURE 11
100
10
1
0.1
0.01
0.001
% ERROR
0
0.5
1.0
1.5
2.0
2.5
ρ
IBP - 9 TERMS
[EQN. 110]
PADÉ
P [4,4]

very abrupt, compared to the smooth and slow roll-off of the truncated integration-by-parts series.

Since the diagonal Padé element is of more interest than the off-diagonal ones, no effort is made to calculate the off-diagonal Padé elements.

A computer program is written in which the quadratic approximation method is used in our problem in a rather simple case;

$$f^2(x)(\gamma_0+\gamma_1x+\gamma_2x^2) + f(x)(\beta_0+\beta_1x) + (\alpha_0+\alpha_1x+\alpha_2x^2) = O(x^7) \tag{113}$$

We find that no significant improvement can be obtained by the quadratic approach.

B. ORTHOGONAL POLYNOMIAL

Here I investigate further another method, the τ method, which is found to be satisfactory at large values of ρ.

In the τ-method,[23] one sets up a differential equation pertinent to a given approximation problem, and admits an error term to the differential equation. The error term is set to be proportional to an orthogonal polynomial. A series solution for such a modified differential equation, with the error term, is then obtained. The proportionality constant for the error term, τ, is undetermined a priori but is evaluated later in connection with certain boundary conditions. The net effect of the τ-method is to spread out the error of approximation throughout a certain range of expansion, rather than achieving a high degree of accuracy near one point at the expense of poorer results from the center of expansion. The τ-method has been successfully applied to[13,14] the problem of approximation of the reduced partition function ratio, ln $\frac{s}{s'} f$, for systems of harmonic oscillators. It is, therefore, a natural extension to attempt an application of τ-method to the present problem.

Our purpose here is to find an approximation for the inner integral of γ_{cl}, Eq.(12). Set

$$\int_0^{y_2} e^{-t^2}\, dt = e^{-y_2^2} f(y_2) = e^{-y_2^2} \sum_{i=1}^{n} a_i y_2^{\,i} \qquad (114)$$

Since the left-hand side of Eq.(114) is an odd function of y_2, we seek the right-hand side of Eq.(114) containing only odd i-terms. Eq.(114) can be rewritten as

$$f(x) = e^{\rho^2 x^2} \int_0^{\rho x} e^{-t^2}\, dt \qquad (115)$$

where

$$x \equiv \frac{y_2}{\rho} \qquad (116)$$

Then we have

$$0 \leq x \leq 1 \tag{117}$$

Differentiating Eq.(115) with respect to x, we get

$$\frac{df(x)}{dx} - 2\rho^2 x f(x) - \rho = 0 \tag{118}$$

Inserting the error term into Eq.(118),

$$f' - 2\rho^2 x f - \rho = \tau T_{n+1}(x) \tag{119}$$

where $T_{n+1}(x)$ is the Chebyshev polynomial of (n+1)-th order, which is defined in $0 \leq x \leq 1$:

$$T_{n+1}(x) = \sum_{i=0}^{n+1} C_{n+1}^{i} x^{i} \tag{120}$$

Only odd n's are employed in the above equation. A series solution of Eq.(119) in the form of

$$f(x) = \sum_{i=1}^{n} a_i x^{i} \tag{121}$$

leads to

$$\gamma_{c1} = \frac{2e^{-\rho^2} \sum\limits_{k=0}^{\frac{n-1}{2}} \frac{\rho^{2k+2}}{(2k+1)k!} \sum\limits_{i=k+1}^{\frac{n+1}{2}} J_n^{i}(\rho)}{C_{n+1}^{0} + \sum\limits_{i=1}^{\frac{n+1}{2}} J_n^{i}(\rho)} \tag{122}$$

where

$$J_n^i(\rho) \equiv \frac{(2i-1)!}{(i-1)!\ 2^{2i-1}} \rho^{-2i} C_{n+1}^{2i} \tag{123}$$

The error of the above approximation, Eq.(122), is found to oscillate as expected. However, the approximation of Eq.(122) has at least one singular point, due to the alternating signs of C_{n+1}^{j}. The approximation is, therefore, found unsatisfactory after the first such singular point, and such points are generally at values of ρ which are smaller than the corresponding values of ρ for the 1% accuracy quoted for the approximation of γ_{c1}.

C. NIELSEN'S RESULT

Nielsen has derived relationships, correct through second-order of approximation, relating the vibrational energies and rotational constants to the cubic and quantic terms in the potential energy expressed in normal coordinate space. In the absence of resonance, the vibrational frequencies are given, in the notation of Ref. 16, Eq.(34.12), by:

$$E_{vib/hc} = E_{0/hc} + \sum_s \omega_s (v_s + \frac{1}{2} g_s)$$

$$+ \sum_s \sum_{s'} \chi_{ss'} (v_s + \frac{1}{2} g_s)(v_s + \frac{1}{2} g_{s'}) +$$

$$+ \sum_{t,t'} \chi_{\ell_t \ell_{t'}} \ell_t \ell_{t'} \tag{124}$$

where

$$\chi_{ss} = \frac{1}{4}\left[6k_{ssss} - 15\left(\frac{k_{sss}^{2}}{\omega_s}\right)\right.$$

$$\left. - \sum_{s'}\left(\frac{k_{sss'}^{2}}{\omega_{s'}}\right)\frac{8\omega_s^{2} - 3\omega_s^{2}}{4\omega_s^{2} - \omega_{s'}^{2}}\right] , \tag{125}$$

$$\chi_{ss'} = \frac{1}{2}\left[k_{sss's'} - 6\left(\frac{k_{sss}k_{ss's'}}{\omega_s}\right)\right.$$

$$- 4k_{sss'}^{2}\left(\frac{\omega_s}{4\omega_s^{2} - \omega_{s'}^{2}}\right) - \sum_{s''}\left(\frac{k_{sss''}k_{s''s's'}}{\omega_{s''}}\right)$$

$$- \sum_{s''}\left(\frac{k_{ss's''}^{2}}{2(g_s+g_{s'}-2)!}\right)\omega_{s''}$$

$$\left(\frac{\omega_{s''}^{2} - \omega_s^{2} - \omega_{s'}^{2}}{(\omega_s+\omega_{s'}+\omega_{s''})(\omega_s+\omega_{s'}-\omega_{s''})(\omega_s-\omega_{s'}+\omega_{s''})(\omega_s-\omega_{s'}-\omega_{s''})}\right)$$

$$\left. + \left(\frac{2}{g_s g_{s'}}\right)\sum_{\alpha}\sum_{\sigma\sigma'}\left(\xi_{s\sigma s'\sigma'}^{(\alpha)}\right)^{2} Be^{(\alpha\alpha)}\left(\frac{\omega_{s'}}{\omega_s}\right)\right] .$$

$$\tag{126}$$

$$\chi_{\ell_t\ell_t} = \frac{1}{4}\left\{2k_{tttt} + \sum_{s'} k_{tts'}{}^2\left[\omega_{s'}/(4\omega_t{}^2 - \omega_{s'}{}^2)\right]\right\} \tag{127}$$

and

$$\chi_{\ell_t\ell_{t'}} = \frac{1}{2}\sum_{s''}(k_{tt's''}{}^2)$$

$$\frac{\omega_t\omega_{t'}\omega_{s''}}{(\omega_t+\omega_{t'}+\omega_{s''})(\omega_t+\omega_{t'}-\omega_{s''})(\omega_t-\omega_{t'}+\omega_{s''})(\omega_t-\omega_{t'}-\omega_{s''})}$$

$$+ \Sigma\,\frac{1}{2}\,(Be^{(\alpha\alpha)})(\xi_{t_1t'_1}{}^{(\alpha)}\xi_{t_2t'_2}{}^{(\alpha)} - \xi_{t_1t'_2}{}^{(\alpha)}\xi_{t_2t'_1}{}^{(\alpha)}) \tag{128}$$

The sum over σ indicates a sum over the components of a degenerate vibration and the index t takes on those values of s corresponding to doubly degenerate vibrations. $\xi^{(\alpha)}_{s\sigma s'\sigma'}$ is the Coriolis coupling factor: ℓ_s is the quantum number of total vibrational angular momentum associated with a two- or three-fold degenerate vibration; $Be^{(\alpha\alpha)}$ is reciprocal of inertia $(h/8\pi^2 I^{(e)}_{\alpha\alpha}c)$.

For calculation, all data for ω_2 are taken from Ref. 18.

D.

In evaluating Eq. (90) we have used the relationship[10]

$$e^{a}be^{-a} = b + [a,b] + \frac{1}{2!}\Big[a,[a,b]\Big] + \ldots \qquad (129)$$

where a,b are operators.

For a simple illustration, let

$$a = \frac{\beta t}{2}\,[\omega_i'(a_i a_i^{\dagger} + a_i^{\dagger} a_i)]$$

$$= \frac{\beta t}{2}\,[\omega_i'(2a_i^{\dagger} a_i + 1)] \qquad (130)$$

$$b = a_i a_j \qquad (131)$$

Then we have, by employing Eq.(129)

$$e^{a}be^{-a} = a_i a_j + \frac{\beta t}{2}\,[2\omega_i'(a_i^{\dagger} a_i a_i a_j - a_i a_j a_i^{\dagger} a_i)]$$

$$= a_i a_j + \frac{\beta t}{2}\,[2\omega_i(a_i^{\dagger} a_i a_i a_j - a_i a_i^{\dagger} a_i a_j)]$$

$$= a_i a_j - \beta t\omega_i' a_i a_j + \frac{(\beta t)^2}{2}\,\omega_i^{2} a_i a_j + \ldots$$

$$= a_i a_j\, e^{-\beta t\omega_i'} \qquad (132)$$

Likewise, it can be shown that if $b = a_i^{\dagger} a_j^{\dagger}$ instead of $b = a_i a_j$, then

$$e^{a}be^{-a} = a_i^{\dagger} a_j^{\dagger} e^{\beta t\omega_i} \qquad (133)$$

By applying the above method and recalling that all terms with uncompensated raising or lowering operators will give zero when averaged in a state $<n_1 n_2 \dots n_n|$, we arrive at Eq. (90).

From the relationship $a_i^{\dagger} a_i |n_i> = n_, |n_i>$ and $n_i = \frac{1}{e^{\beta\hbar\omega_i}-1}$,[24] we can simplify Eq. (90) to Eq. (91) with the help of Eq. (93).

E. LISTINGS OF COMPUTER PROGRAMS

```
// JOB 'MMMMMM',REGION=140K,TIME=9
//*MAIN LINES=3
//PROC EXEC FORTGCG
//FORT.SYSPRINT DD DUMMY,DCB=(RECFM=FBA,LRECL=120,BLKSIZE=1920)
//FORT.SYSIN DD *
C PROGRAM FEXACT FOR  2-D SYSTEM
C Q-QM AND Q-CL WILL BE CALCULATED EXACTLY AND LN(S/S')F
C EQUALS (Q-QM/Q-CL)/(Q-QM'/Q-CL') .

      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION G122(20),G122PI(20),W(20),QQM(20),QQMPI(20),C1(20),C2(20
     1),Y(2,20),YPI(2,20),ALPHA1(20),ALPHA2(20),FSU2(20),FSU2PI(20)
      DIMENSION YNPU(2,20),X(2,20),WE(2,20),YNPUPI(2,20),XPI(2,20),WEPI(
     12,20),QUO(20),QUOPI(20),EXACT(20)
      DIMENSION FSUB(20),F111(20),EH(20),FSUBPI(20),F111PI(20),EHPI(20),
     1X12(20),X12PI(20),V12(20),V12PI(20),EHO(20),EHOPI(20),T(2,20),TPI(
     22,20),ALF1PI(20),ALF2PI(20),F122(20),F122PI(20),PEN(20),PENPI(20)
      DIMENSION GPI(20),F(20),PERHAR(20),PFRANH(20),AT(20),ET(20),DT(20)
 1311 READ(5,300) INDEX,NP,F112,F222,TEMP
  300 FORMAT(2I3,3F8.3)
      HC=6.62559D0*2.997925D-17
      VALKT=1.38054D-16*TEMP
      IF(INDEX+1) 200,311,200
  311 WRITE(6,313) INDEX,NP,F112,F222,TEMP
  313 FORMAT(1H1,'  INDEX= ',I3,'NUMBER OF POINTS = ',I3,' F112= ',F8.3,
     2' F222= ',F8.3,' TEMP= ',F8.3)
      DO 305 I=1,NP
      READ(5,307) (WEPI(J,I),XPI(J,I),WE(J,I),X(J,I),J=1,2)
  307 FORMAT(4F12.5)
  305 CONTINUE
      DO 309 I=1,NP
      PEN(I)=(4.0*WE(2,I)**2-WE(1,I)**2)/(8.0*WE(2,I)**2-3.0*WE(1,I)**2)
      PENPI(I)=(4.0*WEPI(2,I)**2-WEPI(1,I)**2)/(8.0*WEPI(2,I)**2-3.0*WEP
     1I(1,I)**2)
      F122(I)=-DSQRT(4.0*X(2,I)*WE(2,I)*WE(1,I)*PEN(I))
      F122PI(I)=-DSQRT(4.0*XPI(2,I)*WEPI(2,I)*WEPI(1,I)*PENPI(I))
  309 CONTINUE
      DO 601 I=1,NP
      DO 601 J=1,2
      YNPU(J,I)=WE(J,I)/(VALKT/HC)
      YNPUPI(J,I)=WEPI(J,I)/(VALKT/HC)
      Y(J,I)=-X(J,I)*WE(J,I)*(HC/VALKT)
      YPI(J,I)=-XPI(J,I)*WEPI(J,I)*(HC/VALKT)
      T(J,I)=-X(J,I)*WE(J,I)
      TPI(J,I)=-XPI(J,I)*WEPI(J,I)
      F112PI=F112*WEPI(1,I)/WE(1,I)
  601 CONTINUE
      CONST2=8.0D0*(3.14159D0**2)*2.9979D10/6.6262D-27
      CONST=DSQRT(CONST2)
      DO 512 I=1,NP
      FSUB(I)=(F112**2/WE(2,I))*(8.0*WE(1,I)**2-3.0*WE(2,I)**2)/(4.0*WE(
     41,I)**2-WE(2,I)**2)
      FSUBPI(I)=(F112PI**2/WEPI(2,I))*(8.0*WEPI(1,I)**2-3.0*WEPI(2,I)**2
     4)/(4.0*WEPI(1,I)**2-WEPI(2,I)**2)
      DU=WE(1,I)/15.0D0
      DUPI=WEPI(1,I)/15.0D0
      F111(I)=-DSQRT(-4.0D0*T(1,I)*DU-FSUB(I)*DU)
      F111PI(I)=-DSQRT(-4.0D0*TPI(1,I)*DUPI-FSUBPI(I)*DUPI)
      FSU2(I)=(F122(I)**2/WE(1,I))*(8.0*WE(2,I)**2-3.0*WE(1,I)**2)/(4.0*
     4WE(2,I)**2-WE(1,I)**2)
      FSU2PI(I)=(F122PI(I)**2/WEPI(1,I))*(8.0*WEPI(2,I)**2-3.0*WEPI(1,I)
     4**2)/(4.0*WEPI(2,I)**2-WEPI(1,I)**2)
```

```
      DUE=WE(2,I)/15.0D0
      DUEPI=WEPI(2,I)/15.0D0
      F222PI=0.0D0
      ALPHA1(I)=DSQRT(4.0*3.14159*X(1,I))
      ALPHA2(I)=DSQRT(4.0*3.14159*X(2,I))
      ALF1PI(I)=DSQRT(4.0*3.14159*XPI(1,I))
      ALF2PI(I)=DSQRT(4.0*3.14159*XPI(2,I))
C      WRITE(6,702) ALPHA1(I),ALPHA2(I),F111(I),F111PI(I),F122(I),F122PI
C    1(I)
 702   FORMAT(///,'  ALPHA1,2, F111,PI, F122,PI ARE ',6E14.3)
      X12(I)=0.5D0*((-6.0D0*F111(I)*F122(I)/WE(1,I))-4.0D0*(F112**2)*WE(
     51,I)/(4.0D0*WE(1,I)**2-WE(2,I)**2))
     1          +0.5D0*((-6.0D0*F222*F112/WE(2,I))-4.0D0*(F122(I)**2)*WE(
     52,I)/(4.0D0*WE(2,I)**2-WE(1,I)**2))
      X12PI(I)=0.5D0*((-6.0D0*F111PI(I)*F122PI(I)/WEPI(1,I))-4.0D0*(F112
     5PI**2)*WEPI(1,I)/(4.0D0*WEPI(1,I)**2-WEPI(2,I)**2))
     1           +0.5D0*((-6.0D0*F222PI*F112PI/WEPI(2,I))-4.0D0*(F122PI(
     5I)**2)*WEPI(2,I)/(4.0D0*WEPI(2,I)**2-WEPI(1,I)**2))
      WRITE(6,713) I,X12(I),X12PI(I)
 713  FORMAT(/,' I,X12,X12PI ARE  ',I4,2E14.5)
      SUM=0.0
      C2(I)=(1.0D0-X(2,I))/(2.0D0*X(2,I))
      NC2PI=(1.0D0-XPI(2,I))/(2.0*XPI(2,I))
      NC2=C2(I)
      V12(I)=X12(I)*(HC/VALKT)
      V12PI(I)=X12PI(I)*(HC/VALKT)
      DO 401 N2=1,NC2
      V22=N2*1.0D0+0.5D0-1.0D0
      C1(I)=(WE(1,I)-X(1,I)*WE(1,I)+X12(I)*V22)/(2.0*X(1,I)*WE(1,I))
      NC1=C1(I)
      DO 401 N1=1,NC1
      V11=N1*1.0D0+0.5D0 -1.0D0
      EH(I)=YNPU(1,I)*V11+YNPU(2,I)*V22+Y(1,I)*V11**2+Y(2,I)*V22**2+V12(
     5I)*V11*V22
      CHECK=EH(I)
      IF(CHECK-70) 405,405,401
  405 SUM=SUM+DEXP(-EH(I))
  401 CONTINUE
      RHO1=0.5D0*DSQRT(YNPU(1,I)/X(1,I))
      RHO2=0.5D0*DSQRT(YNPU(2,I)/X(2,I))
C      WRITE(6,703) VALKT,RHO1,RHO2
 703   FORMAT(///,' KT=  ',E16.5,' RHO1= ',E16.5,' RHO2= ',E16.5)
       G112=HC*F112/((ALPHA1(I)**2*ALPHA2(I)*VALKT*RHO1**2*RHO2)*DSQRT(8
     1.0D0))
       G122(I)=HC*F122(I)/((ALPHA2(I)**2*ALPHA1(I)*VALKT*RHO2**2*RHO1)*D
     1SQRT(8.0D0))
C703  WRITE(6,701) G112,G122(I)
 701  FORMAT(///,' G112= ',E15.5,' G122=',E15.5)
 707  CALL QUAD(I,RHO1,RHO2,G112,G122,W)
      EHO(I)=0.5D0*(YNPU(1,I)+YNPU(2,I))+0.25D0*(YNPU(1,I)*Y(1,I)/WE(1,I
     1)+YNPU(2,I)*Y(2,I)/WE(2,I)+YNPU(1,I)*V12(I)/WE(1,I))
      QCM(I)=SUM
      QUO(I)=((YNPU(1,I)*YNPU(2,I))*QCM(I))/W(I)
      SUM1=0.0
      DO 507 N2=1,NC2PI
      V22=N2*1.0D0+0.5D0-1.0D0
      NC1PI=(WEPI(1,I)-XPI(1,I)*WEPI(1,I)+X12PI(I)*V22)/(2.0*XPI(1,I)*WE
     1PI(1,I))
      DO 507 N1=1,NC1PI
      V11=N1*1.0D0+0.5D0 -1.0D0
      EHPI(I)=YNPUPI(1,I)*V11+YNPUPI(2,I)*V22+YPI(1,I)*V11**2+YPI(2,I)*V
     522**2+V12PI(I)*V11*V22
      CHECK2=EHPI(I)
      IF(CHECK2-70)  505,505,507
  505 SUM1=SUM1+DEXP(-EHPI(I))
  507 CONTINUE
```

```
      RHO1PI=0.5D0*DSQRT(YNPUPI(1,I)/XPI(1,I))
      RHO2PI=0.5D0*DSQRT(YNPUPI(2,I)/XPI(2,I))
       G112PI=HC*F112PI/((ALF1PI(I)**2*ALF2PI(I)*VALKT*RHO1PI**2*RHO2PI)
     1*DSQRT(8.0D0))
       G122PI(I)=HC*F122PI(I)/((ALF2PI(I)**2*ALF1PI(I)*VALKT*RHO2PI**2*R
     1HO1PI)*DSQRT(8.0D0))
      CALL QUAD(I,RHO1PI,RHO2PI,G112PI,G122PI,W)
      EHOPI(I)=0.5D0*(YNPUPI(1,I)+YNPUPI(2,I))+0.25D0*(YNPUPI(1,I)*YPI(1
     1,I)/WEPI(1,I)+YNPUPI(2,I)*YPI(2,I)/WEPI(2,I)+YNPUPI(1,I)*V12PI(I)/
     2WEPI(1,I))
      OQMPI(I)=SUM1
      QUOPI(I)=((YNPUPI(1,I)*YNPUPI(2,I))*OQMPI(I))/W(I)
C     WRITE(6,511) I,OQM(I),OQMPI(I)
  511 FORMAT(//,' I= ',I3,' OQM = ',F12.5,' OQMPI = ',F12.5)
C     WRITE(6,521) I,QUO(I),QUOPI(I)
  521 FORMAT(//,' I= ',I3,' QUO = ',F12.5,' QUOPI = ',F12.5)
      EXACT(I)=DLOG(QUO(I))-DLOG(QUOPI(I))
C     WRITE(6,531) EXACT(I)
 531  FORMAT(//, ' LNF-EXACT = ',F12.4)
      CALL INFANH(I,TEMP,F112,F122,F112PI,F122PI,YNPU,X,YNPUPI,XPI,EXACT
     1,GPI,F,PERHAR,PERANH,AT,ET,DT)
  512 CONTINUE
      WRITE(6,5001)
 5001 FORMAT(1H1)
      WRITE(6,5003) TEMP,WEPI(1,1),WE(1,1),WEPI(2,1),WE(2,1)
 5003 FORMAT(1X,9(/),' T =',F8.3,10X,9HWE'(1) = ,F8.2,10X,'WE(1) = ',F8.
     12,10X,9HWE'(2) = ,F8.2,10X,'WE(2) = ',F8.2)
      WRITE(6,6001)
 6001 FORMAT(1H0,10(/),24X,9HLN(S/S')F,14X,7H% ERROR)
      WRITE(6,6003)
 6003 FORMAT(15X,28('-'),2X,13('-'))
      WRITE(6,6005)
 6005 FORMAT(3X,'X1',5X,'X2',5X,'EXACT',5X,'HARM.',4X,'ANHARM.',2X,'HARM
     1.',1X,'ANHARM.',5X,'A',10X,'E',10X,'D',6X,12H(F122,F122'),2X,12H(F
     2111,F111'))
      WRITE(6,6007)
 6007 FORMAT(2X,4('-'),2X,5('-'),2X,8('-'),2X,8('-'),2X,8('-'),2X,5('-')
     1,1X,7('-'),1X,9('-'),2X,9('-'),2X,9('-'),2X,13('-'),1X,14('-'))
      WRITE(6,6008) X(1,1),X(2,1),EXACT(1),GPI(1),F(1),PERHAR(1),PERANH(
     11),AT(1),ET(1),DT(1),F122(1),F122PI(1),F111(1),F111PI(1)
 6008 FORMAT(1X,F5.3,F7.3,3F10.6,2F7.3,3F11.6,1X,'(',F6.1,',',F6.1,')','
     1(',F6.1,',',F6.1,')')
      DO 6015 I=2,3
      WRITE(6,6011)         X(2,I),EXACT(I),GPI(I),F(I),PERHAR(I),PERANH(
     1I),AT(I),ET(I),DT(I),F122(I),F122PI(I),F111(I),F111PI(I)
 6011 FORMAT(6X,F7.3,3F10.6,2F7.3,3F11.6,1X,'(',F6.1,',',F6.1,')','(',F6
     1.1,',',F6.1,')')
 6015 CONTINUE
      WRITE(6,6037)
 6037 FORMAT(/)
      WRITE(6,6008) X(1,4),X(2,4),EXACT(4),GPI(4),F(4),PERHAR(4),PERANH(
     14),AT(4),ET(4),DT(4),F122(4),F122PI(4),F111(4),F111PI(4)
      DO 6025 I=5,6
      WRITE(6,6021)         X(2,I),EXACT(I),GPI(I),F(I),PERHAR(I),PERANH(
     1I),AT(I),ET(I),DT(I),F122(I),F122PI(I),F111(I),F111PI(I)
 6021 FORMAT(6X,F7.3,3F10.6,2F7.3,3F11.6,1X,'(',F6.1,',',F6.1,')','(',F6
     1.1,',',F6.1,')')
 6025 CONTINUE
      WRITE(6,6037)
      WRITE(6,6008) X(1,7),X(2,7),EXACT(7),GPI(7),F(7),PERHAR(7),PERANH(
     17),AT(7),ET(7),DT(7),F122(7),F122PI(7),F111(7),F111PI(7)
      DO 6035 I=8,9
      WRITE(6,6031)         X(2,I),EXACT(I),GPI(I),F(I),PERHAR(I),PERANH(
     1I),AT(I),ET(I),DT(I),F122(I),F122PI(I),F111(I),F111PI(I)
 6031 FORMAT(6X,F7.3,3F10.6,2F7.3,3F11.6,1X,'(',F6.1,',',F6.1,')','(',F6
     1.1,',',F6.1,')')
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```
 6035 CONTINUE
      WRITE(6,6041)
 6041 FORMAT(1X,9(/),62H T IS IN 0 K, WE'S AND F'S IN CM-1, THE REST ARE
     1 DIMENSIONLESS)
      GO TO  1311
  200 CALL EXIT
      END
       SUBROUTINE QUAD(I,R,R2,G112,G122,W)
C  SUBROUTINE TO INTEGRATE QUAD INTEGRAL
      IMPLICIT REAL*8(A-H,O-Z)
C  GCL : FOR COMPUTING THE ANHARMONICITY CORRECTION FACTOR FOR
C          G(CL.,EXACT), A FUNCTION OF RHO AND GAMMA , A 2-D SITUATION
       DIMENSION G122(20),W(20),NUP(12),NDOWN(12)
       U=1.0D0
       PI=1.772453851
       N=4
      NUP(1)=100
      NUP(2)=100
      NUP(3)=100
      NDOWN(1)=1000
      NDOWN(2)=250
      NDOWN(3)=200
       NUP(4)=2000
   60 CONTINUE
      IF(R-2.3) 2,2,5
    2 NDOWN(4)=500/(48.0-3.0*R*R)
      GO TO 10
    5 NDOWN(4)=7.0*R
      WRITE(6,311) N,U,R,G112,G122(I),R2
 311  FORMAT(/,' N,U,R,G112,G122,R2 ARE ',I3,5E12.3)
   10 CALL SUBCL2(I,N,U,R,G112,G122,R2,NUP,NDOWN,Q,C1,C2)
      W(I)=C1
      WRITE(6,3002) I,W(I)
 3002 FORMAT(1H0,' I = ',I3,' CI = ',F16.7)
      RETURN
      END
      SUBROUTINE SUBCL2(II,N,U,R,G112,G122,R2,N1,N2,A,B,C)
      IMPLICIT REAL*8(A-H,O-Z)
C   INPUT: U=U : R=0.5*SQRT(U/X): N=NO. OF SUBRANGES
C   IN EACH OF WHICH THE RANGE IS EQUALLY DIVIDED: N1(I)=NO.OF
C   EQUAL INTERVALS IN I-TH RANGE:N2(I)=NO. INTO WHICH R*LN2
C   IS DIVIDED TO OBTAIN EQUAL INTERVALS IN I-TH SUBRANGE
C   SUBCLS WILL BE CALLED TO EVALUATE THE INNER INTEGRALS .
      DIMENSION G122(20),N1(12),N2(12)
      STOP=1.0D-7
      N=4
      PI=1.772453851
      CALL FREN(R,YYMAX)
      YYSTOP =YYMAX*STOP
      S=0.0D0
      RR=R*DLOG(2.0D0)
      X=-RR
C         FOR EVERY SUBRANGE:
      DO 100 I=1,N
      DX=RR/N2(I)
      X=X+DX/2.0D0
      NM=N1(I)
C         FOR EVERY SUBDIVISION:
      DO 50  J=1,NM
      IF(X/R-100)2,1,1
    1 V=1.0D0
      Y=0.0D0
      GO TO 7
    2 V=(1.0D0-(EXP(-X/R))**2
      Y=R*DSQRT(1.0D0-V)
      VRR=V*R*R
```

```
      IF(VRR-100) 3,3,7
    3 EX=DEXP(-VRR)
      IF(Y-1.0D-30/EX) 7,4,4
    4 CALL ERFN(Y,E)
      CALL SUBCLS(II,N,R,X,G112,G122,VRR,R2,N1,N2,A1,B1)
      YY=E*B1
      GO TO 10
    7 YY=0.0D0
   10 CONTINUE
      S=S+YY*DX
      X=X+DX
      IF(I-N) 50,20,200
  200 CALL EXIT
   20 IF(YY-YYSTOP) 150,150,50
   50 CONTINUE
      X=X-DX/2.0D0
  100 CONTINUE
      S=S*1.0D10
  150 B=S/PI
C     WRITE(6,205) B,S
  205 FORMAT(/,' B AND S =' ,2E14.4)
      A=1.0D0/U
      C=1.0D0+0.5D0/(R*R)
      RETURN
      END
      SUBROUTINE SUBCLS(II,N,R,X1,G112,G122,VRR,R2,N1,N2,A1,B1)
C  SUBCLS TAKES CARE OF THE INNER INTEGRAL
      IMPLICIT REAL*8(A-H,O-Z)
C   INPUT: U=U : R=0.5*SQRT(U/X); N=NO. OF SUBRANGES
C   IN EACH OF WHICH THE RANGE IS EQUALLY DIVIDED; N1(I)=NO.OF
C   EQUAL INTERVALS IN I-TH RANGE;N2(I)=NO. INTO WHICH R*LN2
C   IS DIVIDED TO OBTAIN EQUAL INTERVALS IN I-TH SUBRANGE
C   SUBCLS WILL BE CALLED TO EVALUATE THE INNER INTEGRALS .
      DIMENSION G122(20),N1(12),N2(12)
      STOP=1.0D-7
      N=4
      PI=1.772453851
      IF(R.EQ.R2) GO TO 110
      IF(R2-2.3) 21,21,25
   21 N2(4)=500/(48.0-3.0*R2*R2)
      GO TO 110
   25 N2(4)=7.0*R2
  110 CALL ERFN(R2,YYMAX)
      CALL NEWTON(II,R,X1,G112,G122,R2,RMAX)
      YYSTOP =YYMAX*STOP
      S=0.0D0
      RR=R2*DLOG(2.0D0)
      X=-RR
C        FOR EVERY SUBRANGE:
      DO 100 I=1,N
      IF(I-4) 30,35,35
   35 TES=G122(II)*X1
      IF(TES-0.0D0) 37,30,30
   37 CONTINUE
      IF(RMAX.GE.200) GO TO 30
      DX=RMAX/N1(I)
      GO TO 32
   30 DX=RR/N2(I)
   32 X=X+DX/2.0D0
      NM=N1(I)
C        FOR EVERY SUBDIVISION:
      DO 50  J=1,NM
      IF(X/R2-100)2,1,1
    1 V=1.0D0
      Y=0.0D0
      GO TO 7
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    2 V=(1.0D0-DEXP(-X/R2))**2
      V1=(1.0D0-DEXP(-X1/R))**2
      Y=DSQRT(R2*R2*(1.0D0-V))
      YH=R2*R2*(1.0D0-V)-G112*X*X1*X1-G122(II)*X*X1*X
      YR=R2*R2*(1.0D0-V)
      IF(YH.GE.YR) GO TO 300
      IF(YH.LE.1.0D-30) GO TO 300
      YL=R2*R2*(1.0D0-(1.0D0-DEXP(-RMAX/R2))**2)-G112*X1*X1*RMAX-G122(II
     2)*RMAX*RMAX*X1
      IF(YL.LE.0.0) GO TO 300
      Y=DSQRT(YL)
  300 CONTINUE
      VRR2=V*R2*R2
      CHEK=VRR+VRR2+G112*X*X1*X1+G122(II)*X*X*X1
      IF(CHEK-100) 3,3,7
    3 YJ=-VRR-VRR2-G112*X*X1*X1-G122(II)*X*X*X1
      IF(YJ.GT.0.0) GO TO 301
      EX=DEXP(YJ)
      IF(Y-1.0D-30/EX) 7,14,14
  14  TEST=G122(II)*X1
      IF(TEST-0.0D0) 4,4,4
    4 CALL ERFN(Y,F)
      GO TO 45
   44 F=0.5*PI
   45 YY=F*EX
      GO TO 10
    7 YY=0.0D0
   10 CONTINUE
      S=S+YY*DX
      X=X+DX
      IF(I-N) 50,20,200
  301 WRITE(6,310) YJ
  310 FORMAT(/,' OFF-DIAG TERMS TOO LARGE ',E14.4)
  200 CALL EXIT
   20 IF(YY-YYSTOP) 150,150,50
   50 CONTINUE
      X=X-DX/2.0D0
  100 CONTINUE
      WRITE(6,350) YY,YYSTOP
  350 FORMAT(/,' YY AND YYSTOP ARE ',2E16.7)
      S=S*1.0D10
  150 S1=S/PI
      A1=1.0D0/U
      C1=1.0D0+0.5D0/(R2*R2)
      RETURN
      END
      SUBROUTINE ERFN(Y,F)
      IMPLICIT REAL*8(A-H,O-Z)
C      FOR EVALUATING THE ERROR FUNCTION E=ERFN(X) AS
C      ERFN(X)=2*P(1.4141...*X) - 1   . SEE ABRAMOWITZ .
       X=1.41421356*Y
       AX=DABS(X)
       T=1.0D0/(1.0D0+0.2316419D0*AX)
       IF(X*X-100)12,11,11
   11 D=0.0D0
       P=1.0D0
       GO TO 13
   12 CONTINUE
       D=0.3989422804*DEXP(-X*X/2.0D0)
       P=1.0D0-D*T*((((1.330274429*T-1.821255978)*T+1.781477939)*T-
     10.356563782)*T+0.319381530)
   13 CONTINUE
       IF(X) 1,2,2
    1 P=1.0D0-P
    2 IF(P) 3,5,5
    3 WRITE(6,3001)
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 3001 FORMAT(35H0 TROUBLE IN DISTRIBUTION FUNCTION.)
    4 WRITE(6,3002) X,P
 3002 FORMAT(4H X= E14.7,4H P= E14.7)
       CALL EXIT
    5 E=2.0D0*P-1.0D0
       IF(E) 6,7,7
    6 WRITE(6,3003)
 3003 FORMAT(28H0 TROUBLE IN ERROR FUNCTION.)
       GO TO 4
    7 RETURN
       END
      SUBROUTINE LNFANH(I,TEMP,F112,F122,F112PI,F122PI,YNPU,X,YNPUPI,XPI
     2,EXACT,GPI,F,PERHAR,PERANH,AT,ET,DT)
      IMPLICIT REAL*8(A-H,O-Z)
C     SUBROUTINE LNFANH
C     LN(S/S')F WILL BE CALCULATED IN TERMS OF LN(S/S')F(HAR)
C     + MORSE POTENTIAL CORRECTION TERMS (A'S) , CUBIC OFF-
C     DIAG TERMS (D& E'S) FOR OUR MODEL 2-D SYSTEM AT VARIOUS
C     U AND X VALUES .
      DIMENSION D(20),E(20),AT(20),U1(20),U2(20),GPI(20),EXACT(20) ,F(2
     10),EPI(20),DPI(20),U1PI(20),U2PI(20),ET(20),DT(20)
      DIMENSION A(2,20),API(2,20),B(2,20),BPI(2,20),DA1(2,20),DA2(2,20),
     1DA3(2,20),EUI(2,20),WE(2,20),WEPI(2,20),EUIPI(2,20)
      DIMENSION YNPU(2,20),YNPUPI(2,20),X(2,20),XPI(2,20),RHO(2,20),RHOP
     2I(2,20),PROD(2,20),PRODPI(2,20),GUO(2,20)
      DIMENSION DAA1(2,20),DAA2(2,20),DAA3(2,20),DAA4(2,20),AA(2,20),TEM
     61(2,20),TEM2(2,20),TEM1PI(2,20),TEM2PI(2,20)
      DIMENSION GUM(20),GUMPI(20),PG(2,20),PGPI(2,20),F122(20),F122PI(20
     1),PERHAR(20),PERANH(20)
C     WRITE(6,181)
C     WRITE(6,75)
   75 FORMAT(////////////)
C     WRITE(6,417) I,EXACT(I)
  417 FORMAT(/,' I  = ',I3,' EXACT = ',F12.4)
  161 FORMAT(72('*'))
C     WRITE(6,75)
C     WRITE(6,181)
      HC=6.62559D0*2.997925D-17
      VALKT=1.38054D-16*TEMP
      DO 50 J=1,2
      RHO(J,I)=0.5D0*DSQRT(YNPU(J,I)/X(J,I))
      RHOPI(J,I)=0.5D0*DSQRT(YNPUPI(J,I)/XPI(J,I))
      WE(J,I)=(VALKT/HC)*YNPU(J,I)
   50 WEPI(J,I)=(VALKT/HC)*YNPUPI(J,I)
      VAL3=F112/(WE(1,I)*DSQRT(8.0D0))
      VAP3=F122(I)/(WE(2,I)*DSQRT(8.0D0))
      DO 15   J=1,2
      B(J,I)=YNPU(J,I)*X(J,I)
      BPI(J,I)=YNPUPI(J,I)*XPI(J,I)
      PROD(J,I)=(YNPU(J,I)*DEXP(-YNPU(J,I)/2.0D0))/(1.0D0-DEXP(-YNPU(J,I
     1)))
      PRODPI(J,I)=(YNPUPI(J,I)*DEXP(-YNPUPI(J,I)/2.0D0))/(1.0D0-DEXP(-YN
     1PUPI(J,I)))
      GUO(J,I)=DLOG(PROD(J,I))-DLOG(PRODPI(J,I))
      DA1(J,I)=(2.0D0*B(J,I))/(DEXP(YNPU(J,I))-1.0D0)-(2.0D0*BPI(J,I))/(
     1DEXP(YNPUPI(J,I))-1.0D0)
      CHECK=YNPU(J,I)
      IF(CHECK-70.0D0) 37,37,39
  37  CHECK2=YNPUPI(J,I)
      IF(CHECK2-70.0D0) 47,47,39
   47 EUI(J,I)=DEXP(-YNPU(J,I)+2.0D0*B(J,I))
      EUIPI(J,I)=DEXP(-YNPUPI(J,I)+2.0D0*BPI(J,I))
      GO TO 38
   39 EUI(J,I)=0.0D0
      EUIPI(J,I)=0.0D0
   38 DA2(J,I)=B(J,I)*EUI(J,I)*(1.0D0+EUI(J,I))/(1.0D0-EUI(J,I))**2-BPI(
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     2J,I)*EUIPI(J,I)*(1.0D0+EUIPI(J,I))/(1.0D0-EUIPI(J,I)**2)
      DA3(J,I)=0.5D0/(RHOPI(J,I)**2)-0.5D0/(RHO(J,I)**2)
C     A(J,I)=1/4(B-B')+... WILL BE BYPASSED TO ALLOW BETTER APPROX.
      DAA1(J,I)=((1.0D0-DEXP(-YNPU(J,I)))/(1.0D0-EUI(J,I)))/((1.0D0-DEXP
     1(-YNPUPI(J,I)))/(1.0D0-EUIPI(J,I)))
      DAA2(J,I)=DEXP((B(J,I)-BPI(J,I))/4.0)
      TEM1(J,I)=2.0/(DEXP(YNPU(J,I)-2.0*B(J,I)))**2
      TEM1PI(J,I)=2.0/(DEXP(YNPUPI(J,I)-2.0*BPI(J,I)))**2
      TEM2(J,I)=EUI(J,I)/(1.0D0-EUI(J,I))+2.0*EUI(J,I)**2/(1.0D0-EUI(J,I
     2)**2)
      TEM2PI(J,I)=EUIPI(J,I)/(1.0D0-EUIPI(J,I))+2.0*EUIPI(J,I)**2/(1.0D0
     2-EUIPI(J,I)**2)
      DAA3(J,I)=(1.0D0+B(J,I)*TEM1(J,I)+0.5*B(J,I)**2*TEM2(J,I))/(1.0D0+
     3BPI(J,I)*TEM1PI(J,I)+0.5*BPI(J,I)**2*TEM2PI(J,I))
      PG(J,I)=DEXP(-YNPU(J,I)*0.5+B(J,I)*0.25)*(1.0D0+B(J,I)*TEM1(J,I)+0
     2.5*B(J,I)**2*TEM2(J,I))/(1.0-EUI(J,I))
      PGPI(J,I)=DEXP(-YNPUPI(J,I)*0.5+BPI(J,I)*0.25)*(1.0D0+BPI(J,I)*TEM
     21PI(J,I)+0.5*BPI(J,I)**2*TEM2PI(J,I))/(1.0-EUIPI(J,I))
      DAA4(J,I)=(1.0D0+0.5/(RHOPI(J,I)**2))/(1.0D0+0.5/(RHO(J,I)**2))
C     WRITE(6,519) J,DAA1(J,I),DAA2(J,I),DAA3(J,I),DAA4(J,I)
  519 FORMAT(/,' DAA FOLLOW, J=',I3,4F10.4)
      AA(J,I)=DLOG(DAA1(J,I))+DLOG(DAA2(J,I))+DLOG(DAA3(J,I))+DLOG(DAA4(
     1J,I))
C     A(J,I)=0.25D0*(B(J,I)-BPI(J,I))+DA1(J,I)+DA2(J,I)+DA3(J,I)
   15 CONTINUE
      GPI(I)=QUO(1,I)+QUO(2,I)
      GUN(I)=PG(1,I)*PG(2,I)
      GUNPI(I)=PGPI(1,I)*PGPI(2,I)
      VN1=DEXP(YNPU(1,I))/(DEXP(YNPU(1,I))-1.0D0)
      VN11=VN1/(DEXP(YNPU(1,I))-1.0D0)
      VN12=VN11*((DEXP(YNPU(1,I))+1.0D0)/(DEXP(YNPU(1,I))-1.0D0))
      VN2=DEXP(YNPU(2,I))/(DEXP(YNPU(2,I))-1.0D0)
      VN21=VN2/(DEXP(YNPU(2,I))-1.0D0)
      VN22=VN21*((DEXP(YNPU(2,I))+1.0D0)/(DEXP(YNPU(2,I))-1.0D0))
      VN1PI=DEXP(YNPUPI(1,I))/(DEXP(YNPUPI(1,I))-1.0D0)
      VN11PI=VN1PI/(DEXP(YNPUPI(1,I))-1.0D0)
      VN12PI=VN11PI*((DEXP(YNPUPI(1,I))+1.0D0)/(DEXP(YNPUPI(1,I))-1.0D0)
     1)
      VN2PI=DEXP(YNPUPI(2,I))/(DEXP(YNPUPI(2,I))-1.0D0)
      VN21PI=VN2PI/(DEXP(YNPUPI(2,I))-1.0D0)
      VN22PI=VN21PI*((DEXP(YNPUPI(2,I))+1.0D0)/(DEXP(YNPUPI(2,I))-1.0D0)
     1)
      U112=((DEXP(2.0*YNPU(1,I)+YNPU(2,I))-1.0D0)/(2.0*YNPU(1,I)+YNPU(2,
     3I)))*(VN12-VN11)*VN21
      U118=((DEXP(2.0*YNPU(1,I)-YNPU(2,I))-1.0D0)/(2.0*YNPU(1,I)-YNPU(2,
     3I)))*(VN12-VN11)*(VN21+VN2)
      U992=((DEXP(-2.0*YNPU(1,I)+YNPU(2,I))-1.0D0)/(-2.0*YNPU(1,I)+YNPU(
     32,I)))*(VN12+3.0*VN11+2.0*VN1)*VN21
      U998=((1.0D0-DEXP(-2.0*YNPU(1,I)-YNPU(2,I)))/(2.0*YNPU(1,I)+YNPU(2
     3,I)))*(VN12+2.0*VN11+VN1)*(VN21+VN2)
      U221=((DEXP(2.0*YNPU(2,I)+YNPU(1,I))-1.0D0)/(2.0*YNPU(2,I)+YNPU(1,
     3I)))*(VN22-VN21)*VN11
      U229=((DEXP(2.0*YNPU(2,I)-YNPU(1,I))-1.0D0)/(2.0*YNPU(2,I)-YNPU(1,
     3I)))*(VN22-VN21)*(VN11+VN1)
      U881=((DEXP(-2.0*YNPU(2,I)+YNPU(1,I))-1.0D0)/(-2.0*YNPU(2,I)+YNPU(
     31,I)))*(VN22+3.0*VN21+2.0*VN2)*VN11
      U889=((1.0D0-DEXP(-2.0*YNPU(2,I)-YNPU(1,I)))/(2.0*YNPU(2,I)+YNPU(1
     3,I)))*(VN22+2.0*VN21+VN2)*(VN11+VN1)
      W112=((DEXP(2.0*YNPUPI(1,I)+YNPUPI(2,I))-1.0D0)/(2.0*YNPUPI(1,1)+Y
     3NPUPI(2,I)))*(VN12PI-VN11PI)*VN21PI
      W118=((DEXP(2.0*YNPUPI(1,I)-YNPUPI(2,I))-1.0D0)/(2.0*YNPUPI(1,I)-Y
     3NPUPI(2,I)))*(VN12PI-VN11PI)*(VN21PI+VN2PI)
      W992=((DEXP(-2.0*YNPUPI(1,I)+YNPUPI(2,I))-1.0D0)/(-2.0*YNPUPI(1,I)
     3+YNPUPI(2,I)))*(VN12PI+3.0*VN11PI+2.0*VN1PI)*VN21PI
      W998=((1.0D0-DEXP(-2.0*YNPUPI(1,I)-YNPUPI(2,I)))/(2.0*YNPUPI(1,I)+
     3YNPUPI(2,I)))*(VN12PI+2.0*VN11PI+VN1PI)*(VN21PI+VN2PI)
```

```
      W221=((DEXP(2.0*YNPUPI(2,I)+YNPUPI(1,I))-1.0D0)/(2.0*YNPUPI(2,I)+Y
     3NPUPI(1,I)))*(VN22PI-VN21PI)*VN11PI
      W229=((DEXP(2.0*YNPUPI(2,I)-YNPUPI(1,I))-1.0D0)/(2.0*YNPUPI(2,I)-Y
     3NPUPI(1,I)))*(VN22PI-VN21PI)*(VN11PI+VN1PI)
      W881=((DEXP(-2.0*YNPUPI(2,I)+YNPUPI(1,I))-1.0D0)/(-2.0*YNPUPI(2,I)
     3+YNPUPI(1,I)))*(VN22PI+3.0*VN21PI+2.0*VN2PI)*VN11PI
      W889=((1.0D0-DEXP(-2.0*YNPUPI(2,I)-YNPUPI(1,I)))/(2.0*YNPUPI(2,I)+
     3YNPUPI(1,I)))*(VN22PI+2.0*VN21PI+VN2PI)*(VN11PI+VN1PI)
C     U112 STANDS FOR U11-2, U992 STANDS FOR U-1-12 ETC.,
C     WRITE(6,423) U112,U118,U998,U992,VN1,VN2
 423  FORMAT(/,' U112,U118,U998,U992,VN1,VN2 ARE ',6F12.4)
      U1AD=(4.0*VN12+4.0*VN11+VN1)*(VN21*DEXP(YNPU(2,I)-1.0D0))/YNPU(2,I
     1)+(VN21+VN2)*(1.0D0-DEXP(-YNPU(2,I)))/YNPU(2,I)
      U2AD=(4.0*VN22+4.0*VN21+VN2)*(VN11*DEXP(YNPU(1,I)-1.0D0))/YNPU(1,I
     1)+(VN11+VN1)*(1.0D0-DEXP(-YNPU(1,I)))/YNPU(1,I)
      U1ADPI=(4.0*VN12PI+4.0*VN11PI+VN1PI)*(VN21PI*DEXP(YNPUPI(2,I)-1.0D
     10))/YNPUPI(2,I)+(VN21PI+VN2PI)*(1.0D0-DEXP(-YNPUPI(2,I)))/YNPUPI(2
     2,I)
      U2ADPI=(4.0*VN22PI+4.0*VN21PI+VN2PI)*(VN11PI*DEXP(YNPUPI(1,I)-1.0D
     10))/YNPUPI(1,I)+(VN11PI+VN1PI)*(1.0D0-DEXP(-YNPUPI(1,I)))/YNPUPI(1
     2,I)
      U1(I)=U112+U118+U998+U992+U1AD
      U2(I)=U221+U229+U889+U881+U2AD
      U1PI(I)=W112+W118+W998+W992+U1ADPI
      U2PI(I)=W221+W229+W889+W881+U2ADPI
      FACTO1=DEXP(-YNPU(1,I)/2.0)*DEXP(-YNPU(2,I)/2.0)/GUN(I)
      FACTO2=DEXP(-YNPUPI(1,I)/2.0)*DEXP(-YNPUPI(2,I)/2.0)/GUNPI(I)
      D(I)=(0.5*(YNPU(1,I)**2)*VAL3*VAL3*U1(I)+0.5*(YNPU(2,I)**2)*VAR3*V
     1AR3*U2(I))*FACTO1
      WAL3=F112PI/(WEPI(1,I)*DSQRT(8.0D0))
      WAR3=F122PI(I)/(WEPI(2,I)*DSQRT(8.0D0))
      E(I)=12.0D0*(VAL3**2/YNPU(2,I)+VAR3**2/YNPU(1,I))/((1.0D0+1.0/(2.0*
     1RHO(1,I)))*(1.0D0+1.0/(2.0*RHO(2,I))))
      DPI(I)=(0.5*(YNPUPI(1,I)**2)*WAL3*WAL3*U1PI(I)+0.5*(YNPUPI(2,I)**2
     1)*WAR3*WAR3*U2PI(I))*FACTO2
      EPI(I)=12.0D0*(WAL3**2/YNPUPI(2,I)+WAR3**2/YNPUPI(1,I))/((1.0D0+1.0
     1/(2.0*RHOPI(1,I)))*(1.0D0+1.0/(2.0*RHOPI(2,I))))
      AT(I)=AA(1,I)+AA(2,I)
C     DT(I)=D(I)-DPI(I)
C     ET(I)=EPI(I)-E(I)
      WRITE(6,421) I,VAL3,VAR3,U1(I),U2(I),D(I),DPI(I)
 421  FORMAT(/,' I,VAL3,VAR3,U1,U2,D,DPI ARE ',I3,6F9.3)
      DT(I)=DLOG(1.0D0+D(I))-DLOG(1.0D0+DPI(I))
      ET(I)=DLOG(1.0D0+EPI(I))-DLOG(1.0D0+E(I))
      F(I)=GPI(I)+AT(I)+DT(I)+ET(I)
      PERHAR(I)=((GPI(I)-EXACT(I))/EXACT(I))*100
      PERANH(I)=((F(I)-EXACT(I))/EXACT(I))*100
       RETURN
      END
      SUBROUTINE NEWTON(I,P,X1,G112,G122,R2,RMAX)
      IMPLICIT REAL*8(A-H,O-Z)
C     THIS SUBROUTINE SERVES TO FIND THE UPPER LIMIT OF Q2 FOR CASE 1
C     WHEN G112*X IS LESS THAN 0 USING NEWTON'S METHOD
C     NEWTON IS NOW CALCULATED POINT BY POINT
      DIMENSION G122(20),Z(500),UMAX(500)
      USTAN=R2*R2-1.0D-4
      M=1
      Z(1)=1.0
      UMAX(1)=R2*R2*(1.0D0-DEXP(-Z(1)/R2))**2-G112*Z(1)*X1*X1-G122(I)*X1
     1*(Z(1)**2)
    1 IF(UMAX(M).GE.USTAN) GO TO 23
      M=M+1
      Z(M)=Z(M-1)+1.0
      UMAX(M)=R2*R2*(1.0D0-DEXP(-Z(M)/R2))**2-G112*Z(M)*X1*X1-G122(I)*X1
     1*(Z(M)**2)
      IF(UMAX(M).LT.UMAX(M-1)) GO TO 23
```

```
      IF(M.EQ.500) GO TO 12
      GO TO 1
   23 RMAX=Z(M)
      IF(RMAX.LE.0.0) GO TO 12
      GO TO 43
   12 CONTINUE
C     WRITE(6,15) M,Z(M)
   15 FORMAT(/,' ERROR IN CONVERGENCE M ',I4,E14.4)
   43 RETURN
      END
//GO.SYSIN DD *
-01  9     0.0     0.0     100.0
  500.0         0.002        475.0        0.002
 3200.0         0.002       3140.0        0.002
  500.0         0.002        475.0        0.002
 3200.0         0.005       3140.0        0.005
  500.0         0.002        475.0        0.002
 3200.0         0.010       3140.0        0.010
  500.0         0.005        475.0        0.005
 3200.0         0.002       3140.0        0.002
  500.0         0.005        475.0        0.005
 3200.0         0.005       3140.0        0.005
  500.0         0.005        475.0        0.005
 3200.0         0.010       3140.0        0.010
  500.0         0.010        475.0        0.010
 3200.0         0.002       3140.0        0.002
  500.0         0.010        475.0        0.010
 3200.0         0.005       3140.0        0.005
  500.0         0.010        475.0        0.010
 3200.0         0.010       3140.0        0.010
-01  9    0.0     0.0     300.0
  500.0         0.002        475.0        0.002
 3200.0         0.002       3140.0        0.002
  500.0         0.002        475.0        0.002
 3200.0         0.005       3140.0        0.005
  500.0         0.002        475.0        0.002
 3200.0         0.010       3140.0        0.010
  500.0         0.005        475.0        0.005
 3200.0         0.002       3140.0        0.002
  500.0         0.005        475.0        0.005
 3200.0         0.005       3140.0        0.005
  500.0         0.005        475.0        0.005
 3200.0         0.010       3140.0        0.010
  500.0         0.010        475.0        0.010
 3200.0         0.002       3140.0        0.002
  500.0         0.010        475.0        0.010
 3200.0         0.005       3140.0        0.005
  500.0         0.010        475.0        0.010
 3200.0         0.010       3140.0        0.010
 09
/*
//
```

```
// JOB 'ACTIVE',REGION=140K,TIME=7
//*MAIN LINES=3
//PROC EXEC FORTGCG
//FORT.SYSIN DD *
C PROGRAM FEXACT FOR 3-D SYSTEM
C Q-GM AND Q-CL WILL BE CALCULATED EXACTLY AND LN(S/S')F
C EQUALS (Q-GM/Q-CL)/(Q-QM'/Q-CL') .

      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION G122(20),G122PI(20),W(20),QGM(20),QQMPI(20),C1(20),C2(20
     1),Y(3,20),YPI(3,20),ALPHA1(20),ALPHA2(20),FSU2(20),FSU2PI(20)
      DIMENSION YNPU(3,20),X(3,20),WE(3,20),YNPUPI(3,20),XPI(3,20),WEPI(
     13,20),QUO(20),QUOPI(20),EXACT(20)
      DIMENSION FSUB(20),F111(20),FH(20),FSUBPI(20),F111PI(20),EHPI(20),
     1X12(20),X12PI(20),V12(20),V12PI(20),EHO(20),EHOPI(20),T(3,20),TPI(
     23,20),ALF1PI(20),ALF2PI(20),F122(20),F122PI(20),PEN(20),PENPI(20)
      DIMENSION CPI(20),F(20),PERHAR(20),PERANH(20),AT(20),ET(20),DT(20)
      DIMENSION V13(20),V23(20),V13PI(20),V23PI(20),ALPHA3(20),ALF3PI(20
     1),C3(20),C3PI(20)
      DIMENSION X13(20),X13PI(20),X23(20),X23PI(20)
 1311 READ(5,300) INDEX,NP,F133,F133PI,TEMP
  300 FORMAT(2I3,3F8.3)
      HC=6.62559D0*2.997925D-17
      VALKT=1.38054D-16*TEMP
      IF(INDEX+1) 200,311,200
  311 WRITE(6,313) INDEX,NP,F133,F133PI,TEMP
  313 FORMAT(1H1,'  INDEX= ',I3,'NUMBER OF POINTS = ',I3,' F133= ',F8.3,
     2' F133PI= ',F8.3,' TEMP= ',F8.3)
      READ(5,1309) F122(1),F122PI(1)
 1309 FORMAT(2F12.5)
      WRITE(6,671)
 671  FORMAT(/,' WEPI , XPI , WE, X ..123 ARE ')
      DO 305 I=1,NP
      DO 305 J=1,3
      READ(5,307) WEPI(J,I),XPI(J,I),WE(J,I),X(J,I)
      WRITE(6,307) WEPI(J,I),XPI(J,I),WE(J,I),X(J,I)
  307 FORMAT(4F12.5)
  305 CONTINUE
      WRITE(6,672)
  672 FORMAT(/,' X12,X13,X23,X12PI,X13PI,X23PI ARE ')
      READ(5,6001) X12(1),X13(1),X23(1),X12PI(1),X13PI(1),X23PI(1)
      WRITE(6,6001) X12(1),X13(1),X23(1),X12PI(1),X13PI(1),X23PI(1)
 6001 FORMAT(6F12.5)
      DO 601 I=1,NP
      DO 601 J=1,3
      YNPU(J,I)=WE(J,I)/(VALKT/HC)
      YNPUPI(J,I)=WEPI(J,I)/(VALKT/HC)
      X(J,I)=-X(J,I)/WE(J,I)
      XPI(J,I)=-XPI(J,I)/WEPI(J,I)
      Y(J,I)=-X(J,I)*WE(J,I)*(HC/VALKT)
      YPI(J,I)=-XPI(J,I)*WEPI(J,I)*(HC/VALKT)
  601 CONTINUE
      WRITE(6,747)
  747 FORMAT(//,' HERE FOLLOW PAIRS OF U UPRIME 123')
      WRITE(6,757)(YNPU(J,I),YNPUPI(J,I),J=1,3)
  757 FORMAT(/,6F12.4)
      DO 512 I=1,NP
      ALPHA1(I)=DSQRT(4.0*3.14159*X(1,I))
      ALPHA2(I)=DSQRT(4.0*3.14159*X(2,I))
      ALPHA3(I)=DSQRT(4.0*3.14159*X(3,I))
      ALF1PI(I)=DSQRT(4.0*3.14159*XPI(1,I))
      ALF2PI(I)=DSQRT(4.0*3.14159*XPI(2,I))
```

```
      ALF3PI(I)=DSQRT(4.0*3.14159*XPI(3,I))
C      WRITE(6,702) ALPHA1(I),ALPHA2(I),F111(I),F111PI(I),F122(I),F122PI
C    1(I)
 702  FORMAT(///,'  ALPHA1,2, F111,PI, F122,PI ARE ',6E14.3)
      SUM=0.0
      C2(I)=(1.0D0-X(2,I))/(2.0D0*X(2,I))
      NC2PI=(1.0D0-XPI(2,I))/(2.0*XPI(2,I))
      NC2=C2(I)
      V12(I)=X12(I)*(HC/VALKT)
      V23(I)=X23(I)*(HC/VALKT)
      V13(I)=X13(I)*(HC/VALKT)
      V12PI(I)=X12PI(I)*(HC/VALKT)
      V23PI(I)=X23PI(I)*(HC/VALKT)
      V13PI(I)=X13PI(I)*(HC/VALKT)
      DO 401 N2=1,NC2
      V22=N2*1.0D0+0.5D0-1.0D0
      C1(I)=(WE(1,I)-X(1,I)*WE(1,I)+X12(I)*V22)/(2.0*X(1,I)*WE(1,I))
      NC1=C1(I)
      DO 401 N1=1,NC1
      V11=N1*1.0D0+0.5D0-1.0D0
      C3(I)=(WE(3,I)-X(3,I)*WE(3,I)+X13(I)*V11+X23(I)*V22)/(2.0*X(3,I)*W
     2E(3,I))
      NC3=C3(I)
      DO 401 N3=1,NC3
      V33=N3*1.0D0+0.5D0-1.0D0
      DO 401 N4=1,NC3
      V44=N4*1.0D0+0.5D0-1.0D0
      EH(I)=YNPU(1,I)*V11+YNPU(2,I)*V22+Y(1,I)*V11**2+Y(2,I)*V22**2+V12(
     5I)*V11*V22+YNPU(3,I)*V33+Y(3,I)*V33**2+V23(I)*V22*V33+V13(I)*V11*V
     633+YNPU(3,I)*V44+Y(3,I)*V44**2+V23(I)*V22*V44+V13(I)*V11*V44
      CHECK=EH(I)
      IF(CHECK-60) 405,405,401
  405 SUM=SUM+DEXP(-EH(I))
  401 CONTINUE
      RHO1=0.5D0*DSQRT(YNPU(1,I)/X(1,I))
      RHO2=0.5D0*DSQRT(YNPU(2,I)/X(2,I))
      RHO3=0.5D0*DSQRT(YNPU(3,I)/X(3,I))
       WRITE(6,703) VALKT,RHO1,RHO2,RHO3
 703   FORMAT(///,' KT=  ',E16.5,' RHO1 , RHO2 , RHO3 ARE ',3E15.4)
       G133=HC*F133/((ALPHA3(I)**2*ALPHA1(I)*VALKT*RHO3**2*RHO1)*DSQRT(8
     1.0D0))
       G122(I)=HC*F122(I)/((ALPHA2(I)**2*ALPHA1(I)*VALKT*RHO2**2*RHO1)*D
     1SQRT(8.0D0))
C708  WRITE(6,701) G133,G122(I)
 701  FORMAT(///,' G112= ',E15.5,' G122=',E15.5)
      WRITE(6,778)I,RHO1,RHO2,RHO3,G133,G122(I)
 778  FORMAT(/,' I,R1,R2,R3,G133,G122 ',I3,5E12.4)
 707  CALL QUAN(I,RHO1,RHO2,RHO3,G133,G122,W)
      EHO(I)=0.5D0*(YNPU(1,I)+YNPU(2,I))+0.25D0*(YNPU(1,I)*Y(1,I)/WE(1,I
     1)+YNPU(2,I)*Y(2,I)/WE(2,I)+YNPU(1,I)*V12(I)/WE(1,I))
      QQM(I)=SUM
      QUO(I)=((YNPU(1,I)*YNPU(3,I)**2*YNPU(2,I))*QQM(I))/W(I)
      SUM1=0.0
      DO 507 N2=1,NC2PI
      V22=N2*1.0D0+0.5D0-1.0D0
      NC1PI=(WEPI(1,I)-XPI(1,I)*WEPI(1,I)+X12PI(I)*V22)/(2.0*XPI(1,I)*WE
     1PI(1,I))
      DO 507 N1=1,NC1PI
      V11=N1*1.0D0+0.5D0-1.0D0
      C3PI(I)=(WEPI(3,I)-XPI(3,I)*WEPI(3,I)+X13PI(I)*V11+X23PI(I)*V22)/(
     22.0*XPI(3,I)*WEPI(3,I))
      NC3PI=C3PI(I)
      DO 507 N3=1,NC3PI
      V33=N3*1.0D0+0.5D0-1.0D0
      DO 507 N4=1,NC3PI
      V44=N4*1.0D0+0.5D0-1.0D0
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      EHPI(I)=YNPUPI(1,I)*V11+YNPUPI(2,I)*V22+YPI(1,I)*V11**2+YPI(2,I)*V
     522**2+V12PI(I)*V11*V22+YNPUPI(3,I)*V33+YPI(3,I)*V33**2+V23PI(I)*V2
     62*V33+V13PI(I)*V11*V33+YNPUPI(3,I)*V44+YPI(3,I)*V44**2+V23PI(I)*V2
     72*V44+V13PI(I)*V11*V44
      CHECK2=EHPI(I)
      IF(CHECK2-60)  505,505,507
  505 SUM1=SUM1+DEXP(-EHPI(I))
  507 CONTINUE
      RHO1PI=0.5D0*DSQRT(YNPUPI(1,I)/XPI(1,I))
      RHO2PI=0.5D0*DSQRT(YNPUPI(2,I)/XPI(2,I))
      RHO3PI=0.5D0*DSQRT(YNPUPI(3,I)/XPI(3,I))
       G133PI=HC*F133PI/((ALF3PI(I)**2*ALF1PI(I)*VALKT*RHO3PI**2*RHO1PI)
     1*DSQRT(8.0D0))
       G122PI(I)=HC*F122PI(I)/((ALF2PI(I)**2*ALF1PI(I)*VALKT*RHO2PI**2*R
     1HO1PI)*DSQRT(8.0D0))
      WRITE(6,779) I,RHO1PI,RHO2PI,RHO3PI,G133PI,G122PI(I)
 779  FORMAT(/,' I,R1,R2,R3,G133,G122 ALL PRIME ',I3,5E12.4)
      CALL QUAD(I,RHO1PI,RHO2PI,RHO3PI,G133PI,G122PI,W)
      EHOPI(I)=0.5D0*(YNPUPI(1,I)+YNPUPI(2,I))+0.25D0*(YNPUPI(1,I)*YPI(1
     1,I)/WEPI(1,I)+YNPUPI(2,I)*YPI(2,I)/WEPI(2,I)+YNPUPI(1,I)*V12PI(I)/
     2WEPI(1,I))
      QOMPI(I)=SUM1
      QUOPI(I)=((YNPUPI(1,I)*YNPUPI(3,I)**2*YNPUPI(2,I))*QOMPI(I))/W(I)
      WRITE(6,511) I,QOM(I),QOMPI(I)
  511 FORMAT(//,' I= ',I3,' QOM = ',E12.4,' QOMPI = ',E12.4)
      WRITE(6,521) I,QUO(I),QUOPI(I)
  521 FORMAT(//,' I= ',I3,' QUO = ',F12.4,' QUOPI = ',E12.4)
      EXACT(I)=DLOG(QUO(I))-DLOG(QUOPI(I))
      WRITE(6,531) EXACT(I)
 531  FORMAT(//, ' LNF-EXACT = ',F12.4)
  512 CONTINUE
      GO TO  1311
  200 CALL EXIT
      END
       SUBROUTINE QUAD(I,R,R2,R3,G133,G122,W)
C  SUBROUTINE TO INTEGRATE QUAD INTEGRAL
      IMPLICIT REAL*8(A-H,O-Z)
C  QCL : FOR COMPUTING THE ANHARMONICITY CORRECTION FACTOR FOR
C         Q(CL.,EXACT), A FUNCTION OF RHO AND GAMMA , A 2-D SITUATION
       DIMENSION G122(20),W(20),NUP(12),NDOWN(12)
       U=1.0D0
       PI=1.772453851
       N=4
      NUP(1)=40
      NUP(2)=40
      NUP(3)=40
      NDOWN(1)=400
      NDOWN(2)=100
      NDOWN(3)=80
       NUP(4)=800
   60 CONTINUE
      IF(R-2.3) 2,2,5
    2 NDOWN(4)=500/(48.0-3.0*R*R)
      GO TO 10
    5 NDOWN(4)=7.0*R
      WRITE(6,311) N,U,R,G133,G122(I),R2,R3
 311  FORMAT(/,' N,U,R,G133,G122,R2,R3 ARE ',I3,6E12.3)
   10 CALL SUBCL2(I,N,U,R,R2,R3,G133,G122,NUP,NDOWN,Q,C1,C2)
      W(I)=C1
      WRITE(6,3002) I,W(I)
 3002 FORMAT(1H0,' I = ',I3,' CI = ',F16.7)
      RETURN
      END
      SUBROUTINE SUBCL2(II,N,U,R,R2,R3,G133,G122,N1,N2,A,B,C)
      IMPLICIT REAL*8(A-H,O-Z)
C   INPUT: U=U : R=0.5*SQRT(U/X): N=NO. OF SUBRANGES
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C   IN EACH OF WHICH THE RANGE IS EQUALLY DIVIDED: N1(I)=NO.OF
C   EQUAL INTERVALS IN I-TH RANGE:N2(I)=NO. INTO WHICH R*LN2
C   IS DIVIDED TO OBTAIN EQUAL INTERVALS IN I-TH SUBRANGE
C   SUBCLS WILL BE CALLED TO EVALUATE THE INNER INTEGRALS .
      DIMENSION G122(20),N1(12),N2(12)
      STOP=1.0D-7
      N=4
      PI=1.772453851
      CALL ERFN(R,YYMAX)
      YYSTOP =YYMAX*STOP
      S=0.0D0
      RR=R*DLOG(2.0D0)
      X=-RR
C        FOR EVERY SUBRANGE:
      DO 100 I=1,N
      DX=RR/N2(I)
      X=X+DX/2.0D0
      NM=N1(I)
C        FOR EVERY SUBDIVISION:
      DO 50  J=1,NM
      IF(X/R-100)2,1,1
    1 V=1.0D0
      Y=0.0D0
      GO TO 7
    2 V=(1.0D0-DEXP(-X/R))**2
      Y=R*DSQRT(1.0D0-V)
      VRP=V*R*R
      IF(VRR-100) 3,3,7
    3 EX=DEXP(-VPR)
      IF(Y-1.0D-30/EX) 7,4,4
   4  CALL ERFN(Y,E)
      CALL SUBCLS(II,N,R,R2,R3,X,G133,G122,VRR,A1,B1)
      YY=E*B1*DEXP(-VRR)
      GO TO 10
    7 YY=0.0D0
   10 CONTINUE
      S=S+YY*DX
      X=X+DX
      IF(I-N) 50,20,200
  200 CALL EXIT
   20 IF(YY-YYSTOP) 150,150,50
   50 CONTINUE
      X=X-DX/2.0D0
  100 CONTINUE
      S=S*1.0D10
  150 B=S/PI
      WRITE(6,205) B,S
  205 FORMAT(/,' B AND S =' ,2E14.4)
      A=1.0D0/U
      C=1.0D0+0.5D0/(R*R)
      RETURN
      END
      SUBROUTINE SUBCLS(II,N,R,R2,R3,X1,G133,G122,VRR,A1,B1)
C  SUBCLS TAKES CARE OF THE INNER INTEGRAL
      IMPLICIT REAL*8(A-H,O-Z)
C   INPUT: U=U ; R=0.5*SQRT(U/X): N=NO. OF SUBRANGES
C   IN EACH OF WHICH THE RANGE IS EQUALLY DIVIDED: N1(I)=NO.OF
C   EQUAL INTERVALS IN I-TH RANGE;N2(I)=NO. INTO WHICH R*LN2
C   IS DIVIDED TO OBTAIN EQUAL INTERVALS IN I-TH SUBRANGE
C   SUBCLS WILL BE CALLED TO EVALUATE THE INNER INTEGRALS .
      DIMENSION G122(20),N1(12),N2(12)
      STOP=1.0D-7
      N=4
      PI=1.772453851
      N2(1)=400
      N2(2)=100
```

```
      N2(3)=80
      N1(1)=40
      N1(2)=40
      N1(3)=40
      N1(4)=800
      IF(R.EQ.R2) GO TO 110
      IF(R2-2.3) 21,21,25
   21 N2(4)=500/(48.0-3.0*R2*R2)
      GO TO 110
   25 N2(4)=7.0*R2
  110 CALL ERFN(R2,YYMAX)
      CALL NEWTON(II,R,X1,G122,R2,RMAX)
      YYSTOP =YYMAX*STOP
      S=0.0D0
      RR=R2*DLOG(2.0D0)
      X=-RR
C        FOR EVERY SUBRANGE:
      DO 100 I=1,N
      IF(I-4) 30,35,35
   35 TES=G122(II)*X1
      IF(TES-0.0D0) 37,30,30
   37 CONTINUE
      IF(RMAX.GE.200) GO TO 30
      DX=RMAX/N1(I)
      GO TO 32
   30 DX=RR/N2(I)
   32 X=X+DX/2.0D0
      NM=N1(I)
C        FOR EVERY SUBDIVISION:
      DO 50  J=1,NM
      IF(X/R2-100)2,1,1
    1 V=1.0D0
      Y=0.0D0
      GO TO 7
    2 V=(1.0D0-DEXP(-X/R2))**2
      V1=(1.0D0-DEXP(-X1/R))**2
      Y=DSQRT(R2*R2*(1.0D0-V))
      YH=R2*R2*(1.0D0-V)-G122(II)*X*X1*X
      YR=R2*R2*(1.0D0-V)
      IF(YH.GE.YR) GO TO 300
      IF(YH.LE.1.0D-30) GO TO 300
      YL=R2*R2*(1.0D0-(1.0D0-DEXP(-RMAX/R2))**2)-0.00*X1*X1*RMAX-G122(II
     2)*RMAX*RMAX*X1
      IF(YL.LE.0.0) GO TO 300
      Y=DSQRT(YL)
  300 CONTINUE
      VRR2=V*R2*R2
      IF(VRR2-100) 3,3,7
    3 EX=DEXP(-VRR2)
      IF(Y-1.0D-30/EX) 7,4,4
    4 CALL ERFN(Y,E)
      CALL SUBCLI(II,N,R,R2,R3,X1,X,G133,G122,VRR,VRR2,A2,R2)
      GO TO 45
   44 E=0.5*PI
   45 CHEK=VRR2+G122(II)*X1*X*X
      IF(CHEK-100) 9,9,7
    9 YY=E*(R2**2)*DEXP(-CHEK)
      GO TO 10
    7 YY=0.0D0
   10 CONTINUE
      S=S+YY*DX
      X=X+DX
      IF(I-N) 50,20,200
  200 CALL EXIT
   20 IF(YY-YYSTOP) 150,150,50
   50 CONTINUE
```

```
          X=X-DX/2.0D0
      100 CONTINUE
          WRITE(6,350) YY,YYSTOP
      350 FORMAT(/,' YY AND YYSTOP ARE ',2E16.7)
          S=S*1.0D10
      150 B1=S/PI
          A1=1.0D0
          C1=1.0D0+0.5D0/(R2*R2)
          RETURN
          END
          SUBROUTINE SUBCLL(II,N,R,R2,R3,X1,X2,G133,G122,VRR,VRR2,A2,B2)
C  SUBCLL TAKES CARE OF THE INNERMOST INTEGRAL
          IMPLICIT REAL*8(A-H,O-Z)
C   INPUT: U=U ; R=0.5*SQRT(U/X); N=NO. OF SUBRANGES
C   IN EACH OF WHICH THE RANGE IS EQUALLY DIVIDED: N1(I)=NO.OF
C   EQUAL INTERVALS IN I-TH RANGE:N2(I)=NO. INTO WHICH R*LN2
C   IS DIVIDED TO OBTAIN EQUAL INTERVALS IN I-TH SUBRANGE
C   SUBCLS WILL BE CALLED TO EVALUATE THE INNER INTEGRALS .
          DIMENSION G122(20),N1(12),N2(12)
          STOP=1.0D-7
          N=4
          PI=1.772453851
          N2(1)=800
          N2(2)=200
          N2(3)=160
          N1(1)=60
          N1(2)=60
          N1(3)=80
          N1(4)=1600
          IF(R.EQ.R3) GO TO 110
          IF(R3-2.3) 21,21,25
       21 N2(4)=500/(48.0-3.0*R3*R3)
          GO TO 110
       25 N2(4)=7.0*R3
      110 CALL FREN(R3,YYMAX)
          CALL NEWTN2(II,R,X1,G133,R3,RMAX)
          YYSTOP =YYMAX*STOP
          S=0.0D0
          RR=R3*DLOG(2.0D0)
          X=-RR
C            FOR EVERY SUBRANGE:
          DO 100 I=1,N
          IF(I-4) 30,35,35
       35 TES=G133*X1
          IF(TES-0.0D0) 37,30,30
       37 CONTINUE
          IF(RMAX.GE.200) GO TO 30
          DX=RMAX/N1(I)
          GO TO 32
      30  DX=RR/N2(I)
      32  X=X+DX/2.0D0
          NM=N1(I)
C            FOR EVERY SUBDIVISION:
          DO 50  J=1,NM
          IF(X/R3-100)2,1,1
        1 V=1.0D0
          Y=0.0D0
          GO TO 7
        2 V=(1.0D0-DEXP(-X/R3))**2
          V1=(1.0D0-DEXP(-X1/R))**2
          Y=DSQRT(R3*R3*(1.0D0-V))
          YH=R3*R3*(1.0D0-V)-G133*X*X1*X
          YR=R3*R3*(1.0D0-V)
          IF(YH.GE.YR) GO TO 300
          IF(YH.LE.1.0D-30) GO TO 300
          YL=R3*R3*(1.0D0-(1.0D0-DEXP(-RMAX/R3))**2)-G133*X1*RMAX*RMAX
```

```
      IF(YL.LE.0.0) GO TO 300
      Y=DSQRT(YL)
  300 CONTINUE
      VRR3=V*R3*R3
      CHEK=VRR3+G133*X*X*X1
      IF(CHEK-100) 3,3,7
    3 YJ=-CHEK
      IF(YJ.GT.0.0) GO TO 301
      EX=DEXP(YJ)
      IF(Y-1.0D-30/EX) 7,14,14
 14   TEST=G133*X1
      IF(TEST-0.0D0) 4,4,4
    4 CALL ERFN(Y,E)
      GO TO 45
   44 E=0.5*PI
   45 YY=E*EX
      GO TO 10
    7 YY=0.0D0
   10 CONTINUE
      S=S+YY*DX
      X=X+DX
      IF(I-N) 50,20,200
  301 WRITE(6,310) YJ
  310 FORMAT(/,' OFF-DIAG TERMS TOO LARGE ',E14.4)
  200 CALL EXIT
   20 IF(YY-YYSTOP) 150,150,50
   50 CONTINUE
      X=X-DX/2.0D0
  100 CONTINUE
      WRITE(6,350) YY,YYSTOP
  350 FORMAT(/,' YY AND YYSTOP ARE ',2E16.7)
      S=S*1.0D10
  150 B2=S/PI
      A2=1.0D0
      C2=1.0D0+0.5D0/(R3*R3)
      RETURN
      END
      SUBROUTINE ERFN(Y,E)
      IMPLICIT REAL*8(A-H,O-Z)
C       FOR EVALUATING THE ERROR FUNCTION E=ERFN(X) AS
C       ERFN(X)=2*P(1.4141...*X) - 1   . SEE ABRAMOWITZ .
       X=1.41421356*Y
       AX=DABS(X)
       T=1.0D0/(1.0D0+0.2316419D0*AX)
       IF(X*X-100)12,11,11
   11 D=0.0D0
       P=1.0D0
       GO TO 13
   12 CONTINUE
       D=0.3989422804*DEXP(-X*X/2.0D0)
       P=1.0D0-D*T*((((1.330274429*T-1.821255978)*T+1.781477939)*T-
     10.356563782)*T+0.31938153)
   13 CONTINUE
       IF(X) 1,2,2
    1 P=1.0D0-P
    2 IF(P) 3,5,5
    3 WRITE(6,3001)
 3001 FORMAT(35H0 TROUBLE IN DISTRIBUTION FUNCTION.)
    4 WRITE(6,3002) X,P
 3002 FORMAT(3H X= E14.7,4H P= E14.7)
       CALL EXIT
    5 E=2.0D0*P-1.0D0
       IF(E) 6,7,7
    6 WRITE(6,3003)
 3003 FORMAT(28H0 TROUBLE IN ERROR FUNCTION.)
       GO TO 4
```

```
    7 RETURN
       END
      SUBROUTINE NEWTON(I,R,X1,G122,R2,RMAX)
      IMPLICIT REAL*8(A-H,O-Z)
C     THIS SUBROUTINE SERVES TO FIND THE UPPER LIMIT OF Q2 FOR CASE 1
C     WHEN G112*X IS LESS THAN 0 USING NEWTON'S METHOD
C     NEWTON IS NOW CALCULATED POINT BY POINT
      DIMENSION G122(20),Z(500),UMAX(500)
      USTAN=R2*R2-1.0D-4
      M=1
      Z(1)=1.0
      UMAX(1)=R2*R2*(1.0D0-DEXP(-Z(1)/R2))**2-0.00*Z(1)*X1*X1-G122(I)*X1
     1*(Z(1)**2)
    1 IF(UMAX(M).GE.USTAN) GO TO 23
      M=M+1
      Z(M)=Z(M-1)+1.0
      UMAX(M)=R2*R2*(1.0D0-DEXP(-Z(M)/R2))**2-0.00*Z(M)*X1*X1-G122(I)*X1
     1*(Z(M)**2)
      IF(UMAX(M).LT.UMAX(M-1)) GO TO 23
      IF(M.EQ.500) GO TO 12
      GO TO 1
   23 RMAX=Z(M)
      IF(RMAX.LE.0.0) GO TO 12
      GO TO 43
   12 CONTINUE
C     WRITE(6,15) M,Z(M)
   15 FORMAT(/,' ERROR IN CONVERGENCE M ',I4,E14.4)
   43 RETURN
      END
      SUBROUTINE NEWTN2(I,R,X1,G133,R3,RMAX)
      IMPLICIT REAL*8(A-H,O-Z)
C     THIS SUBROUTINE SERVES TO FIND THE UPPER LIMIT OF Q2 FOR CASE 1
C     WHEN G112*X IS LESS THAN 0 USING NEWTON'S METHOD
C     NEWTON IS NOW CALCULATED POINT BY POINT
      DIMENSION Z(500),UMAX(500)
      USTAN=R3*R3-1.0D-4
      M=1
      Z(1)=1.0
      UMAX(1)=R3*R3*(1.0D0-DEXP(-Z(1)/R3))**2-G133*Z(1)**2*X1
    1 IF(UMAX(M).GE.USTAN) GO TO 23
      M=M+1
      Z(M)=Z(M-1)+1.0
      UMAX(M)=R3*R3*(1.0D0-DEXP(-Z(M)/R3))**2-G133*Z(M)**2*X1
     1*(Z(M)**2)
      IF(UMAX(M).LT.UMAX(M-1)) GO TO 23
      IF(M.EQ.500) GO TO 12
      GO TO 1
   23 RMAX=Z(M)
      IF(RMAX.LE.0.0) GO TO 12
      GO TO 43
   12 CONTINUE
C     WRITE(6,15) M,Z(M)
   15 FORMAT(/,' ERROR IN CONVERGENCE M ',I4,E14.4)
   43 RETURN
      END
//GO.SYSIN DD *
-01  1 0067.86 0069.84  300.0
-238.54     -245.53
 1349.97      -2.38      1349.97     -2.38
 2395.69     -12.40      2327.41    -11.64
  674.65      -2.30       655.65     -2.20
-18.05        0.9900     -11.82     -18.500       01.010       -12.61
 09
/*
//
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