On the Operator Formulation of the Polyatomic Molecule Partition Function

J. Bohmann and W. Witschel
Department of Chemistry, Universität Ulm

Z. Naturforsch. **38 a**, 167 – 183 (1983); received October 29, 1982

Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

The Nielsen Hamiltonian of the general polyatomic molecule including anharmonicity and its resonances, Coriolis-coupling and its resonances, and rotation-vibration interaction are treated by statistical perturbation theory in its operator form. By generating function methods and operator theorems, which are treated in an appendix, cumbersome calculations with non-commuting operators are avoided. The results for H_2O and SO_2 agree very well with accurate numerical calculations from the literature. Qualitative conclusions on the convergence of the perturbation series are drawn from the numerical calculations for model systems.

1. Introduction

The calculation of thermodynamic properties of ideal gases by statistical methods was reviewed some time ago by Frankiss and Green [1]. They concluded that the methods have been developed between 1935 and 1950. Unfortunately, they overlooked important theoretical work summarized by Godnev [2], Rowlinson [3] and Gurvich [4] and also extended numerical work. The article concentrated on the solution of the Schrödinger equation by perturbation methods, introduction of molecular constants from high resolution spectroscopy and numerical summation of the appropriate Boltzmann factors. An example for these types of calculations are the precise thermodynamic functions of NH_3, calculated by Haar [5]. Extended systematic work can be found in the JANAF-tables [6], together with a critical discussion of the methods used [7].

If one considers the polyatomic molecule in the Nielsen-Watson approximation as system of coupled anharmonic oscillators with polynomial or exponential interactions, the problem of eigenvalues and level densities is unsolved. This model system is investigated intensively in mathematical physics, as it is a prototype in quantum field and elementary particle theory, in statistical mechanics and ergodicity, in energy transfer, in phase transitions and laser isotope separation. A lot of different powerful techniques were developed in these fields, but unfortunately they are often unknown to workers in neighbouring areas. We shall take the opportunity to refer to some of these techniques.

Beginning in 1968 we investigated the possibilities of Schwinger-perturbation theory (SPT) for the calculation of thermodynamic data and level densities for molecules. As SPT deals with noncommuting operators, we tried to eliminate the difficulties and present the results in terms of ordinary *c*-number functions. Though we calculated the partition function (PF) a long time ago [9], [10] we did publish it only in part because of the difficulties of the calculus of noncommuting operators. Meanwhile, we were interested again because of simplifications, of the introduction of variation-perturbation theory, and because of the possibility to check our results against high quality calculations by Isaacson, Truhlar and Overend [11].

The aim of the present article is, therefore, twofold: First, we wish to show that SPT can be evaluated exactly to arbitrary order, including all resonances and couplings; second, by comparing our results to different techniques, we want to show that SPT and its improvements lead to compact, analytical expressions which, by simple differentiation, can be easily converted to the thermodynamic functions H, C_p, C_v, S and level densities.

The article is organized as follows: in Sect. 2 we discuss the Nielsen-Watson Hamiltonian and techniques for calculating eigenvalues of coupled anharmonic oscillators. Section 3 sketches various techniques for the calculation of the PF; SPT is applied to the vibrational part in Section 4 and to the

---

Reprint requests to Prof. Dr. W. Witschel, Department of Chemistry, Universität Ulm, Oberer Eselsberg, D-7900 Ulm.

0340-4811 / 83 / 0200-0167 $ 01.3 0/0. – Please order a reprint rather than making your own copy.

rotation-vibration part in Section 5. Numerical results are discussed in Section 6. In some appendices we try to discuss qualitatively the convergence of SPT for a perturbed harmonic oscillator and for diatomic molecules in fourth and third order SPT, respectively.

The article is long because of the complexity of the polyatomic molecular Hamiltonian, but we think it necessary to present the fairly long expressions for further applications.

2. The molecular Hamiltonian and its eigenvalues

2.1. The Darling-Dennison-Nielsen-Hamiltonian

In high resolution spectroscopy one uses a Hamiltonian worked out and used extensively by Nielsen [12]. The basic work is associated with Wilson and Howard, and with Darling and Dennison. We shall use a slightly truncated form of this "Nielsen-Hamiltonian" where too small effects are neglected. Our notation differs from Nielsen's insofar as we use the angular frequency ω (unit: $\sec^{-1}$) instead of the wavenumber $\tilde{\omega}$ (unit: cm^{-1}). Accordingly, the definition of the constants $a_i^{(gg')}$, $G_{ij}^{(gg')}$, $\zeta_{r,s}^{(\alpha)}$ etc. is altered [15].

$$\hat{H} = \hat{H}^{(0)} + \Lambda \hat{H}^{(1)} + \Lambda^2 \hat{H}^{(2)}\,, \tag{1}$$

$$\hat{H}^{(0)} = \sum_j \hat{\mathscr{H}}_0^{(j)} + \frac{1}{2} \sum_g \frac{\hat{P}_g^2}{I_{gg}^e}\,, \tag{2}$$

$$\begin{aligned} \hat{H}^{(1)} = {} & \sum_{ijk} k_{ijk}\, \hat{q}_i \hat{q}_j \hat{q}_k - \sum_g \left(\frac{\hat{P}_g \hat{p}_g}{I_{gg}^e} \right) \\ & - \sum_{gg'} \sum_i \frac{\hat{P}_g \hat{P}_{g'}}{I_{gg}^e I_{g'g'}^e} \frac{a_i^{(gg')}}{(\omega_i)^{1/2}} \hat{q}_i \\ & + \frac{1}{2} \sum_{gg'} \sum_i \frac{\hat{P}_g}{I_{gg}^e I_{g'g'}^e} \frac{a_i^{(gg')}}{(\omega_i)^{1/2}} (\hat{p}_{g'} \hat{q}_i + \hat{q}_i \hat{p}_{g'}) \end{aligned} \tag{3}$$

$$\begin{aligned} \hat{H}^{(2)} = {} & \sum_{ijkl} k_{ijkl}\, \hat{q}_i \hat{q}_j \hat{q}_k \hat{q}_l + \frac{1}{2} \sum_g \frac{\hat{p}_g^2}{I_{gg}^e} \\ & - \frac{1}{2} \sum_{gg'} \sum_{ij} \frac{\hat{p}_g \hat{p}_{g'}}{I_{gg}^e I_{g'g'}^e} \frac{G_{ij}^{(gg')}}{(\omega_i \omega_j)^{1/2}} \hat{q}_i \hat{q}_j\,, \end{aligned} \tag{4}$$

where $\hat{\mathscr{H}}_0^{(j)}$ denotes the harmonic oscillator Hamiltonian corresponding to the j-th normal coordinate:

$$\hat{\mathscr{H}}_0^{(j)} = \tfrac{1}{2}\hbar\, \omega_j (\hat{p}_j^2 + \hat{q}_j^2)\,. \tag{5}$$

This Hamiltonian contains anharmonicity, Coriolis-coupling and rotation-vibration-coupling. For details see the authoratative handbook article and the excellent reviews by Mills [13], [14]. Λ is an ordering parameter also indicating the order of magnitude of the effects.

A slightly different form was given by Watson (see Mills) [13] with a consistent order of magnitude classification and an additional mass-dependent term U, which is usually neglected both in spectroscopic and thermodynamic calculations. Using Mills' notation with a meaning of the several symbols different from the one used in this article it reads

$$\begin{aligned} \hat{H}/hc = {} & \tfrac{1}{2} \sum_r \tilde{\omega}_r (\hat{p}_r + \hat{q}_r^2) + V_{\mathrm{anh}}(\hat{q}_r)/hc \\ & + \sum_{\alpha,\beta} (\hbar^2/2hc)\, \hat{\mu}_{\alpha\beta} (\hat{J}_\alpha - \hat{j}_\alpha)(\hat{J}_\beta + \hat{j}_\beta) + U/hc\,; \end{aligned} \tag{6}$$

$$V_{\mathrm{anh}}/hc = (1/6)\, \varphi^{rst}\, \hat{q}_r \hat{q}_s \hat{q}_t + (1/24)\, \varphi^{rstu}\, \hat{q}_r \hat{q}_s \hat{q}_t \hat{q}_u$$

$\hat{J}_\alpha$ ≡ rotation angular momentum,

$\hat{j}_\alpha$ ≡ vibration angular momentum,

$$\hat{\mu}_{\alpha\beta} = \mu_{\alpha\beta}^{(e)} + \sum_r \mu_{\alpha\beta}^{(r)} \hat{q}_r + \cdots\,; \tag{7}$$

$$\mu_{\alpha\beta}^{(e)} = I_\alpha^{-1} \delta_{\alpha\beta}\,;\ \mu_{\alpha\beta}^{(r)} = -\,(a_r^{(\alpha\beta)}/\gamma_r^{1/2} I_\alpha I_\beta)\,;$$

$$\gamma_r = (2\pi c\, \omega_r/h)\,;\ \hat{j}_\alpha = \sum_{r,s} \zeta_{r,s}^{(\alpha)} \hat{q}_r \hat{p}_s (\omega_s/\omega_r)^{1/2}\,; \tag{7'}$$

$\zeta_{rs}^{(\alpha)}$ ≡ Coriolis-Coupling constant.

As the handbook article is easily available, we still prefer the Nielsen notation, slightly modified by using latin-type indices. For all details and the meaning of the constants see Nielsen [12].

2.2. The eigenvalue problem of the Nielsen-Hamiltonian

If the eigenvalues of the Nielsen-Hamiltonian would have been known, the summation of the appropriate Boltzmann factors would be a programming exercise. Unfortunately the polyatomic Schrödinger equation can only be solved approximately.

Recently Carney, Sprandel and Kern [15] published an extended review on the variational (and perturbational) approaches to vibration-rotation spectroscopy for polyatomic molecules where they critically summarized present techniques used in high resolution spectroscopy. The most comprehensive publication of conventional perturbation theory is by Amat, Nielsen and Tarrago [16], so that it is only necessary to discuss developments in different fields.

Only in few cases is it possible to prove convergence of perturbation series. For one-dimensional anharmonic oscillators of the types

$$\begin{aligned} \hat{H} &= \hat{\mathscr{H}}_0 + \lambda\, \hat{q}^{2k} \quad \text{and} \\ \hat{H} &= \hat{\mathscr{H}}_0 + \lambda\, \hat{q}^{2k+1} \end{aligned} \tag{8}$$

it was proved that the Rayleigh-Schrödinger perturbation theory is divergent for arbitrary small λ [17, 18]. It is possible, however, to sum the divergent series to infinite order by Padé-approximants, continued fraction and Stieltjes-summation [19]. For coupled anharmonic oscillators the calculations become even more complicated, but Banks, Bender and Wu [20] proved, that Rayleigh-Schrödinger-perturbation theory is divergent for coupled quartic anharmonic oscillators. Non-perturbational techniques are, therefore, investigated by Montroll [21] and co-workers who, by a combination of analytical and numerical techniques calculated eigenvalues for coupled and spherical anharmonic oscillators with quartic anharmonicity. Unfortunately, oscillators with mixed cubic and quartic anharmonicity are not treated. Even more interesting is their WKB-type technique for calculating level densities, so that one can compare high temperature PF with bounds from different techniques.

It should also be mentioned that direct variational techniques become more and more important. Marcus and Noid [22] calculated precise eigenvalues of the Henon-Heiles Hamiltonian, a standard model of celestial mechanics, ergodicity, and energy migration in molecules.

$$\hat{H} = \hat{\mathscr{H}}_0^{(1)} + \hat{\mathscr{H}}_0^{(2)} + \lambda\, (\hat{q}_1\, \hat{q}_2^2 - \tfrac{1}{2}\, \hat{q}_1^3)\,. \tag{9}$$

They diagonalized a 1200×1200 matrix. Another interesting approach was the application of the algebraic computer language MACSYMA to high order perturbation theory [23], which will facilitate cumbersome and error-proned analytical calculations by hand. Another interesting approach is by Bowman [24] who calculated energy levels by SCF-techniques. All these techniques may also lead to precise eigenvalues of the Nielsen-Hamiltonian, especially at higher excitation energies.

3. Methods for calculating partition functions

As the article mentioned in the introduction does not present modern techniques for calculating partition functions, we take the opportunity to sketch various methods and refer to scattered results. We assume that in general the vibration rotation Hamiltonian $\hat{H}$ can be split up in some way into two parts

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \tag{10}$$

where $\hat{H}_0$ corresponds to an exactly solvable problem.

3.1. Customary techniques for the PF of polyatomic molecules

Customarily the partition function Z is defined as a sum over the Boltzmann factors formed with the eigenvalues E_m of the discrete spectrum of $\hat{H}$.

$$Z = \sum_m g_m \exp(-\beta E_m)\,; \tag{11}$$

where g_m is the degeneracy.

Besides the difficulties with the eigenvalue problem mentioned above, this summation requires approximations. Pennington and Kobe, and Wooley developed expansion techniques for the various sums over rotation and vibration quantum numbers [25]. Durand and Brandmaier [25] evaluated the various higher order corrections to the PF numerically. It was pointed out by Evans [26] that these unrestricted summations of questionable energy levels at higher energies will lead to wrong results. For diatomic molecules one introduces cutoffs for both rotational and vibrational quantum numbers, which was not done as yet for polyatomic molecules.

3.2. Variational techniques

Non-perturbative treatments based on the trace formulation of the PF are exact upper and lower bounds given by the Gibbs-Bogoliubov and the Golden-Thompson inequalities. As there exist excellent reviews by Girardeau and Mazo [27], Huber [28], and Falk [29] for the lower bound, we only give the essential formulas:

$$Z \;= \mathrm{Tr}\{\exp(-\beta \hat{H})\} = \mathrm{Tr}\{\exp[-\beta(\hat{H}_0 + \hat{H}_1)]\}\,, \tag{12}$$

$$\begin{aligned} Z_{\mathrm{LB}} &= \mathrm{Tr}\{\exp(-\beta \hat{H}_0)\exp(-\beta\langle \hat{H}_1\rangle_0)\}\,, \\ \langle \hat{H}_1\rangle_0 &= \mathrm{Tr}\{\exp(-\beta \hat{H}_0)\,\hat{H}_1\}/\mathrm{Tr}\{\exp(-\beta \hat{H}_0)\}\,, \end{aligned} \tag{13}$$

$$Z_{\mathrm{UB}} = \mathrm{Tr}\{\exp(-\beta \hat{H}_0)\exp(-\beta \hat{H}_1)\}\,, \tag{14}$$

Z_{LB} (Gibbs-Bogoliubov) $\leqq Z \leqq Z_{\mathrm{UB}}$ (Golden-Thompson).

They are valid under fairly general conditions for $\hat{H}_0$ and $\hat{H}_1$, especially $\hat{H}_1$ needs not to be small in the sense of perturbation theory. The lower bound with and without variational parameters can be evaluated easily for the linear harmonic oscillator with exponential, Gauß-type or arbitrary polynomial interactions, and for the polyatomic molecule with arbitrary polynomial interactions. The upper bound, as yet, is only solved for special cases of anharmonic oscillator systems.

3.3. *Semiclassical techniques*

Semiclassical techniques are well known since the classical work by Kirkwood and Wigner and its improvements [30]. They can be applied easily to linear anharmonic systems, but lead for coupled systems to difficulties. Only for the spherical Einstein model closed analytical results could be given [31]. Recent advances by modified Feynman path integrals have been achieved by W. Miller [32] and co-workers, and by Jorish and Zitserman [33] for linear anharmonic oscillators, corresponding to diatomic molecules. The latter authors applied the local approximation to two-dimensional systems and calculated the PF of the planar quartic oscillator. A somewhat related path integral technique was suggested by Papadopoulos [34] for the polyatomic molecule, but the path integrals have to be performed numerically. A Monte-Carlo-type semiclassical calculation was performed recently [35] to show the validity of an old approximation by Pitzer and Gwinn [36]. They suggested

$$Z(T) \simeq Z_c(T)\,[Z^R(T)/Z_c^R(T)]\,, \qquad (15)$$

where the exact quantum statistical PF of an anharmonic oscillator $Z(T)$ was assumed to be proportional to the corresponding classical PF $Z_c(T)$ multiplied with the quotient of the quantum ($Z^R(T)$) and the classical ($Z_c^R(T)$) PF of a reference oscillator. Isaacson and Truhlar [37] investigated this approximation systematically for some one-dimensional model potentials, and Isaacson, Truhlar, Scanlon and Overend [11] calculated the PF of triatomics in various force field approximations in the Pitzer-Gwinn technique. Comparison with their results will be given below.

3.4. *Thermodynamic perturbation theory*

Thermodynamic perturbation theory in connection with molecular problems is not new. Already in 1933 Serber [38] introduced a perturbation treatment of the canonical density matrix for the Kerr-effect. His technique is similar to the perturbation method of Peierls [39] developed in connection with the diamagnetism of conduction electrons. Nakajima [40] reviewed perturbation theory in statistical mechanics in 1955. In the same year Saenz and O'Rourke [41] gave an application of Schwinger-operator perturbation theory, and also a WKB-type perturbation expansion, which contains SPT. Further applications to solid state physics can be found in Choquard's [42] book on phonon anharmonicity. Resonances in polyatomic molecules have been treated by SPT [43], as well as the diatomic and the polyatomic molecule. Because of the calculus of noncommuting operators, the results are fairly complicated. Independently Naya [44], and Naya and Siegel [45] treated the linear anharmonic oscillator PF. Calculation of operator traces in the perturbation series were greatly simplified by a generating function method which was used for level densities of polyatomics [45a] and for the isotopic dependence of the diatomic dissociation equilibrium [46].

Wolfsberg and co-workers [47] applied SPT successfully to the isotopic equilibria of polyatomic molecules, and Lew and Ishida [48] also investigated isotope effects by SPT. The well-known SPT is to second order

$$\begin{aligned}\mathrm{Tr}\{\exp[-\beta(\hat{H}_0+\hat{H}_1)]\} &= \mathrm{Tr}\{\exp(-\beta\hat{H}_0)\}\\ &\quad-\beta\,\mathrm{Tr}\{\hat{H}_1\exp(-\beta\hat{H}_0)\}\\ &\quad+(\beta^2/2)\int_0^1 \mathrm{d}s_1\,\mathrm{Tr}\{\hat{H}_1\exp[-\beta\hat{H}_0(1-s_1)]\\ &\quad\cdot\hat{H}_1\exp[-\beta\hat{H}_0 s_1]\}\mp\cdots\,. \qquad (16)\end{aligned}$$

$\hat{H}_1$ must be small in the sense of perturbation theory. It will be shown in the appendices, that this condition is not sufficient. We, therefore, tried to improve the range of validity by considering a combination of variational techniques with SPT.

3.5. *Variation-perturbation theory*

It was mentioned in 3.2 that the Gibbs-Bogoliubov inequality can be evaluated including variational parameters. A variation of the equilibrium positions and the frequencies of the harmonic reference oscillators is appropriate in the case of polyatomic molecules with polynomial interaction. Calculations for one-dimensional oscillators show a strong improvement of the lower bound. As the choice of $\hat{H}_0$ in SPT is fairly arbitrary, we calculated an optimized $\hat{H}_0$ from the variational lower bound and took it as zero order Hamiltonian in the subsequent SPT. As an example, where precise eigenvalues were known, we took the quartic anharmonic oscillator

$$\hat{H}^{\mathrm{q}} = \frac{\hbar\,\omega}{2}(\hat{p}^2 + \hat{q}^2) + \lambda\,\hbar\,\omega\,\hat{q}^4 \tag{17}$$

and introduced

$$\mathscr{H}_0(\Omega) = \frac{\hbar\,\Omega}{2}(\hat{p}^{*2} + \hat{q}^{*2}) , \tag{18}$$

$$\hat{H}^{\mathrm{q}}_1(\Omega) = \frac{\hbar\,\omega}{2}\left(\frac{\omega^2 - \Omega^2}{\omega\,\Omega}\right)\hat{q}^{*2} + \hbar\,\omega\,\lambda\left(\frac{\omega}{\Omega}\right)^2 \hat{q}^{*4} , \tag{19}$$

where Ω (or $k = \omega/\Omega$) is the variation parameter. For details and the fairly long formulas we refer to [49], but we wish to show the improvement of the results in Table 1.

For the constants chosen in this example the numerical PF from the Hioe-Montroll eigenvalues is $Z^{\mathrm{q}}_{\mathrm{HM}} = 2.2153$. For completeness we also give the exact Golden-Thompson bound including the variation of Ω: $Z^{\mathrm{V}}_{\mathrm{UB}} = 2.2225$. One sees that SPT ($k = 1$) is wrong to the extent of several orders of magnitude. With decreasing values of k, the result is improved till very good agreement with $Z^{\mathrm{q}}_{\mathrm{HM}}$ is reached. The case corresponding to the optimal value of the lower bound is in bold type.

It will be interesting to see whether variation-perturbation techniques work as well for coupled oscillator systems. Unfortunately, only few exact or high precision numerical results are known for these systems.

Table 1. Variation-perturbation theory for the quartic anharmonic oscillator. Improvement of SPT with variation of $k = (\omega/\Omega)$. $Z^{\mathrm{V}}_{\mathrm{SPT}} \equiv$ Variation perturbation theory based on second order SPT, $Z^{\mathrm{V}}_{\mathrm{LB}}(\Omega) \equiv$ Lower bound including the variational parameter Ω. $\beta\,\hbar\,\omega = 0.2$, $\lambda = 1$.

k	$Z^{\mathrm{V}}_{\mathrm{SPT}}$	$Z^{\mathrm{V}}_{\mathrm{LB}}(\Omega)$
1	6518.72	1.3815 (−6)
0.9	2494.48	2.4234 (−4)
0.8	844.30	9.6242 (−3)
0.7	242.83	0.1171
0.6	55.97	0.5694
0.5	10.14	1.3868
0.4	2.688	2.0368
0.3456	**2.2381**	**2.1373**
0.3	2.1640	2.0712
0.2	1.7234	1.5682
0.1	0.8945	0.8128

4. Vibrational PF of anharmonic oscillators, application of second quantization and operator techniques

We shall evaluate the PF in the trace formulation. As the potential energy ends with an even power, the harmonic oscillator basis can be extended to infinity and no cutoff-problems because of dissociation arise. Evidently, this is an unphysical approximation. For linear anharmonic systems of the $r^{-(2m+2)} - r^{-2m}$-type theorems exist giving the exact number of bound states, a given potential can support [50]. For polyatomic systems such theorems seem not to exist. The problem of cutoff, treated extensively for atoms [51] and diatomics [52], was solved recently by inclusion of the continuum. Whereas the results for atoms seem to be satisfying, the treatment of the Morse-oscillator merits further consideration. For intermediate temperatures, considered here for polyatomic molecules, we tried to control the influence of limited numbers of quanta in the trace calculations. The results are fairly insensible for both rotational and vibrational cutoffs.

4.1. Direct evaluation

Following the technique given by Messiah [53], one sees that

$$\hat{q}_j = (\hat{a}^+_j + \hat{a}_j)/\sqrt{2} , \tag{20}$$

$$\hat{p}_j = i\,(\hat{a}^+_j - \hat{a}_j)/\sqrt{2} \tag{21}$$

with $[\hat{a}_j, \hat{a}^+_k]_- = \delta_{jk}$. For simplicity, we count degeneracy separately to avoid the double index.

The technique, following [9, 10], will be explained for the term proportional to k^2_{jkk} appearing in second order SPT where also the effect of Fermi-resonance can be seen. The notation $Z^{[lm]}_2$ which is used subsequently indicates an arbitrary numeration m of l-th order potential terms contributing to second order SPT.

$$\begin{aligned} Z^{[35]}_2 = \tfrac{1}{16}\,\beta^2 k^2_{jkk} \int_0^1 \mathrm{Tr}\,\{&\exp[-\beta(\hat{\mathscr{H}}^{(j)}_0 + \hat{\mathscr{H}}^{(k)}_0)] \\ &\cdot [\hat{a}^+_k \exp(\beta\,\hbar\,\omega_k s_1) + \hat{a}_k \exp(-\beta\,\hbar\,\omega_k s_1)]^2 \\ &\cdot [\hat{a}^+_j \exp(\beta\,\hbar\,\omega_j s_1) + \hat{a}_j \exp(-\beta\,\hbar\,\omega_j s_1)] \\ &\cdot (\hat{a}^+_k + \hat{a}_k)^2 (\hat{a}^+_j + \hat{a}_j)\}\,\mathrm{d}s_1 . \end{aligned} \tag{22}$$

Using the formulas of Appendix C and the commutation properties of the trace, we get in terms of the diagonal number operators $\hat{n}_i$

$$
\begin{aligned}
Z_2^{[35]} = \tfrac{1}{16}\,\beta^2 k_{jkk}^2 \int_0^1 \mathrm{Tr}\{&\exp[-\beta(\hat{\mathscr{H}}_0^{(j)} + \hat{\mathscr{H}}_0^{(k)})] \\
&\cdot [(\hat{n}_k^2 - \hat{n}_k)(\hat{n}_j \exp\{(2\varepsilon_k + \varepsilon_j)s_1\} \\
&+ (\hat{n}_j + 1)\exp\{(2\varepsilon_k - \varepsilon_j)s_1\}) \\
&+ (2\hat{n}_k + 1)^2(\hat{n}_j \exp\{\varepsilon_j s_1\} + (\hat{n}_j + 1)\exp\{-\varepsilon_j s_1\}) \\
&+ (\hat{n}_k^2 + 3\hat{n}_k + 2)(\hat{n}_j \exp\{-(2\varepsilon_k - \varepsilon_j)s_1\} \\
&+ (\hat{n}_j + 1)\exp\{-(2\varepsilon_k + \varepsilon_j)s_1\})]\}\,\mathrm{d}s_1\,, \qquad (23)
\end{aligned}
$$

where the abbreviation $\varepsilon_i = \beta\hbar\omega_i$ was introduced.

The traces are known to be of the geometric series form $\sum_n n^k \exp(-\varepsilon_i n)$, which can be written down after differentiation of the ordinary geometric series:

$$\sum_n \exp(-\varepsilon_i n) = \exp(\varepsilon_i)/(\exp(\varepsilon_i) - 1)\,. \qquad (24)$$

The ordering integrals are

$$Y(z) = \int_0^1 \exp(z s_1)\,\mathrm{d}s_1 = [\exp(z) - 1]/z\,, \qquad (25)$$

so that the final result reads with the abbreviation

$$Z_{kj} = \exp(-\varepsilon_j/2) \sum_{n_j=0}^{\infty} n_j^k \exp(-\varepsilon_j n_j) \qquad (26)$$

$$
\begin{aligned}
Z_2^{[35]} = \tfrac{1}{16}\,\beta^2 k_{jkk}^2 \{&(Z_{2k} - Z_{1k})[Z_{1j}\,Y(2\varepsilon_k + \varepsilon_j) \\
&+ (Z_{1j} + Z_{0j})\,Y(2\varepsilon_k - \varepsilon_j)] \\
&+ (4Z_{2k} + 4Z_{1k} + Z_{0k}) \\
&\cdot [Z_{1j}\,Y(\varepsilon_j) + (Z_{1j} + Z_{0j})\,Y(-\varepsilon_j)] \\
&+ (Z_{2k} + 3Z_{1k} + 2Z_{0k})[Z_{1j}\,Y(\varepsilon_j - 2\varepsilon_k) \\
&+ (Z_{1j} + Z_{0j})\,Y(-2\varepsilon_k - \varepsilon_j)]\}\,. \qquad (27)
\end{aligned}
$$

It was already shown [43] that in contrast to ordinary perturbation theory, resonances of all types are included consistently. For $2\omega_k \approx \omega_j$ we get Fermi-resonance which is solved by L'Hospital's rule. Anharmonic resonances change the simple molecular level pattern and lead to irregularities which are closely related to the irregular trajectories found in numerical investigations of the classical and quantum dynamics of anharmonic oscillator systems. With increasing number of vibrational modes, the possibility of accidental resonances increases, so that SPT is a valuable means to incorporate these irregularities. With increasing powers in the potential and in higher orders, the direct methods become very complicated. We, therefore, tried to avoid the difficulties of the operator calculus by a generating function method.

4.2. Generating function method

For simplicity we explain the method for the one-dimensional case, details will be found elsewhere [10].

In SPT of arbitrary order expressions of the form

$$
\begin{aligned}
\mathrm{Tr}\{&\exp(-\beta\hat{\mathscr{H}}_0)(\hat{a}^+\alpha_1^* + \hat{a}\,\alpha_1)^k(\hat{a}^+\alpha_{12}^* + \hat{a}\,\alpha_{12})^j \\
&\cdot (\hat{a}^+\alpha_{123}^* + \hat{a}\,\alpha_{123})^m \cdots\} \qquad (28)
\end{aligned}
$$

arise, where $\alpha_1^* = \exp(\beta\hbar\omega s_1)$, $\alpha_1 = \exp(-\beta\hbar\omega s_1)$ etc. Repeated normal-ordering according to Appendix C will be very cumbersome. On the other hand, it is easy to define a generating function GF

$$
\begin{aligned}
\mathrm{GF} = \mathrm{Tr}\{&\exp(-\beta\hat{\mathscr{H}}_0)\exp[k_1(\hat{a}^+\alpha_1^* + \hat{a}\,\alpha_1)] \\
&\cdot \exp[k_2(\hat{a}^+\alpha_{12}^* + \hat{a}\,\alpha_{12})]\cdots\}\,. \qquad (29)
\end{aligned}
$$

The exponentials are united by repeated application of the BCH-formula leading, to second order, to

$$
\begin{aligned}
\mathrm{GF} = \mathrm{Tr}\{&\exp(-\beta\hat{\mathscr{H}}_0)\exp[(k_1\alpha_1^* + k_2\alpha_{12}^* + \cdots)\hat{a}^+ \\
&+ (k_1\alpha_1 + k_2\alpha_{12} + \cdots)\hat{a}]\} \\
&\cdot \exp\{k_1 k_2(\alpha_1\alpha_{12}^* - \alpha_1\alpha_{12}^*)/2 + \cdots\}\,. \qquad (30)
\end{aligned}
$$

This is exactly the form of the characteristic function of the harmonic oscillator probability distribution, which is

$$
\begin{aligned}
\mathrm{GF} = Z_0 \exp\Big\{&\left(\frac{R}{2}\right)(k_1 a_1^* + k_2\alpha_{12}^* + \cdots) \\
&\cdot (k_1\alpha_1 + k_2\alpha_{12} + \cdots)\Big\} \\
&\cdot \exp\{k_1 k_2(\alpha_1\alpha_{12}^* - \alpha_1^*\alpha_{12})/2 + \cdots\}, \qquad (31)
\end{aligned}
$$

where Z_0 denotes the harmonic oscillator PF

$$Z_0 = [2\sinh(\varepsilon/2)]^{-1}, \qquad \varepsilon = \beta\hbar\omega$$

and

$$R = \coth(\varepsilon/2)\,. \qquad (32)$$

One sees that the non-commuting operators disappear. It remains to find the various traces either by series expansion and comparison, or by differentiation according to the order parameters k_i. The latter technique was used in an application of the algebraic programming language REDUCE II to higher order perturbation theory, but because of computer difficulties we did not succeed. An application of MACSYMA which also can integrate the ordering integrals would, hopefully, be more successful. As detailed formulas for the various anharmonic terms are not published as yet, we give the fairly lengthy formulas for fourth order potential and second order SPT. Higher order corrections are treated by Bohmann (a limited number of this thesis can be requested).

4.3. Formulas for anharmonic oscillators

In the present section we give several terms contributing to the vibrational PF of polyatomic molecules in first and second order SPT. Third and fourth order potential terms are considered. The vibrational sum which can thus be calculated must be multiplied by the appropriate rotational sum, a discussion of which is given in Chapter 5. We use the notation

$$\begin{aligned} \omega_j &= \text{angular frequency of the normal mode } j, \\ \varepsilon_j &= \beta \hbar \omega_j, \\ R_j &= \coth(\varepsilon_j/2), \\ Z_0^{(j)} &= [2\sinh(\varepsilon_j/2)]^{-1}. \end{aligned} \tag{33}$$

4.3.1. First order SPT

Generally, terms of the form

$$Z_1^{(n)} = -\beta \operatorname{Tr}\{k_{ijkm} \hat{q}_i \hat{q}_j \hat{q}_k \hat{q}_m \exp(-\beta \hat{H}_0')\} \tag{34}$$

arise, where the superscript n in brackets indicates an arbitrary numeration. Subsequently we assume that H_0' consists only of the harmonic oscillator Hamiltonians which correspond to the indices of the anharmonicity constant k_{jklm}; Z_0' is the PF corresponding to $\hat{H}_0'$, for example $Z_0' = Z_0^{(j)} \cdot Z_0^{(k)}$ for a term proportional to k_{jjkk}.

From the structure of the GF (Eq. (31)) it is clear that terms containing odd powers of the normal coordinates do not contribute to the PF. Additionally, it should be mentioned at this point that the Gibbs-Bogoliubov lower bound is closely related to first order SPT, as can be seen by comparison of Eqs. (16) and (13). Therefore, the following equations can also be used for the calculation of Z_{LB}:

$$Z_1^{(1)} = -\beta Z_0' (3/4)\, k_{jjjj} R_j^2, \tag{35}$$

$$Z_1^{(2)} = -\beta Z_0' (1/4)\, k_{jjkk} R_j R_k. \tag{36}$$

4.3.2. Second order SPT

In second order we get expressions of the forms

$$\begin{aligned} Z_2^{[3n]} = (\beta^2/2) \Big\{ k_{ijk} k_{rst} \operatorname{Tr} \Big\{ \int_0^1 \mathrm{d}s_1 \\ \cdot \exp(-\beta \hat{H}_0'(1-s_1))\, \hat{q}_i \hat{q}_j \hat{q}_k \\ \cdot \exp(-\beta \hat{H}_0' s_1)\, \hat{q}_r \hat{q}_s \hat{q}_t \Big\} \Big\}, \end{aligned} \tag{37}$$

$$\begin{aligned} Z_2^{[4n]} = (\beta^2/2) \Big\{ k_{ijkm} k_{rstw} \operatorname{Tr} \Big\{ \int_0^1 \mathrm{d}s_1 \\ \cdot \exp(-\beta \hat{H}_0'(1-s_1)\, \hat{q}_i \hat{q}_j \hat{q}_k \hat{q}_m \\ \cdot \exp(-\beta \hat{H}_0' s_1)\, \hat{q}_r \hat{q}_s \hat{q}_t \hat{q}_w \Big\} \Big\}, \end{aligned} \tag{38}$$

where the superscripts $[3n]$ and $[4n]$ correspond to the arbitrary numbering of third and fourth order terms.

Low order indices contributions are easily calculated by the direct method, whereas higher powers are calculated more economically by the GF-method. As the results are very long, we only give the third order terms completely and the fourth order terms which are necessary for bent triatomic molecules of the type XYX. The complete list can be requested or easily calculated.

$$\begin{aligned} Z_2^{[31]} = \frac{1}{16} \beta^2 k_{jkm}^2 \{ & Z_{1j} Z_{1k} Z_{1m} Y(\varepsilon_j + \varepsilon_k + \varepsilon_m) \\ & + Z_{1j} Z_{1k} (Z_{1m} + Z_{0m}) Y(\varepsilon_j + \varepsilon_k - \varepsilon_m) \\ & + Z_{1j} Z_{1m} (Z_{1k} + Z_{0k}) Y(\varepsilon_j - \varepsilon_k + \varepsilon_m) \\ & + Z_{1k} Z_{1m} (Z_{1j} + Z_{0j}) Y(\varepsilon_k + \varepsilon_m - \varepsilon_j) \\ & + Z_{1j} (Z_{1k} + Z_{0k}) (Z_{1m} + Z_{0m}) Y(\varepsilon_j - \varepsilon_k - \varepsilon_m) \\ & + Z_{1k} (Z_{1j} + Z_{0j}) (Z_{1m} + Z_{0m}) Y(\varepsilon_k - \varepsilon_j - \varepsilon_m) \\ & + Z_{1m} (Z_{1j} + Z_{0j}) (Z_{jk} + Z_{0k}) Y(\varepsilon_m - \varepsilon_j - \varepsilon_k) \\ & + (Z_{1j} + Z_{0j}) (Z_{1k} + Z_{0k}) (Z_{1m} + Z_{0m}) \\ & \cdot Y(-\varepsilon_j - \varepsilon_k - \varepsilon_m). \end{aligned} \tag{39}$$

This expression is calculated by the direct method. One observes a Fermi-type resonance for $\omega_j \approx \omega_k + \omega_m$ which is treated consistently by L'Hospital's rule. For the expressions calculated by the GF-method we introduce

$$Y_+(z) = 2[\cosh(z) - 1]/z, \tag{40}$$

$$Y_-(z) = 2\sinh(z)/z \tag{41}$$

for which the limits for $z \to 0$ (anharmonic resonances) also exist.

$$\begin{aligned} Z_2^{[32]} = \frac{3}{64}\,\beta^2 Z_0' k_{jjj}^2 \{ & R_j^3 [9\,Y_-(\varepsilon_j) + Y_-(3\,\varepsilon_j)] \\ & - 3\,R_j^2 [3\,Y_+(\varepsilon_j) + Y_+(3\,\varepsilon_j)] \\ & + 3\,R_j [Y_-(3\,\varepsilon_j) - Y_-(\varepsilon_j)] \\ & - [Y_+(3\,\varepsilon_j) - 3\,Y_+(\varepsilon_j)]\}\,, \end{aligned} \tag{42}$$

$$\begin{aligned} Z_2^{[33]} = \frac{1}{32}\,\beta^2 Z_0' & k_{jkk} k_{jmm} R_k R_m \\ & \cdot \{R_j\,Y_-(\varepsilon_j) - Y_+(\varepsilon_j)\}\,, \end{aligned} \tag{43}$$

$$\begin{aligned} Z_2^{[34]} = \frac{3}{32}\,\beta^2 Z_0' & k_{jjj} k_{jkk} R_j R_k \\ & \cdot \{R_j\,Y_-(\varepsilon_j) - Y_+(\varepsilon_j)\}\,, \end{aligned} \tag{44}$$

$$\begin{aligned} Z_2^{[35]} = \frac{1}{64}\,\beta^2 Z_0' k_{jkk}^2 \{ & R_j R_k^2 [4\,Y_-(\varepsilon_j) \\ & + Y_-(\varepsilon_j + 2\,\varepsilon_k) + Y_-(\varepsilon_j - 2\,\varepsilon_k)] \\ & - R_k^2 [4\,Y_+(\varepsilon_j) + Y_+(\varepsilon_j + 2\,\varepsilon_k) \\ & + Y_+(\varepsilon_j - 2\,\varepsilon_k)] \\ & - 2\,R_j R_k [Y_+(\varepsilon_j + 2\,\varepsilon_k) - Y_+(\varepsilon_j - 2\,\varepsilon_k)] \\ & + 2\,R_k [Y_-(\varepsilon_j + 2\,\varepsilon_k) - Y_-(\varepsilon_j - 2\,\varepsilon_k)] \\ & + R_j [Y_-(\varepsilon_j + 2\,\varepsilon_k) + Y_-(\varepsilon_j - 2\,\varepsilon_k) \\ & - 2\,Y_-(\varepsilon_j)] - [Y_+(\varepsilon_j + 2\,\varepsilon_k) \\ & + Y_+(\varepsilon_j - 2\,\varepsilon_k) - 2\,Y_+(\varepsilon_j)]\}\,. \end{aligned} \tag{45}$$

$Z_2^{[35]}$ is identical to (27), though, because of the different methods it looks quite different.

The contributions due to fourth order potential constants are:

$$\begin{aligned} Z_2^{[41]} = \frac{3}{64}\,\beta^2 Z_0' & k_{jjjj}^2 \\ & \cdot \{R_j^4 [Y_-(4\,\varepsilon_j) + 16\,Y_-(2\,\varepsilon_j) + 36] \\ & - 4\,R_j^3 [Y_+(4\,\varepsilon_j) + 8\,Y_+(2\,\varepsilon_j)] \\ & + 6\,R_j^2 [Y_-(4\,\varepsilon_j) + Y_-(2\,\varepsilon_j) - 6] \\ & - 4\,R_j [Y_+(4\,\varepsilon_j) - 2\,Y_+(2\,\varepsilon_j)] \\ & + [Y_-(4\,\varepsilon_j) - 4\,Y_-(2\,\varepsilon_j) + 6]\}\,, \end{aligned} \tag{46}$$

$$\begin{aligned} Z_2^{[42]} = \frac{1}{128}\,\beta^2 Z_0' k_{jjkk}^2 \{ & R_j^2 R_k^2 [4\,Y_-(2\,\varepsilon_j) + 4\,Y_-(2\,\varepsilon_k) \\ & + Y_-(2\,\varepsilon_j + 2\,\varepsilon_k) + Y_-(2\,\varepsilon_j - 2\,\varepsilon_k) + 16] \\ & + 4\,R_j R_k [Y_-(2\,\varepsilon_j + 2\,\varepsilon_k) - Y_-(2\,\varepsilon_j - 2\,\varepsilon_k)] \\ & + [Y_-(2\,\varepsilon_j + 2\,\varepsilon_k) + Y_-(2\,\varepsilon_j - 2\,\varepsilon_k) \\ & - 2\,Y_-(2\,\varepsilon_j) - 2\,Y_-(2\,\varepsilon_k) + 4] \\ & + \sum_{\substack{0\\ jk}} (R_j^2 [Y_-(2\,\varepsilon_j + 2\,\varepsilon_k) + Y_-(2\,\varepsilon_j - 2\,\varepsilon_k) \\ & + 4\,Y_-(2\,\varepsilon_k) - 2\,Y_-(2\,\varepsilon_j) - 8] \\ & - 2\,R_j R_k^2 [4\,Y_+(2\,\varepsilon_j) + Y_+(2\,\varepsilon_j + 2\,\varepsilon_k) \\ & + Y_+(2\,\varepsilon_j - 2\,\varepsilon_k)] - 2\,R_j [Y_+(2\,\varepsilon_j + 2\,\varepsilon_k) \\ & + Y_+(2\,\varepsilon_j - 2\,\varepsilon_k) - 2\,Y_+(2\,\varepsilon_j)])\}\,, \end{aligned} \tag{47}$$

where the symbol ${}^{\,0}_{jk}$ in the sum denotes a permutation of the indices j, k.

$$\begin{aligned} Z_2^{[43]} = \frac{3}{32}\,\beta^2 Z_0' k_{jjjj} k_{jjkk} R_j R_k \{ & R_j^2 [Y_-(2\,\varepsilon_j) + 3] \\ & - 2\,R_j\,Y_+(2\,\varepsilon_j) + Y_-(2\,\varepsilon_j) - 2\}\,, \end{aligned} \tag{48}$$

$$Z_2^{[44]} = \frac{9}{32}\,\beta^2 Z_0' k_{jjjj} k_{kkkk} R_j^2 R_k^2\,, \tag{49}$$

$$Z_2^{[45]} = \frac{3}{32}\,\beta^2 Z_0' k_{jjjj} k_{kkmm} R_j^2 R_k R_m\,, \tag{50}$$

$$\begin{aligned} Z_2^{[46]} = \frac{1}{64}\,\beta^2 Z_0' & k_{jjkk} k_{kkmm} R_j R_m \\ & \cdot \{R_k^2 [Y_-(2\,\varepsilon_k) + 4] \\ & - 2\,R_k\,Y_+(2\,\varepsilon_k) - Y_-(2\,\varepsilon_k) - 2\}\,. \end{aligned} \tag{51}$$

5. Rotation-vibration interaction, large amplitude motions

5.1. *Rotational PF*

As the PFs of rigid rotation are well known, but often overlooked in textbooks and reviews, they are sketched briefly.

5.1.1. Spherical top

The eigenvalues

$$E_j = (\hbar^2/2\,I)\,J\,(J+1) \tag{52}$$

are $(2J+1)^2$-fold degenerate, so that the PF can be evaluated by means of θ-transforms. For high temperatures Fox [54] gave a detailed discussion, whereas for low temperatures the classical work by Maue is still important, where the symmetry of nuclear spin and rotation is taken into account [54].

5.1.2. Symmetric top

The eigenvalues

$$\begin{aligned} E_{JK} = {} & (\hbar^2/2\,I_{xx})\,J\,(J+1) \\ & + \{(\hbar^2/2)\,(1/I_{zz} - 1/I_{xx})\,K^2\} \end{aligned} \tag{53}$$

are $(2J+1)$-fold degenerate. Depending on the prolate or oblate form, the equilibrium moments of inertia can be commuted. One can calculate the PF by various methods, the customary one is by Euler-MacLaurin asymptotic series [55].

Following Kassel [56], the different terms arising in the perturbation expansion

$$Z^{\mathrm{ST}}_{\mathrm{ROT}}(\Phi) = \sum_{J=0}^{\infty} \sum_{|K|=J}^{\infty} (2J+1)\Phi \cdot \exp\{-\sigma_x J(J+1) - \gamma\sigma_x K^2\}$$

$$\sigma_\alpha = \beta\hbar^2/2I_{\alpha\alpha}; \quad \gamma = (I_{xx}/I_{zz}) - 1\,, \tag{54}$$

which are characterized by the different values of Φ, can be calculated by parameter differentiation. The zero and first order terms are

$$Z^{\mathrm{ST}}_{\mathrm{ROT}}(1) = \pi^{1/2}\sigma_x^{-3/2}\exp(\sigma_x/4)(\gamma+1)^{-1/2} \cdot \{1+\gamma\sigma_x/12(\gamma+1)+\cdots\}\,, \tag{55}$$

$$Z^{\mathrm{ST}}_{\mathrm{ROT}}(K^2) = \pi^{1/2}\sigma_x^{-5/2}\exp(\sigma_x/4)(\gamma+1)^{-3/2} \cdot \{1+(\gamma-2)\sigma_x/12(\gamma+1)+\cdots\}\,, \tag{56}$$

$$Z^{\mathrm{ST}}_{\mathrm{ROT}}(J(J+1)) = \pi^{1/2}\sigma_x^{-5/2}\exp(\sigma_x/4)(\gamma+1)^{-1/2} \cdot \{(2\gamma+3)/2(\gamma+1)+\cdots\}\,. \tag{57}$$

If the exponential factor in $Z^{\mathrm{ST}}_{\mathrm{ROT}}(1)$ is expanded too, (55) becomes

$$Z^{\mathrm{ST}}_{\mathrm{ROT}}(1) = (\pi/\sigma_z)^{1/2}\sigma_x^{-1}\{1+(4\sigma_x-\sigma_x^2/\sigma_z)/12 + (32\sigma_x^2-24\sigma_x^3/\sigma_z+7\sigma_x^4/\sigma_z^2)/480+\cdots\} \tag{58}$$

which will be compared to the PF of the asymmetric top.

For completeness we also give the matrix elements in the symmetric top basis which are necessary for the subsequent applications of SPT to Coriolis effects and rotation-vibration interaction.

$$\langle K,J|\hat{P}_x^2|K,J\rangle = \langle K,J|\hat{P}_y^2|K,J\rangle = \hbar^2/2\{J(J+1)-K^2\}\,, \tag{59}$$

$$\langle K,J|\hat{P}_z^2|K,J\rangle = \hbar^2K^2\,,$$

$$\langle K,J|\hat{P}_x^4|K,J\rangle = \langle K,J|\hat{P}_y^4|K,J\rangle = (\hbar^4/8)\{3J^2(J+1)^2-2J(J+1) - 6J(J+1)K^2+5K^2+3K^4\}\,, \tag{60}$$

$$\langle K,J|\hat{P}_z^4|K,J\rangle = \hbar^4K^4\,. \tag{61}$$

For some recent developments on the symmetric top PF we refer to Kayser and Kilpatrick [57].

5.1.3. Asymmetric top PF

It is well known that the asymmetric top eigenvalues cannot be given in closed form, but extended tables for the numerical calculation are available. For an excellent review on the asymmetric top see van Winter [58]. An elegant semiclassical Wigner-Kirkwood expansion leads to simple closed expressions. Stripp and Kirkwood derived [59]

$$Z^{\mathrm{AT}}_{\mathrm{ROT}} = (\pi/\sigma_x\sigma_y\sigma_z)^{1/2}[1+(1/12)(2\sigma_x+2\sigma_y + 2\sigma_z-\sigma_x\sigma_y/\sigma_z-\sigma_y\sigma_z/\sigma_x-\sigma_z\sigma_x/\sigma_y)+\cdots] \tag{62}$$

which in the symmetric top limit agrees with Viney's result. Independently Kaplan [60] derived the same asymptotic expansion using Feynman's ordering technique. We shall use their results in the zero order terms. For perturbation calculations, however, these formulas are not suited. We prefer a symmetric top approximation which was similarly used by Gordon [61]. One writes

$$\hat{H} = (\hat{P}_x^2/I_{xx}+\hat{P}_y^2/I_{yy}+\hat{P}_z^2/I_{zz})/2 = \hat{H}_0+\hat{H}_1\,, \tag{63}$$

$$\begin{aligned}\hat{H}_0 &= (\hat{P}_x^2/I_{xx}+\hat{P}_y^2/(I_{yy}I_{zz})^{1/2}+\hat{P}_z^2/(I_{yy}I_{zz})^{1/2})/2\,,\\ \hat{H}_1 &= (1/I_{yy}-1/(I_{yy}I_{zz})^{1/2})\,\hat{P}_y^2/2 + (1/I_{zz}-1/(I_{yy}I_{zz})^{1/2})\,\hat{P}_z^2/2\,,\end{aligned} \tag{64}$$

so that $\hat{H}_1$ is small because of the difference of the inverse moments of inertia and can be neglected to a good approximation. The pseudo symmetric top is used in the following calculations with a second approximation. For the anharmonic oscillators the ordering transformation can be performed easily as the set $\{\hat{a},\hat{a}^+,1\}$ is closed under a commutator operation and $[\hat{a},\hat{a}^+]_-=1$ leads to a c-number which commutes with $\hat{a}$ and $\hat{a}^+$ respectively. Matters are more complicated for $\{\hat{J}_x,\hat{J}_y,\hat{J}_z\}=\{\hat{P}_x,\hat{P}_y,\hat{P}_z\}$. The commutator no longer leads to a c-number, but to an operator. The Hausdorff-ordering transform (Appendix C) can no longer be summed easily. We, therefore, neglect the higher terms of the series and take only the first (constant) one.

5.2. Coriolis-coupling

Coriolis-coupling is usually associated with the vibrational angular momentum of degenerate modes and is, therefore, treated in connection with the spherical and symmetrical top. This Coriolis effect is called of first order. The quantum mechanics for the symmetric top is simple, but for the spherical top it is a field of active research. In addition, Jahn (see Nielsen [12]) showed that Coriolis-coupling of second order arises in asymmetric top molecules like formaldehyde and water. Though this effect is small, it should be treated for completeness.

5.2.1. Sketch of first-order Coriolis-coupling

As the influence of Coriolis-coupling was treated recently for degenerate modes [62], only the method will be outlined: after translation to occupation number representation the vibrational angular momentum operators read:

$$\begin{aligned}\hat{p}_x &= i\sum_\mu \zeta^{(x)}_{\mu 2,\mu 3}(\hat{a}_{\mu 2}\hat{a}^+_{\mu 3}-\hat{a}^+_{\mu 2}\hat{a}_{\mu 3})\,,\\ \hat{p}_y &= i\sum_\mu \zeta^{(y)}_{\mu 3,\mu 1}(\hat{a}_{\mu 3}\hat{a}^+_{\mu 1}-\hat{a}^+_{\mu 3}\hat{a}_{\mu 1})\,, \qquad (65)\\ \hat{p}_z &= i\sum_\mu \zeta^{(z)}_{\mu 1,\mu 2}(\hat{a}_{\mu 1}\hat{a}^+_{\mu 2}-\hat{a}^+_{\mu 1}\hat{a}_{\mu 2})\,.\end{aligned}$$

It is obvious that the ordering transformation between the components of a degenerate mode does not contribute.

$$\begin{aligned}&\exp\{+\beta\hbar\omega_\mu(\hat{a}^+_{\mu 1}\hat{a}_{\mu 1}+\hat{a}^+_{\mu 2}\hat{a}_{\mu 2}+\hat{a}^+_{\mu 3}\hat{a}_{\mu 3})s_1\}\,\hat{a}_{\mu 1}\hat{a}^+_{\mu 2}\\ &\quad\cdot\exp\{-\beta\hbar\omega_\mu(\hat{a}^+_{\mu 1}\hat{a}_{\mu 1}+\hat{a}^+_{\mu 2}\hat{a}_{\mu 2}+\hat{a}^+_{\mu 3}\hat{a}_{\mu 3})s_1\} \qquad (66)\\ &=\hat{a}_{\mu 1}\exp(-\beta\hbar\omega_\mu s_1)\,\hat{a}^+_{\mu 2}\exp(\beta\hbar\omega_\mu s_1)=\hat{a}_{\mu 1}\hat{a}^+_{\mu 2}\,.\end{aligned}$$

For brevity, the final formulas will not be written down but can be obtained easily by the operator techniques of Appendix C.

5.2.2. Second order Coriolis-coupling

Following Jahn (see [12]) we take H_2O as example

$$\begin{aligned}\hat{H} &= (\hat{P}^2_x/I_{xx})+(\hat{P}_y-\hat{p}^{12}_y-\hat{p}^{13}_y)^2/I_{yy}+\hat{P}^2_z/I_{zz}+\hat{H}_{ViB}\,,\\ \hat{p}^{12}_y &= \zeta_{12}(\hat{q}_1\hat{p}_2-\hat{p}_1\hat{q}_2)=(-i\zeta_{12})(\hat{a}^+_1\hat{a}_2-\hat{a}^+_2\hat{a}_1)\,, \qquad (67)\\ \hat{p}^{13}_y &= \zeta_{13}(\hat{q}_1\hat{p}_3-\hat{p}_1\hat{q}_3)=(-i\zeta_{13})(\hat{a}^+_1\hat{a}_3-\hat{a}^+_3\hat{a}_1)\,.\end{aligned}$$

$\hat{H}$ is separated into a zero order term $\hat{H}_0$ and a perturbational part $\hat{H}_1$ containing the Coriolis operators and anharmonicity.

$$\hat{H}^{\mathrm{RV}}_0=(\hat{P}^2_x/I_{xx})+(\hat{P}^2_y/I_{yy})+(\hat{P}^2_z/I_{zz})+\sum_j\hat{\mathscr{H}}^{(j)}_0\,, \qquad (68)$$

$$\begin{aligned}\hat{H}_1 &= (2\hat{P}_y/I_{yy})\cdot i\{\zeta_{12}(\hat{a}^+_1\hat{a}_2-\hat{a}^+_2\hat{a}_1)\\ &\quad+\zeta_{13}(\hat{a}^+_1\hat{a}_3-\hat{a}^+_3\hat{a}_1)\}\\ &\quad-(1/I_{yy})\{\zeta_{12}(\hat{a}^+_1\hat{a}_2-\hat{a}^+_2\hat{a}_1)\\ &\quad+\zeta_{13}(\hat{a}^+_1\hat{a}_3-\hat{a}^+_3\hat{a}_1)\}^2+\tilde{V}_{\mathrm{anh}}(q)\,, \qquad (69)\end{aligned}$$

where $\tilde{V}_{\mathrm{anh}}(q)$ contains the anharmonic part of the potential energy.

The second term in $\hat{H}_1$ already contributes in first order SPT

$$\begin{aligned}Z^{\mathrm{CC}}_1 &= (\beta/I_{yy})\,Z^{\mathrm{AT}}_{\mathrm{ROT}} \qquad (70)\\ &\quad\cdot\{Z'_0(1,2)\,\zeta^2_{12}[2Z_{11}Z_{12}+Z_{11}Z_{02}+Z_{01}Z_{12}]\\ &\quad+Z'_0(1,3)\,\zeta^2_{13}[2Z_{11}Z_{13}+Z_{11}Z_{03}+Z_{01}Z_{13}]\}\,.\end{aligned}$$

$Z^{\mathrm{AT}}_{\mathrm{ROT}}$ denotes the rotational PF and $Z'_0(j,k)$ the vibrational PF in the harmonic approximation without the PF of the normal modes j and k.

The first term of $\hat{H}_1$ only contributes in second order SPT:

$$\begin{aligned}Z^{\mathrm{CC}}_2 &= 2(\beta/I_{yy})^2\,W_{\mathrm{ROT}}\\ &\quad\cdot\{Z'_0(1,2)\,\zeta^2_{12}[Y(\varepsilon_2-\varepsilon_1)Z_{11}(Z_{12}+Z_{02})\\ &\quad+Y(\varepsilon_1-\varepsilon_2)Z_{12}(Z_{11}+Z_{01})]\\ &\quad+Z'_0(1,3)\,\zeta^2_{13}[Y(\varepsilon_3-\varepsilon_1)Z_{11}(Z_{13}+Z_{03})\\ &\quad+Y(\varepsilon_1-\varepsilon_3)Z_{13}(Z_{11}+Z_{01})]\}\,. \qquad (71)\end{aligned}$$

W_{ROT} contains the rotational part which is approximated in the averaged symmetric top approximation. The matrix element is taken from (59).

$$W_{\mathrm{ROT}}=\hbar^2 Z^{\mathrm{ST}}_{\mathrm{ROT}}(K^2)\,. \qquad (72)$$

In contrast to the symmetric and spherical top the contributions in first and second order SPT do not cancel. The reason is that for degenerate modes the ordering transform vanishes, whereas for different vibrations it contributes to the PF.

5.2.3. Coriolis resonance

Though the effects of Coriolis resonance are even smaller than for ordinary Coriolis-coupling, we shall discuss it to show the generality of the method. Following Nielsen [12] we treat Coriolis resonance between the fundamentals ω_5 and ω_6 of formaldehyde in the symmetric top approximation $I_{xx}=I_{yy}$. The part of the Nielsen Hamiltonian responsible for resonance is in the original notation

$$\hat{T}=[\lambda_6/\lambda_5)^{1/4}\hat{q}_5\hat{p}_6-(\lambda_5/\lambda_6)^{1/4}\hat{q}_6\hat{p}_5]\,\zeta^{(z)}_{56}\,\hat{P}_z/I_{zz}\,, \qquad (73)$$

where $\lambda_s=(2\pi(\tilde{\omega}_s))^2$, $\tilde{\omega}_s$ is the normal frequency in cm^{-1}, not to be confused with ω_j used in the text.

One gets with

$$\begin{aligned}t &= (\omega_6/\omega_5)^{1/2}-(\omega_5/\omega_6)^{1/2}\,,\\ t^* &= (\omega_6/\omega_5)^{1/2}+(\omega_5/\omega_6)^{1/2}\,, \qquad (74)\end{aligned}$$

$$\hat{T}=\{t\,\hat{a}^+_5\hat{a}^+_6-t^*\hat{a}^+_5\hat{a}_6+t^*\hat{a}_5\hat{a}^+_6-t\,\hat{a}_5\hat{a}_6\}\,(i\,\zeta^{(z)}_{56}\hat{P}_z/2I_{zz}) \qquad (75)$$

so that after a simple calculation with the technique discussed for the anharmonic part the results is:

$$\begin{aligned}Z^{\mathrm{CR}}_2 &= \frac{1}{8}(\beta\zeta^{(z)}_{56}/I_{zz})^2\,W_{\mathrm{ROT}}\cdot\{t^2\,Y(-\varepsilon_5-\varepsilon_6)Z_{15}Z_{16}\\ &\quad+t^2\,Y(\varepsilon_5+\varepsilon_6)(Z_{15}+Z_{05})(Z_{16}+Z_{06})\end{aligned}$$

$$
\begin{aligned}
&+t^{*2}\,Y(\varepsilon_5-\varepsilon_6)\,Z_{16}(Z_{15}+Z_{05})\\
&+t^{*2}\,Y(\varepsilon_6-\varepsilon_5)\,Z_{15}(Z_{16}+Z_{06})\}\,. \qquad (76)
\end{aligned}
$$

One sees that the resonance is caused by the Coriolis-coupling and not by anharmonic-coupling terms. The quantum mechanical treatment of this effect is fairly complicated [12, 14], but the present results show that resonance effects and irregularities can be incorporated into the PF easily. Furthermore, it can be seen that the effects are small, so that in contrast to some suggestions they need not be taken into account in level density calculations, as the anharmonic resonances are much more important.

5.3 Rotation-vibration-coupling

For brevity we consider only the most important term, diagonal in the angular momentum operators. As the constants are not of special interest, we abbreviate them all by C^i_{gg} so that the rotation-vibration term reads:

$$
\begin{aligned}
\hat{T}^{\mathrm{RV}} &= -\sum_g\sum_j \{C^j_{gg}\,\hat{P}^2_g\,\hat{q}_j\}\\
&= -\sum_g\sum_j \{2^{-1/2}C^j_{gg}\,\hat{P}^2_g(\hat{a}^+_j+\hat{a}_j)\}\,. \qquad (77)
\end{aligned}
$$

From the generating function given in Sect. 4.2 it follows immediately that only terms of $\hat{H}_1$ containing odd powers of the $\hat{q}_j$ will contribute to the PF in second order SPT, if $\hat{T}^{\mathrm{RV}}$ is taken into account. The most important contribution results from the diagonal cubic anharmonicity $k_{jjj}\,\hat{q}^3_j$. Using the methods discussed above, the respective term reads

$$
\begin{aligned}
Z^{\mathrm{RV}}_2 = &-\frac{1}{2}\beta^2\int_0^1 \mathrm{d}s_1\Big[\mathrm{Tr}\Big\{\exp(-\beta\hat{H}^{\mathrm{RV}}_0)\\
&\cdot\exp(-\beta\hat{H}^{\mathrm{RV}}_0 s_1)\\
&\cdot\Big(\sum_j k_{jjj}\,\hat{q}^3_j\Big)\exp(\beta\hat{H}^{\mathrm{RV}}_0 s_1)\Big[\sum_g\sum_j C^j_{gg}\,\hat{P}^2_g\,\hat{q}_j)\Big]\Big\}\\
&+\mathrm{Tr}\Big\{\exp(-\beta\hat{H}^{\mathrm{RV}}_0)\exp(-\beta\hat{H}^{\mathrm{RV}}_0 s_1)\\
&\cdot\Big[\sum_g\sum_j C^j_{gg}\,\hat{P}^2_g\,\hat{q}_j\Big]\exp(\beta\hat{H}^{\mathrm{RV}}_0 s_1)\Big(\sum_j k_{jjj}\,\hat{q}^3_j\Big)\Big\}\Big]\\
= &-\frac{3}{8}\beta^2\sum_g\sum_j C^j_{gg}k_{jjj}\,W^{\mathrm{RV}}(g,j)\\
&\cdot[Y(\varepsilon_j)+Y(-\varepsilon_j)][2Z_{2j}+2Z_{1j}+Z_{0j}]\,, \qquad (78)
\end{aligned}
$$

where

$$
W^{\mathrm{RV}}(g,j)=\mathrm{Tr}\,\{\hat{P}^2_g\exp[-\beta\hat{H}^{\mathrm{RV}}_0(j)]\,; \qquad (79)
$$

$\hat{H}^{\mathrm{RV}}_0(j)$ is the zero order rotation Hamiltonian plus the zero order vibration Hamiltonian but without the Hamiltonian of the j-th normal mode $\hat{\mathscr{H}}^{(j)}_0$. $W^{\mathrm{RV}}(g,j)$ can be evaluated in the same approximation as for the Coriolis-couplings. Furthermore, second order SPT leads for the diagonal part to rotational powers $\sim\hat{P}^4_g$, which are much smaller than the anharmonic rotation-vibration interaction.

5.4. Internal rotation and large amplitude motion

For completeness we want to refer to molecular motions which are not included in the Nielsen-Hamiltonian and which cannot be treated by perturbation methods.

5.4.1 Internal rotation

The problem of internal rotation was treated from the practical point of view by Frankiss and Green [1], who also gave a large number of examples. They used numerical summation of Boltzmann-factors from available tabulations. Details of the quantum mechanics with extended references are given in Chapt. 8 of [63]. These techniques are not well suited for the calculation of the PF and level densities which are needed in reaction kinetics. Vojta [64] showed that Wigner-Kirkwood semiclassical expansion to order $\hbar^4$ gives good analytical results for symmetric hindered tops in terms of modified Bessel-functions. It is, therefore, easy to incorporate these degrees of freedom in the calculation of level densities. Kaplan [66] used ordering techniques to get analytical results for symmetric hindered tops and Zaitsev [65] applied a resolvent-type technique to the same problem.

5.4.2. Large amplitude motions

A good review on the quantum mechanics and spectroscopy of large amplitude motions like torsion and ring-puckering is given in Chapt. 7 of [63]. One customarily reduces the problem to the Hamiltonian of an one-dimensional single or double well oscillator

$$
\begin{aligned}
&\hat{H}=\tfrac{1}{2}\hbar\omega(\hat{p}^2+\delta\hat{q}^2)+k_3\hat{q}^3+k_4\hat{q}^4\,,\\
&k_4, k_3 \geqq 0\,,\quad \delta=+1 \qquad \text{single well,}\\
&k_4>0,\quad k_3\leqq 0,\quad \delta=-1\quad \text{double well.} \qquad (80)
\end{aligned}
$$

The Wigner-Kirkwood expansion can be evaluated analytically to arbitrary order in series of exponential functions and parabolic cylinder functions. In addition exact upper and lower bounds including variation, and the variation-perturbation series can be evaluated analytically [67].

6. Numerical results and discussion

6.1. Numerical results

As rotational effects are small and well understood, we evaluated only the vibrational part for two examples H_2O and SO_2 with the potential constants from Morino and Kuchitsu [68], for a detailed recent discussion of these constants see Isaacson et al. [11].

Anharmonic force field:

$$\begin{aligned}\hat{H}_1 = {} & k_{111}\,\hat{q}_1^3 + k_{122}\,\hat{q}_1\,\hat{q}_2^2 + k_{133}\,\hat{q}_1\,\hat{q}_3^2 \\ & + k_{211}\,\hat{q}_2\,\hat{q}_1^2 + k_{222}\,\hat{q}_2^3 + k_{233}\,\hat{q}_2\,\hat{q}_3^2 \\ & + k_{1111}\,\hat{q}_1^4 + k_{1122}\,\hat{q}_1^2\,\hat{q}_2^2 + k_{1133}\,\hat{q}_1^2\,\hat{q}_3^2 \\ & + k_{2222}\,\hat{q}_2^4 + k_{2233}\,\hat{q}_2^2\,\hat{q}_3^2 + k_{3333}\,\hat{q}_3^4\,. \end{aligned} \tag{81}$$

The vibrational PF of H_2O in different approximations is given in Table 2 for several temperatures. As expected, the PF Z_B from summed Boltzmann factors agrees very well with second order SPT, as the eigenvalues are calculated by Van Vleck perturbation theory. Good agreement exists also between SPT and the accurate results. The results for high temperatures are only given to show the behaviour of both approximations. Unfortunately the agreement is lost below 1000 K, where the approximation Z_B is valid, whereas SPT, as a high temperature expansion, leads to wrong and at room temperature to meaningless negative values. As will be discussed in the appendix, for molecules with high frequency X-H vibrations SPT does not work well at low temperatures, but sufficiently well at higher temperatures.

Table 2. The vibrational partition function of H_2O. – Comparison of first (Z_{01}) and second (Z_{02}) order SPT with the PF from summed Boltzmann factors Z_B and accurate results from Isaacson et al. [11], Z_I. Molecular constants from [68].

T in K	Z_B	Z_{01}	Z_I	Z_{02}
1000	1.43 (−3)	1.19 (−3)	1.39 (−3)	1.41 (−3)
2000	6.08 (−2)	5.40 (−2)	–	6.07 (−2)
3000	3.01 (−1)	2.65 (−1)	–	3.02 (−1)
4000	8.36 (−1)	7.19 (−1)	8.06 (−1)	8.42 (−1)
5000	1.79	1.50	–	1.81
6000	3.31	2.68	–	3.36

Table 3. Contributions of various orders SPT for SO_2. Z_0 = harmonic PF; $Z_1^{[4]}$ = first order SPT, fourth order potential; $Z_2^{[3]}$ = second order SPT, third order potential; $Z_2^{[4]}$ = second order SPT, third and fourth order potential.

T in K	Z_0	$Z_1^{[4]}$	$Z_2^{[3]}$	$Z_2^{[4]}$
400	4.77 (−3)	−3.87 (−5)	1.96 (−4)	4.10 (−6)
1000	2.94 (−1)	1.71 (−3)	1.04 (−2)	6.18 (−4)
2000	2.93	4.92 (−2)	1.67 (−1)	2.12 (−2)
3000	1.03 (+1)	2.72 (−1)	8.43 (−1)	1.63 (−1)
4000	2.48 (+1)	8.87 (−1)	2.67	6.91 (−1)
5000	4.89 (+1)	2.20	6.51	2.11

Table 4. The vibrational partition function of SO_2. – Comparison of different approximations. Z_I = accurate results from Isaacson et al. [11]; $Z_{01}^{(4)}$ = first order SPT, fourth order potential; $Z_{02}^{(3)}$ = second order SPT, third order potential; $Z_{02}^{(4)}$ = second order SPT, fourth order potential.

T in K	Z_I	$Z_{01}^{(4)}$	$Z_{02}^{(3)}$	$Z_{02}^{(4)}$
400	–	4.73 (−3)	4.93 (−3)	4.93 (−3)
1000	3.06 (−1)	2.95 (−1)	3.05 (−1)	3.06 (−1)
2000	3.17	2.98	3.15	3.17
3000	–	1.06 (+1)	1.14 (+1)	1.16 (+1)
4000	–	2.57 (+1)	2.84 (+1)	2.91 (+1)
5000	–	5.10 (+1)	5.76 (+1)	5.97 (+1)

A comparison of the different contributions to the PF in first and second order SPT is given for SO_2 in Table 3. One sees that the contribution of second order SPT is smaller than the first order form, only, if potential terms up to fourth order are considered rather than a potential limited to third order terms, and if the temperature is not too high. The observation that the contributions of different orders n of SPT may increase with n was also made for other systems [see appendices A and B] and seems to be related to the convergence problems of SPT.

In Table 4 the PF of SO_2 in the different approximations is given. The agreement with the accurate results by Isaacson et al., which differ also little from the perturbation results, is quite good. We expect, therefore, that second order SPT is a good approximation for heavier molecules between room temperature and 2000 K.

6.2. Conclusions

We conclude from the numerical results and their good agreement with accurate independent calculations for selected triatomics that SPT to second order is comparable to conventional numerical methods for calculating PFs. The advantages are:

A) once the force field in normal coordinate representation is given, SPT to arbitrary order even for high powers of the normal coordinates can be performed by GF-methods. The calculations are simple, but tedious and lead to long expressions.

B) the results are given in terms of simple transcendental functions which can be easily differentiated. Thermodynamic functions H, E, S, C can be given in analytical form, no numerical differentiations are necessary. As the specific heat C is closely related to the level density, calculated by steepest descent methods, it can be evaluated analytically in first and second order. We showed in a previous paper the good agreement with level counting [45 a].

C) all resonances which make the level pattern irregular and become more and more important with increasing number of normal vibrations are included consistently.

D) it was mentioned that Wolfsberg and coworkers applied SPT to off-diagonal force fields in the harmonic approximation. Their success suggest the same technique for anharmonic force fields, too. The calculations may, however, be very long.

We shall also mention the disadvantages and open questions.

E) SPT was shown to be equivalent to degenerate Rayleigh-Schrödinger-perturbation theory. For anharmonic oscillators it suffers not only from the principal convergence problems for perturbation theories, but also from the special divergence even for infinitesimal small anharmonicity.

F) SPT is a high temperature expansion which is wrong at low temperatures and also leads to wrong results at very high temperatures. This was shown explicitly for the linear quartic anharmonic oscillator. It happens (see Appendix A and B) often, that the third order SPT is worse than the second order.

6.3. Outlook

We plan further systematic investigations of the convergence behaviour using algebraic computer languages and summation techniques. We hope to get criteria for the range of reliable approximations depending on harmonic frequencies, anharmonicities and temperature. A crucial test will be the calculation of the isotope equilibrium constant for

$$H_2O + D_2O = 2\,HDO$$

by variation-perturbation methods and the comparison with precise numerical results by Wolfsberg with eigenvalues from variational calculations.

Part of this work was performed at UC Irvine. W. W. wishes to thank the Department of Chemistry for the invitation and Prof. M. Wolfsberg for many stimulating discussions. A travel grant by the DFG, and support by the Fonds der Chemischen Industrie is gratefully acknowledged.

Appendix A

Numerical investigation of the convergence behaviour for a perturbed harmonic oscillator.

Harvie, Bopp and Wolfsberg [47] investigated in an important paper the convergence behaviour of SPT to fourth order for polyatomic molecules in the off-diagonal-representation. From the behaviour of the different orders they suggested convergence of this model system. As the perturbation of the nondiagonal operators is not very strong, we consider a one-dimensional oscillator, where the exact result is known and the perturbation can be varied arbitrarily:

$$\hat{H} = \hat{\mathscr{H}}_0 + \hat{H}_1\,; \quad \hat{\mathscr{H}}_0 = (\hbar\omega/2)(\hat{p}^2 + \hat{q}^2)\,, \quad \hat{H}_1 = \hbar\omega\, k_2\, \hat{q}^2\,. \tag{A 1}$$

This corresponds to a harmonic oscillator with a new frequency

$$\omega^* = \omega(1+2k_2)^{1/2}, \quad \text{and} \quad Z_0^* = [2\sinh(\beta\hbar\omega^*/2)]^{-1}. \tag{A 2}$$

We investigate the following questions:

- how does the convergence of SPT depend on the temperature and perturbation
- is $|Z_{n+1}| \leqq |Z_n|$ a reasonable criterium for the applicability of SPT
- how do the different orders of SPT behave?

We calculated SPT to fourth order; the lengthy formulas are given in [10]. For small perturbations $k_2 < 0.1$, the results practically agree with the exact results. The agreement improves with increasing order of SPT for the whole temperature range from 200 – 10 000 K. On the other hand, for the extremely strong perturbation $k_2 = 1.5$, SPT gives completely wrong, divergent results for all orders and all temperatures. We, therefore, investigated the behaviour for different k_2 at 4000 K, where SPT should work, and $\omega = 2\pi \cdot 10^{13}$ [sec^{-1}] in Tables 5, 6, and 7.

Table 5. The partition function of a harmonic oscillator with quadratic perturbation. Contributions of different orders of SPT Z_i as a function of the perturbation parameter k_2. $\omega = 2\pi \cdot 10^{13}\ \mathrm{sec}^{-1}$, $T = 4000$ K.

k_2	Z_0	Z_1	Z_2	Z_3	Z_4
0.30	8.33	−2.50	1.13	−5.62 (−1)	2.95 (−1)
0.40	8.33	−3.33	2.00	−1.33	9.34 (−1)
0.50	8.33	−4.17	3.13	−2.60	2.23
0.60	8.33	−5.00	4.50	−4.50	4.73
0.70	8.33	−5.84	6.13	−7.15	8.75
0.80	8.33	−6.67	8.00	−1.07 (+1)	1.49 (+1)

Table 6. The partition function of a harmonic oscillator with quadratic perturbation. – Dependence of the SPT in different orders n, $Z_{0n} = \sum_i^n Z_i$, on the value of the perturbation parameter k_2. $\omega = 2\pi \cdot 10^{13}\ \mathrm{sec}^{-1}$, $T = 4000$ K.

k_2	Z_0^*	Z_{01}	Z_{02}	Z_{03}	Z_{04}
0.30	6.58	5.82	6.95	6.39	6.68
0.40	6.20	4.99	6.99	5.66	6.59
0.50	5.88	4.07	7.32	4.68	6.96
0.60	5.61	3.32	7.83	3.32	8.05
0.70	5.37	2.49	8.61	1.47	1.02 (+1)
0.80	5.16	1.65	9.66	- 1.01	1.39 (+1)

One observes that the different orders Z_{0i} oscillate. Up to $k \approx 0.5$, the $|Z_n|$ form a monotonically decreasing sequence, whereas for $k \geqq 0.58$ the sequence increases. Below $k \approx 0.5$, the results improve with increasing order SPT, whereas above, the accuracy decreases. For more detailed discussion see [10]. To show this behaviour explicitly, we give the percentage deviation $\Delta Z_{0n} = 100\,(Z_{0n} - Z_0^*)/Z_0^*$ in Table 7.

We conclude that for the harmonic oscillator with quadratic perturbation there exist a perturbation parameter k_2^*, where the SPT gives wrong results with increasing order of SPT. The temperature behaviour is shown in Figs. 1 and 2. In any order of

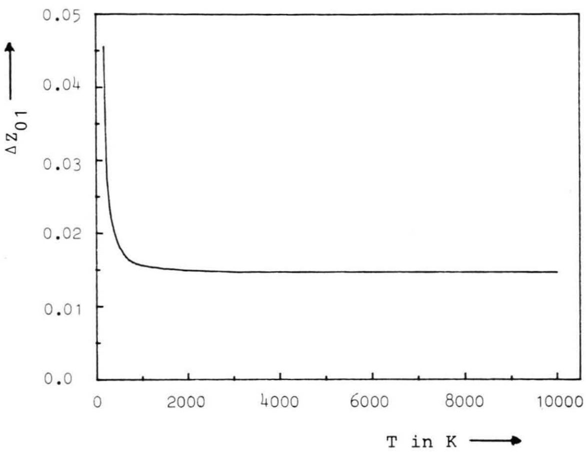

Fig. 1. The partition function of a harmonic oscillator with quadratic perturbation. – The relative (percentage) deviation $\Delta Z_{01} = 100\ (Z_{01} - Z_0^*)/Z_0^*\ (Z_{01} = Z_0 + Z_1)$ as a function of the temperature T for a small perturbation: $k_2 = 0.01$.

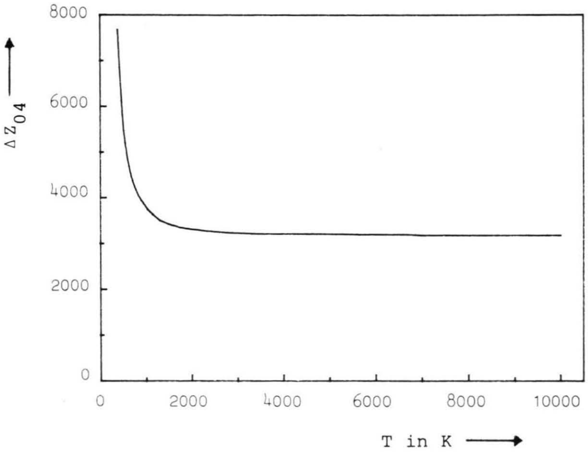

Fig. 2. The partition function of a harmonic oscillator with quadratic perturbation. – The relative (percentage) deviation $\Delta Z_{04} = 100\,(Z_{04} - Z_0^*)/Z_0^*\ (Z_{04} = Z_0 + Z_1 + Z_2 + Z_3 + Z_4)$as a function of the temperature T for a strong perturbation: $k_2 = 1.5$.

Table 7. The partition function of a harmonic oscillator with quadratic perturbation. Percentage deviation ΔZ_{0n} for the approximations in different orders n of SPT. $\omega = 2\pi \cdot 10^{13}\ \mathrm{sec}^{-1}$, $T = 4000$ K.

k_2	ΔZ_0	ΔZ_{01}	ΔZ_{02}	ΔZ_{03}	ΔZ_{04}
0.02	1.98	−3.95 (−2)	1.97 (−3)	−6.90 (−5)	2.48 (−6)
0.10	9.56	−1.41	2.33 (−1)	−4.07 (−2)	7.30 (−3)
0.20	1.83 (+1)	−5.35	1.76	−6.10 (−1)	2.19 (−1)
0.40	3.42 (+1)	−1.95 (+1)	1.27 (+1)	−8.78	6.27
0.60	4.84 (+1)	−4.07 (+1)	3.95 (+1)	−4.07 (+1)	4.35 (+1)
0.80	6.14 (+1)	−6.79 (+1)	8.72 (+1)	−1.20 (+2)	1.70 (+2)
1.00	7.34 (+1)	−1.00 (+2)	1.60 (+2)	−2.74 (+2)	4.85 (+2)
1.20	8.47 (+1)	−1.37 (+2)	2.62 (+2)	−5.36 (+2)	1.14 (+3)
1.40	9.53 (+1)	−1.78 (+2)	3.96 (+2)	−9.44 (+2)	2.34 (+3)

SPT and for arbitrary values of k_2 the relative deviation from the exact PF approaches an asymptotic value for $T \to \infty$. This high temperature behaviour is observed even if SPT leads to meaningless figures. The temperature, where the asymptotic value is practically reached depends on ω and k_2. From these results we conclude that it is necessary to investigate systematically high order perturbation theory for different types of perturbation over a range of anharmonicity constants and temperature.

Appendix B

Third order perturbation results for diatomics to fourth order Dunham-expansion.

Though we dealt in the text with polyatomics, some unpublished results for third order SPT of diatomics should be given to illustrate the behaviour for molecules with cubic and quartic anharmonicity; for brevity we discuss H_2 with large anharmonicity (Tables 8 and 9). HBr, HCl, HF, CO, J_2 are treated in [10].

Generally, it follows from the numerical calculations that third order SPT does not improve the agreement with numerical results, whereas second order SPT gives a good approximation and always lies slightly above the exact upper bound with variation of the internuclear distance and the frequency. The convergence is strongly dependent on the harmonic frequency. As a rule, second order SPT works well for intermediate values of $\varepsilon = \beta \hbar \omega$. It follows, that the results are good for fairly low temperatures, if ω is small, whereas unphysical negative figures are obtained for large values of ω. On the other hand, the results are bad even at intermediate temperatures for small ω, whereas the results for high temperatures are reasonable. We hope to improve the range of validity by variation-perturbation techniques.

Table 8. The vibrational partition function of H_2. – Contributions Z_n arising from zero to third order SPT. Molecular constants calculated from [70].

T in K	Z_0	Z_1	Z_2	Z_3
1000	4.22 (−2)	−5.57 (−3)	7.78 (−3)	−4.12 (−3)
2000	2.14 (−1)	−1.66 (−2)	2.44 (−2)	−1.49 (−2)
4000	5.70 (−1)	−4.30 (−2)	7.64 (−2)	−7.94 (−2)
6000	9.05 (−1)	−8.45 (−2)	1.71 (−1)	−2.54 (−1)
8000	1.23	−1.42 (−1)	3.15 (−1)	−6.06 (−1)
10000	1.55	−2.16 (−1)	5.18 (−1)	−1.21

Appendix C

Formulas of operator calculus.

Though the relevant formulas of operator calculus have been given in previous articles, we wish to give some improvement which facilitate the calculations. More details will be given in a forthcoming lecture note [69].

Hausdorff-formulas:

$$\begin{aligned}\exp(\alpha \hat{A})\, \hat{B} \exp(-\alpha \hat{A}) &= \hat{B} + \alpha [\hat{A}, \hat{B}]_- \\ &\quad + (\alpha^2/2!)\, [\hat{A}[\hat{A}, \hat{B}]_-]_- + \dots \\ &= \sum_{n=0}^{\infty} (\alpha^n/n!)\, \{\hat{A}^n, \hat{B}\}_- = \widetilde{B(\alpha)}\,, \end{aligned} \tag{C 1}$$

$$\exp(\alpha \hat{A})\, \hat{B}^k \exp(-\alpha \hat{A}) = \{\widetilde{B(\alpha)}\}^k, \ \alpha \equiv c\text{-number}, \tag{C 2}$$

$$\exp(\alpha \hat{A}) \exp \hat{B} \exp(-\alpha \hat{A}) = \exp\{\widetilde{B(\alpha)}\}\,. \tag{C 3}$$

Baker-Campbell-Hausdorff-formulas (BCH):

$$\begin{aligned}\exp(\alpha \hat{A}) \exp(\beta \hat{B}) &= \exp\{\alpha \hat{A} + \beta \hat{B} + (\alpha \beta/2)\, [\hat{A}, \hat{B}]_-\}\,, \\ \exp(a \hat{A} + \beta \hat{B}) &= \exp(\alpha \hat{A}) \exp(\beta \hat{B}) \\ &\quad \cdot \exp\{-(\alpha \beta/2)\, [\hat{A}, \hat{B}]_-\} \end{aligned} \tag{C 4}$$

$$\text{if} \quad [\hat{A}, [\hat{A}, \hat{B}]_-]_- = [\hat{B}, [\hat{A}, \hat{B}]_-]_- = 0\,.$$

These formulas can be used as generating functions for ordered expressions formed with the Lie-algebras

Table 9. The vibrational partition function of H_2. – Comparison of first (Z_{01}), second (Z_{02}), and third (Z_{03}) order SPT results with lower (Z_{LB}^V) and upper (Z_{UB}^V) variational bounds and the PF from summed Boltzmann factors Z_B. Molecular constants calculated from [70].

T in K	Z_B	Z_{LB}^V	Z_{01}	Z_{02}	Z_{03}	Z_{UB}^V
1000	4.41 (−2)	3.70 (−2)	3.66 (−2)	4.43 (−2)	4.02 (−2)	5.29 (−2)
2000	2.21 (−1)	1.98 (−1)	1.97 (−1)	2.22 (−1)	2.07 (−1)	2.32 (−1)
4000	5.96 (−1)	5.28 (−1)	5.27 (−1)	6.03 (−1)	5.24 (−1)	5.96 (−1)
6000	9.67 (−1)	8.24 (−1)	8.20 (−1)	9.91 (−1)	7.36 (−1)	9.42 (−1)
8000	1.35	1.10	1.09	1.40	7.97 (−1)	1.28
10000	1.76	1.35	1.33	1.85	6.41 (−1)	1.61

$\{\hat{p}, \hat{q}, c\hat{I}\}$; $[\hat{p}, \hat{q}]_- = c\hat{I}$; $\{\hat{a}, \hat{a}^+, \hat{I}\}$; $[\hat{a}, \hat{a}^+]_- = \hat{I}$; $[\hat{I}, \hat{a}]_- = [\hat{I}, \hat{a}^+]_- = 0$. Differentiation with respect to a characteristic parameter or expansion and comparison leads to ordered expressions.

$$\begin{aligned} \mathrm{GF} &= \exp\{k(\hat{a}^+ + \hat{a})\} \\ &= \exp(k\hat{a}^+)\exp(k\hat{a})\exp(k^2/2) \\ &= \exp(k\hat{a})\exp(k\hat{a}^+)\exp(-k^2/2)\,. \end{aligned} \tag{C 5}$$

Example: $(\hat{a}^+ + \hat{a})^4$

Expansion of the left and right side leads to

$$\begin{aligned} (\hat{a}^+ + \hat{a})^4 &= \hat{a}^+ + 4\hat{a}^{+3}\hat{a} + 6\hat{a}^{+2}\hat{a}^2 + 4\hat{a}^+\hat{a}^3 + \hat{a}^4 \\ &\quad + 6\hat{a}^{+2} + 12\hat{a}^+\hat{a} + 6\hat{a}^2 + 3 \\ &\qquad (\text{“normal-ordering”}) \\ &= \hat{a}^4 + 4\hat{a}^3\hat{a}^+ + 6\hat{a}^2\hat{a}^{+2} + 4\hat{a}\hat{a}^{+3} + \hat{a}^{+4} \\ &\quad - 6\hat{a}^2 - 12\hat{a}\hat{a}^+ - 6\hat{a}^{+2} + 3 \\ &\qquad (\text{“antinormal-ordering”})\,. \end{aligned} \tag{C 6}$$

This is easier to derive than the related compact formula from parameter differentiation.

$$(\hat{p} + \hat{q})^n = \sum_{k=0}^{[n/2]} \sum_{s=0}^{n-2k} \frac{(c/2)^k n!\,\hat{q}^s \hat{p}^{n-2k-s}}{k!\,s!\,(n-2k-s)!}\,. \tag{C 7}$$

In method 4.1 for calculating traces it is often necessary to commute high powers of noncommuting operators. This can be easily performed by a BCH-generating function:

$$\begin{aligned} \exp(k_1\hat{a}^+)\exp(k_2\hat{a}) &= \exp(k_2\hat{a})\exp(k_1\hat{a}^+) \\ &\quad \cdot \exp(-k_1k_2)\,, \\ \exp(k_2\hat{a})\exp(k_1\hat{a}^+) &= \exp(k_1\hat{a}^+)\exp(k_2\hat{a})\exp(k_1k_2). \end{aligned} \tag{C 8}$$

Example:

$$\begin{aligned} \hat{a}^{+2}\hat{a}^2 &= \hat{a}^2\hat{a}^{+2} - 4\hat{a}\hat{a}^+ + 2\,, \\ \hat{a}^2\hat{a}^{+2} &= \hat{a}^{+2}\hat{a}^2 + 4\hat{a}^+\hat{a} + 2\,. \end{aligned} \tag{C 9}$$

This again is to be compared with the corresponding formula from parameter differentiation

$$\hat{p}^m\hat{q}^n = \sum_{j=0}^{m} \frac{m!\,n!\,c^j\hat{q}^{n-j}\hat{p}^{m-j}}{j!\,(m-j)!\,(n-j)!}\,. \tag{C 10}$$

To express operator products in terms of the diagonal number operator, we need diagonal ordering expressions.

For $\hat{n} = \hat{a}^+\hat{a}$ we get

$$\begin{aligned} [\hat{a}^+\hat{a}, \hat{a}^m]_- &= -m\hat{a}^m \\ [\hat{a}^+\hat{a}, \hat{a}^{+m}]_- &= m\hat{a}^{+m} \end{aligned} \tag{C 11}$$

and by repeated application of this formula:

$$\hat{a}^m\hat{a}^{+m} = \prod_{p=1}^{m} (\hat{a}^+\hat{a} + p)\,, \tag{C 12}$$

$$\hat{a}^{+m}\hat{a}^m = \prod_{p=1}^{m} (\hat{a}^+\hat{a} + 1 - p)\,. \tag{C 13}$$

It was mentioned in the introduction that trace calculations are simplified by the characteristic function for the momentum-coordinate probability distribution of the harmonic oscillator. Though there exist a number of derivations, we give it for convenience in Messiah's [53] form:

$$\begin{aligned} \mathrm{Tr}\{\exp(-\beta\hat{\mathscr{H}}_0)\exp\{i\zeta(\gamma^*\hat{a}^+ + \gamma\hat{a})\}\} \\ = Z_0\exp\{-(\gamma^*\gamma/2)\zeta^2 R\}\,, \end{aligned} \tag{C 14}$$

$$R = \coth(\beta\hbar\omega/2)\,; \quad Z_0 = [2\sinh(\beta\hbar\omega/2)]^{-1}\,.$$

Expansion and comparison leads to traces of operator functions.

Example:

$$\mathrm{Tr}\{\exp(-\beta\hat{\mathscr{H}}_0)\,(\hat{a}^+ + \hat{a})^4\} = 3Z_0R^2\,. \tag{C 15}$$

Traces of powers of operators are also important; the generating function is:

$$\begin{aligned} \mathrm{GF} &= \mathrm{Tr}\{\exp(-\beta\hat{\mathscr{H}}_0)\exp(k_1\hat{a}^+)\exp(k_2\hat{a})\} \\ &= \mathrm{Tr}\{\exp(-\beta\hat{\mathscr{H}}_0)\exp(k_1\hat{a}^+ + k_2\hat{a})\exp(-k_1k_2/2) \\ &= Z_0\exp(k_1k_2W)\,, \end{aligned} \tag{C 16}$$

$W = (R-1)/2$ and

$$\begin{aligned} \mathrm{GF} &= \mathrm{Tr}\{\exp(-\beta\hat{\mathscr{H}}_0)\exp(k_2\hat{a})\exp(k_1\hat{a}^+)\} \\ &= Z_0\exp(k_1k_2W^*)\,, \quad W^* = (R+1)/2\,. \end{aligned} \tag{C 17}$$

Example:

$$\mathrm{Tr}\{\exp(-\beta\hat{\mathscr{H}}_0)\,\hat{a}^{+m}\hat{a}^m\} = m!\,W^m\,. \tag{C 18}$$

Application of the different ordering techniques leads to completely different looking expressions, which after tedious manipulations with hyperbolic functions can be brought to identical form.

[1] S. G. Frankiss and J. H. Green, Statistical Methods for Calculating Thermodynamic Functions. In: Thermodynamics I. A Specialist Periodical Report. The Chemical Soc. London 1973, p. 268.

[2] I. N. Godnev, Berechnung thermodynamischer Funktionen aus Moleküldaten, Deutscher Verlag, Berlin 1963.

[3] J. S. Rowlinson, The Perfect Gas. Pergamon Press, Oxford 1963.

[4] L. V. Gurvich et al., The Thermodynamic Properties of Individual Materials. Akad. Nauk. SSSR 1962.

[5] L. Haar, NBS J. of Research Phys. and Chem. **72 A,** 207 (1968).

[6] JANAF: Evaluation and Compilation of the Thermodynamic Properties. NBS Special Publ. **561**, 1581 (1979).
[7] M. Chase, J. R. Downey, and A. N. Syverud. Proc. of the 10th Materials Symposium, (1979), p. 1581.
[8] W. Witschel, Habilitationsschrift TU Braunschweig 1971.
[9] W. Witschel, J. Chem. Soc. Faraday Trans. II **70**, 1441 (1974).
[10] J. Bohmann, Diplomarbeit, Inst. Physik. Chemie TU Braunschweig 1975.
[11] A. D. Isaacson, D. G. Truhlar, K. Scanlon, and J. Overend, J. Chem. Phys. **75**, 3017 (1981).
[12] H. H. Nielsen, The Vibration-Rotation Energies of Molecules. Handbuch der Physik (S. Flügge, ed.), **38**, Springer-Verlag Berlin 1953, p. 173.
[13] I. Mills, Harmonic and Anharmonic Force Field Calculations. Theoretical Chemistry I. A Specialist Periodical Report. The Chemical Soc., London 1974, p. 110.
[14] I. Mills, Molecular Spectroscopy: Modern Research Vol. I (K. N. Rao and C. W. Matthews, eds.), Chapter 6, Acad. Press., New York 1972.
[15] G. D. Carney, L. L. Sprandel, and C. W. Kern, Adv. Chem. Phys. **37**, 305 (1978).
[16] G. Amat, H. H. Nielsen, and G. Tarrago, Rotation-Vibration of Polyatomic Molecules, M. Dekker, New York 1971.
[17] M. Reed and B. Simon, Methods of Modern Mathematical Physics II, Acad. Press, New York 1978.
[18] E. Calceti, S. Graffi, and M. Maioli, Comm. Math. Phys. **75**, 51 (1980).
[19] C. M. Bender and S. A. Orszag, Advanced Mathematical Methods for Scientists and Engineers, McGraw, New York 1978.
[20] T. Banks, C. M. Bender, and T. T. Wu, Phys. Rev. **D 8**, 3346 (1973).
[21] F. T. Hioe and E. Montroll, J. Math. Phys. **16**, 945 (1975). – F. T. Hioe, D. MacMillen, and E. Montroll, Phys. Reports **43**, 307 (1978). – F. T. Hioe, J. Chem. Phys. **69**, 204 (1978).
[22] D. W. Noid and R. A. Marcus, J. Chem. Phys. **67**, 559 (1979). – D. W. Noid, M. L. Koszykowski, M. Tabor, and R. A. Marcus, J. Chem. Phys. **72**, 6199 (1980).
[23] R. T. Swimm and J. B. Delos, in: Lecture Notes in Physics **93** "Stochastic Behaviour in Classical and Quantum Hamiltonian Systems" (G. Casati and J. Ford, ed.), Springer, Berlin 1979, p. 306.
[24] J. Bowman, J. Chem. Phys. **68**, 608 (1978).
[25] J. L. Durand and H. E. Brandmaier, The Effect of Higher Order Corrections to the Thermodynamic Properties of Polyatomic Molecules. In: Kinetics, Equilibria and Performances of High Temperature Systems (G. E. Bahn, ed.), Gordon and Breach, New York 1963.
[26] W. H. Evans, ibid. p. 151.
[27] M. D. Girardeau and R. M. Mazo, Adv. Chem. Phys. **24**, 187 (1973).
[28] A. Huber, in: Methods and Problems of Theoret. Phys. (J. E. Bowcock, ed.), North-Holland PC, Amsterdam 1970.
[29] H. Falk, Amer. J. Phys. **38**, 858 (1970).
[30] H. J. Korsch, J. Phys. A.: Math. Gen. **12**, 1521 (1979).
[31] W. Witschel and M. Wolfsberg, to be submitted to Chem. Phys. Letters.
[32] W. H. Miller, J. Chem. Phys. **55**, 3146 (1971). – W. H. Miller, J. Chem. Phys. **58**, 1664 (1973).
[33] V. S. Jorish, V. F. Baibuz, V. Y. Zitserman, and A. A. Zavalny, Chem. Phys. **18**, 257 (1976).
[34] G. J. Papadopoulos, J. Phys. A.: Math. Gen. **2**, 172 (1969).
[35] J. D. Doll and L. E. Myers, J. Chem. Phys. **71**, 2880 (1979).
[36] K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. **10**, 428 (1942).
[37] A. D. Isaacson and D. G. Truhlar, J. Chem. Phys. **75**, 4090 (1981).
[38] R. Serber, Phys. Rev. **43**, 1011 (1933).
[39] R. Peierls, Z. Phys. **80**, 763 (1933).
[40] S. Nakajima, Adv. Phys. **4**, 367 (1955).
[41] A. W. Saenz and O'Rourke, Rev. Mod. Phys. **27**, 381 (1955).
[42] P. Choquard, The Anharmonic Crystal. W. A. Benjamin, New York 1967.
[43] W. Witschel, Chem. Phys. Letters **2**, 349 (1968).
[44] S. Naya, Progr. Theor. Phys. **48**, 407 (1972).
[45] S. Naya and A. Siegel, Progr. Theor. Phys. **48**, 783 (1972).
[45 a] W. Witschel, B. Großwendt, and J. Bohmann, PTB Mitteilungen **87**, 3 (1977).
[46] J. Bohmann and W. Witschel, J. Chem. Soc. Faraday Trans. II, **74**, 2235 (1978).
[47] G. Singh and M. Wolfsberg, J. Chem. Phys. **62**, 4165 (1975). – C. Harvie, P. Bopp, and M. Wolfsberg, J. Chem. Phys. **72**, 6349 (1980).
[48] P. Lew and T. Ishida, Approx. Methods for the PF of Anharmonic Systems, DOE-Report, COO-3127-30.
[49] W. Witschel, Phys. Letters **77 A**, 107 (1980).
[50] V. Glaser, H. Grosse, and A. Martin, Comm. Math. Phys. **59**, 197 (1978).
[51] F. J. Rogers, Phys. Letters **61 A**, 358 (1977).
[52] B. Talukdar, M. Chatterji, and P. Banerjee, Pramana **13**, 15 (1979).
[53] A. Messiah, Quantum Mechanics I. North-Holland PC, Amsterdam 1964, p. 432.
[54] K. Fox, J. Quant. Spectrosc. Radiat. Transfer **10**, 1335 (1970). – A. Maue, Annalen der Physik **30**, 555 (1937).
[55] I. E. Viney, Proc. Cambridge Phil. Soc. **29**, 142 (1933).
[56] L. S. Kassel, J. Chem. Phys. **1**, 576 (1933).
[57] R. Kayser and J. E. Kilpatrick, J. Chem. Phys. **68**, 1511 (1978).
[58] C. van Winter, Physica **20**, 274 (1954).
[59] K. F. Stripp and J. G. Kirkwood, J. Chem. Phys. **19**, 1131 (1951).
[60] M. I. Kaplan, Sov. Phys. JETP **38**, 1260 (1974).
[61] A. R. Gordon, J. Chem. Phys. **2**, 65 (1934).
[62] W. Witschel, J. Quant. Spectrosc. Radiat. Transfer **25**, 463 (1981).
[63] K. D. Möller and W. G. Rothschild, Far-Infrared Spectroscopy. John-Wiley-Intersci. New York 1971.
[64] G. Vojta, Ann. Physik (7) **9**, 337 (1962).
[65] A. A. Zaitsev, Russ. J. Physik Chem. **36**, 799 (1962).
[66] M. I. Kaplan, Sov. Phys. High Temperature **17**, 976 (1980).
[67] W. Witschel, Chem. Phys. Letters **86**, 558 (1982).
[68] K. Kuchitsu and Y. Morino, Bull. Chem. Soc. Japan **38**, 805 (1965).
[69] W. Witschel, Special Topics in Statistical Thermodynamics; Lectures given in the spring term 1982, University of California Irvine, to be published.
[70] S. Weissman, J. T. Vanderslice, and R. Battino, J. Chem. Phys. **39**, 2226 (1963).