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1980 J. Phys. A: Math. Gen. 13 2735

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On the statistical mechanics of quartic type anharmonic oscillators, application of variational and perturbation methods

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Received 15 November 1978, in final form 21 January 1980

Abstract. The lower and upper bounds including variation of the frequency are calculated for the partition function of oscillators of the quartic type. They are shown to be fair approximations to the partition function calculated from eigenvalues given by Hioe and Montroll. The upper bound presents a very good high-temperature approximation which can be differentiated analytically giving also closed formulae for the thermodynamic functions H, E, S, C_p . Perturbation theory is discussed in terms of operator-free generating functions. As expected, it works well only for intermediate temperatures and for small anharmonicity. Using a technique by Fisher for convex functions, upper and lower bounds for the entropy are also calculated from the exact upper and lower bounds to the partition function.

1. Introduction

Working on problems in the theory of molecular quantum dynamics, we were interested in the level density of strongly anharmonic coupled oscillators. For high excitation energies this is a meaningful description. The level density and partition function are interrelated by a Laplace transform which can be evaluated numerically or, after a steepest-descent approximation, analytically. The problem reduces to the calculation of the partition function.

Eigenvalues can be calculated approximately only for low energies using matrix diagonalisation techniques. For high energies no general method existed to our knowledge, though semiclassical techniques look very promising (Hioe *et al* 1978, Powell and Percival 1979). It seems, therefore, more appropriate to avoid the calculation of eigenvalues and the summation of Boltzmann factors by methods which are applied directly to the partition function. We shall investigate subsequently variational and perturbation methods.

We consider as an example for the application of these techniques the quartic anharmonic oscillator with Hamiltonian

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{H}_1, \\ \hat{H}_0 &= \hat{p}^2/2m + \frac{1}{2}m\omega^2\hat{q}^2 = \hbar\omega(\hat{P}^2 + \hat{Q}^2),\end{aligned}\tag{1.1}$$

$$\hat{H}_1 = k_4 \hat{Q}^4 = \lambda \hbar \omega \hat{Q}^4, \quad k_4, \lambda > 0, \quad (1.2)$$

the standard model for anharmonic vibrations in quantum field theory, solid state and molecular physics. A large variety of analytical and numerical techniques for finding eigenvalues and eigenfunctions has been developed. Though Hioe and Montroll (1975), by a combination of analytical and numerical techniques, derived analytical expressions for the eigenvalues for different regions of the coupling constant λ , suitable for all applications, more than twenty articles have been published since then, dealing with other techniques.

The situation is different for the partition function. Of course one can sum the Boltzmann factors formed with the Hioe–Montroll eigenvalues numerically. This was done by Schwarz (1976) who derived by several unclear approximations analytical expressions for the thermodynamic functions A, S, E, C_v . Pant and Mitra (1979) gave an interpolation formula for the Hioe–Montroll eigenvalues and also derived a numerical partition function. Path integral methods were applied by Miller (1971) and by Jorish and Zitserman (1975, 1976) to the one- and two-dimensional quartic oscillator. A related but complicated technique was also applied by Mathews and Seshadri (1975) in the approximate evaluation of the anharmonic oscillator density matrix in terms of elliptic functions. All these techniques present difficulties for coupled anharmonic oscillator partition functions.

The present paper, therefore, aims at a test of variational and perturbation techniques for the partition function of quartic anharmonic oscillator type model systems. We check our calculations against the numerical partition function from Hioe–Montroll eigenvalues. For coupled systems only the recent important articles by Hioe (1976, 1977, 1978) are known. Their results will be discussed thoroughly in a forthcoming article by Bohmann (1980). The upper bound, which will be derived subsequently, is a good approximation to the high-temperature partition function. As it is given for the quartic oscillator model system in closed form, high-temperature formulae for the thermodynamic functions can be easily derived. Though great progress in trace inequalities for the entropy of coupled systems has been made in recent years, no direct trace inequality for the entropy was found in the literature. A method by Ruelle (1963) and Fisher (1965) will be used to derive upper and lower bounds to the entropy from upper and lower bounds to the partition function. In a previous paper we showed that thermodynamic perturbation theory in the Schwinger form can be used in the evaluation of molecular partition functions (Witschel *et al* 1977). We shall, therefore, discuss generating functions for arbitrary order of the perturbing power of coordinate or momentum and of the order of perturbation theory. It is the only generally applicable method for anharmonic oscillator systems and it takes accidental resonances like Fermi or Darling–Dennison resonance exactly into account. This is important from the point of view of irregularity of spectra, which was discussed recently by Powell and Percival (1979).

The paper is organised as follows. Section 2 sketches the trace inequalities, Bloch's theorem, perturbation theory and the different model Hamiltonians. In § 3 we discuss the lower bounds and in § 4 the upper bounds. Section 5 gives the results for the perturbation theory. In § 6 we derive exact upper and lower bounds to the entropy using the Ruelle–Fisher technique. The extended numerical calculations are discussed in § 7. A short Appendix gives, for convenience, the necessary formulae from the theory of special functions.

2. Trace inequalities, Bloch's theorem, perturbation theory and model Hamiltonians

2.1. Trace inequalities as upper and lower bounds

Trace inequalities are often used in the calculation of the partition function, in the following abbreviated by PF. As a good review is available (Girardeau and Mazo 1973) we do not duplicate the references but only add some important results. Breitenecker and Grumm (1972) treated the upper or Golden–Thompson inequality in detail. Further work was done by Lieb and co-authors (1973a, b, Lieb and Ruskai 1973a, b), who were mainly interested in the sub-additivity of the entropy and in the Wigner–Yanase conjecture. In this connection the comprehensive review by Wehrl (1978) should be consulted. A further interesting development was given recently by Leschke (1979) who derived upper and lower bounds to the PF of boson systems using Feynman path integrals. We can summarise these recent results: no direct trace inequalities are available in the literature for S or C_v .

For the lower bound the Gibbs–Bogoliubov inequality is used. We shall add to the list of references by Girardeau and Mazo a comprehensive review article by Falk (1970) summarising the work on this inequality and its classical counterpart. The Hamiltonian \hat{H} can be split quite arbitrarily into two parts \hat{H}_0 and \hat{H}_1 , where \hat{H}_1 , in contrast to perturbation theory, need not be small. The inequality reads

$$Z = \text{Tr}[\exp(-\beta\hat{H})] \geq Z_0 \exp(-\beta\langle\hat{H}_1\rangle_0) \tag{2.1}$$

where $Z_0 = \text{Tr}[\exp(-\beta\hat{H}_0)]$ and $\beta = (k_B T)^{-1}$. $\langle\hat{H}_1\rangle_0$ is the thermal average of \hat{H}_1 formed with \hat{H}_0 ,

$$\langle\hat{H}_1\rangle_0 = Z_0^{-1} \text{Tr}[\hat{H}_1 \exp(-\beta\hat{H}_0)]. \tag{2.2}$$

The upper bound or Golden–Thompson inequality is

$$Z \leq \text{Tr}[\exp(-\beta\hat{H}_0) \exp(-\beta\hat{H}_1)]. \tag{2.3}$$

By a suitable definition variational parameters can be built in, which can be varied numerically or analytically and which lead to improved upper and lower bounds. In treating operator traces one must be careful, as by invalid trace operations wrong results may occur. It is especially dangerous to use the cyclic invariance of the trace or to introduce commutators.

2.2. Characteristic function of the Bloch theorem

Bloch's theorem (Messiah 1964) for the probability distribution of a linear combination of the coordinate and momentum of the harmonic oscillator states that it is a Gaussian. The characteristic function of this distribution is useful in the calculation of thermal averages of arbitrary powers of coordinate and momentum. We write the characteristic function $\Phi(t)$ in a form useful for our applications.

$$Z_0\Phi(t) = \text{Tr}\{\exp[it(\alpha_1\hat{Q} + \alpha_2\hat{P})] \exp(-\beta\hat{H}_0)\} = \exp[-t^2(\alpha_1^2 + \alpha_2^2)R/4] \tag{2.4}$$

with

$$Z_0 = [2 \sinh(\epsilon/2)]^{-1}, \tag{2.5}$$

$$R = \coth(\epsilon/2), \tag{2.6}$$

$$\epsilon = \beta \hbar \omega, \quad \beta = (k_B T)^{-1}. \tag{2.7}$$

2.3. Thermodynamic perturbation theory

Only for a few cases like the harmonic oscillator or the two-dimensional Ising model is it possible to evaluate the PF exactly. In many cases a form of thermodynamic perturbation theory is used. Different formulations are compared by Saenz and O'Rourke (1955) who attributed the expansion

$$\begin{aligned} & \text{Tr}\{\exp[-\beta(\hat{H}_0 + \hat{H}_1)]\} \\ &= \text{Tr}[\exp(-\beta\hat{H}_0)] - \beta \text{Tr}[\hat{H}_1 \exp(-\beta\hat{H}_0)] \\ &+ (\beta^2/2) \int_0^1 ds_1 \text{Tr}\{\hat{H}_1 \exp[-\beta\hat{H}_0(1-s_1)]\hat{H}_1 \exp(-\beta\hat{H}_0s_1)\} \mp \dots \tag{2.8} \\ &+ \frac{(-\beta)^{n+1}}{(n+1)} \int_0^1 s_1^{n-1} ds_1 \int_0^1 s_2^{n-2} ds_2 \dots \int_0^1 ds_n \text{Tr}\{\hat{H}_1 \exp[-\beta\hat{H}_0(1-s_1)] \\ &\times \hat{H}_1 \exp[-\beta\hat{H}_0s_1(1-s_2)] \dots \hat{H}_1 \exp[-\beta\hat{H}_0s_1s_2 \dots s_n]\} + \dots \end{aligned}$$

to Schwinger. The ordering transformations can be performed with the well known Hausdorff formula (Messiah 1964)

$$\begin{aligned} & \exp(\alpha\hat{A})\hat{B} \exp(-\alpha\hat{A}) \\ &= \hat{B} + \alpha[\hat{A}, \hat{B}]_- + (\alpha^2/2!)[\hat{A}, [\hat{A}, \hat{B}]_-] + \dots \tag{2.9} \\ &= \sum_{m=0}^{\infty} (\alpha^m/m!)\{\hat{S}^m, \hat{B}\}_-. \end{aligned}$$

This type of thermodynamic perturbation theory is closely related to the disentangling of exponential operators. A special example for a related path integral-perturbation method applied to coupled anharmonic oscillators was given by Papadopoulos (1969).

2.4. Anharmonic oscillators of the quartic type

$$\text{H1:} \quad \hat{H} = \hat{p}^2/2m + \frac{1}{2}m\omega^2 \hat{q}^2 + k_4 \hat{q}^4 = \frac{1}{2}\hbar\omega (\hat{P}^2 + \hat{Q}^2) + \lambda \hbar\omega \hat{Q}^4. \tag{2.10}$$

This is the standard quartic anharmonic oscillator (equation (1)) which will be used extensively below.

$$\text{H2:} \quad \hat{H} = \sum_{i=1}^2 \hat{H}_{0i} + \lambda_{12} \hat{q}_1^2 \hat{q}_2^2, \tag{2.11}$$

$$\hat{H}_{0i} = \hat{p}_i^2/2m + \frac{1}{2}m\omega_i^2 \hat{q}_i^2. \tag{2.12}$$

This Hamiltonian was discussed in connection with the regular and irregular spectra of quantum dynamical systems by Pomphrey (1974), but it is of less importance in theory, as it is a system of coupled harmonic oscillators.

$$\text{H3:} \quad \hat{H} = \sum_{i=1}^2 \hat{H}_{0i} + \lambda_1 \hat{q}_1^4 + \lambda_2 \hat{q}_2^4 + \lambda_{12} \hat{q}_1 \hat{q}_2. \tag{2.13}$$

Some authors (see Beck 1976) use this Hamiltonian in the theory of structural phase

transitions. More interest has been found in

$$H4: \quad \hat{H} = \sum_{i=1}^2 \hat{H}_{0i} + \lambda_1 \hat{q}_1^4 + \lambda_2 \hat{q}_2^4 + \lambda_{12} \hat{q}_1^2 \hat{q}_2^2 \quad (2.14)$$

which was treated extensively by Hioe (1977) and by Hioe *et al* (1978) who derived not only the low lying eigenvalues but also, from WKB-type calculations, the level density at high energies.

A system which was, to our knowledge, not discussed in the literature is

$$H5: \quad \hat{H} = \sum_i \hat{H}_{0i} + \left(\sum_i k_i \hat{q}_i \right)^4. \quad (2.15)$$

It is necessary to investigate the eigenvalues of this Hamiltonian in the future.

3. Lower bound with variation

Following a suggestion by Feynman (1972), the lower bound to the partition function of an anharmonic oscillator can be written in a form allowing a later variation of the frequency and the equilibrium position of the harmonic reference oscillator. For symmetric potentials the latter variation does not improve the bound, whereas for asymmetric potentials it gives a strong improvement.

We consider the quartic anharmonic oscillator (QA), equation (1). A term $(m\omega^{*2}/2)\hat{q}^2$ is added and subtracted. The Hamiltonian now reads

$$\hat{H}_0^* = (\hbar\omega^*/2)(\hat{P}^{*2} + \hat{Q}^{*2}), \quad (3.1)$$

$$\hat{H}_1^* = \hbar\omega(\gamma\hat{Q}^{*2} + \Lambda\hat{Q}^{*4}), \quad (3.2)$$

with

$$\gamma = (\omega^2 - \omega^{*2})/2\omega\omega^*, \quad (3.3)$$

$$\Lambda = \lambda(\omega/\omega^*)^2. \quad (3.4)$$

The thermal average $\langle \hat{H}_1^* \rangle_0$ is calculated in the basis of \hat{H}_0^* , using the characteristic function of § 2.3. As a function of ω^* the lower bound is

$$Z \geq Z_{LB} = Z_0^* \exp[-\epsilon(\frac{1}{2}\gamma R^* - \frac{3}{4}\Lambda R^{*2})] \quad (3.5)$$

with

$$Z_0^* = [2 \sinh(\beta\hbar\omega^*/2)]^{-1}, \quad (3.6)$$

$$R^* = \coth(\beta\hbar\omega^*/2). \quad (3.7)$$

Unfortunately ω^* can only be varied numerically as it occurs in the transcendental functions R^* and Z_0^* . For unsymmetrical potentials containing even and odd powers of Q , the simultaneous and independent variation of both the equilibrium position and the frequency ω^* leads to coupled transcendental equations. For some special potentials the variation of the equilibrium position can first be performed algebraically followed by a numerical variation of ω^* . For the Morse oscillator we treated the mathematics and the numerical variations in detail (Bohmann and Witschel 1978).

The lower bounds including variations of the frequencies can be evaluated for the Hamiltonians H1–H5. We vary the frequencies numerically until they show an

extremum. In any case this is an improvement of the bounds though, possibly, we did not obtain the best values for the variational parameters. In addition it should be remarked that we calculated lower bounds for Hamiltonians of the types

$$\hat{H} = \hat{H}_0 + A \exp(-B\hat{q}^2) + C \exp(-D\hat{q}^4) \quad (3.8)$$

and

$$\hat{H} = \sum_i \hat{H}_{0i} + \sum_{ijk} \lambda_{ijk} \hat{q}_i \hat{q}_j \hat{q}_k + \sum_{ijkl} \lambda_{ijkl} \hat{q}_i \hat{q}_j \hat{q}_k \hat{q}_l, \quad (3.9)$$

the Nielsen Hamiltonian of molecular spectroscopy. A special example of this Hamiltonian is the Henon-Heiles Hamiltonian,

$$\hat{H} = \sum_{i=1}^2 \hat{H}_{0i} + \lambda_1 \hat{q}_1^3 + \lambda_2 \hat{q}_1 \hat{q}_2^2, \quad (3.10)$$

the standard model in the recent important investigations of regular and irregular spectra and quantum ergodicity (Powell and Percival 1979). In the latter case we varied frequency and internuclear distance. As operators belonging to different normal vibrations commute, the calculations can be performed after decoupling. For example, we use H5 for two coupled oscillators,

$$\hat{H} = \hat{H}_0^{(1)} + \hat{H}_0^{(2)} + (\lambda_1 \hat{Q}_1 + \lambda_2 \hat{Q}_2)^4, \quad (3.11)$$

where the indices refer to the normal modes '1' and '2'. As a function of the two variation parameters ω_1^* and ω_2^* the lower bound reads

$$Z \geq Z_0^{*(1)} \exp(-\beta \langle \hat{H}_1^{(12)} \rangle_0) \quad (3.12)$$

with

$$\begin{aligned} \langle \hat{H}_1^{(12)} \rangle_0 = & 3\lambda_1^4 (\omega_1 R_1^*/2\omega_1^*)^2 + 3\lambda_2^4 (\omega_2 R_2^*/2\omega_2^*)^2 + \hbar(\omega_1^2 - \omega_1^{*2}) R_1^*/4\omega_1^* \\ & + \hbar(\omega_2^2 + \omega_2^{*2}) R_2^*/4\omega_2^* + 3\lambda_1^2 \lambda_2^2 R_1^* R_2^* \omega_1 \omega_2 / 2\omega_1^* \omega_2^*. \end{aligned} \quad (3.13)$$

4. Upper bounds to the partition function for various model systems

4.1. Illustration of the technique and application to the quartic anharmonic oscillator

Including the variation parameter ω^* , the upper bound to the partition function of the quartic anharmonic oscillator is given by

$$Z_{\text{UB}} = \text{Tr}\{\exp(-\beta \hat{H}_0^*) \exp[-\epsilon(\Lambda \hat{Q}^{*4} + \gamma \hat{Q}^{*2})]\}. \quad (4.1)$$

Using the well known Laplace transform for a Gaussian (Gradshteyn and Ryzhik 1965, no. 3.323-2) twice, we obtain a form of the trace suitable for the application of the characteristic function of § 2.2.

$$Z_{\text{UB}} = \frac{1}{\pi} \int_{-\infty}^{\infty} dx e^{-x^2} \int_{-\infty}^{\infty} dy e^{-y^2} \text{Tr}\{\exp(-\beta \hat{H}_0^*) \exp[-2iy(2ix\sqrt{\epsilon\Lambda + \epsilon\gamma})^{1/2} \hat{Q}^*]\}. \quad (4.2)$$

The trace is evaluated and the first back-transformation performed:

$$Z_{UB} = \frac{1}{\pi} Z_0^* \int_{-\infty}^{\infty} dx e^{-x^2} \int_{-\infty}^{\infty} dy e^{-y^2} \exp[-y^2(2ix\sqrt{\epsilon\Lambda} + \gamma)R^*] \tag{4.3}$$

$$= Z_0^* \pi^{-1/2} \int_{-\infty}^{\infty} dy \exp[-y^2(1 + \epsilon\gamma R^*) - y^4 \epsilon\Lambda R^{*2}]. \tag{4.4}$$

This integral is known (Gradshteyn and Ryzhik 1965, no. 3.323–3) and has already been used in connection with the classical partition function of the quartic anharmonic oscillator and with a certain type of quantum field theory. The final result is

$$Z_{UB} = Z_0^* \sqrt{2\zeta/\pi} (1 + \epsilon\gamma R^*)^{-1/2} \exp(\zeta) K_{1/4}(\zeta) \tag{4.5}$$

with

$$\zeta = (1 + \epsilon\gamma R^*)^2 / 8\epsilon\Lambda R^{*2}. \tag{4.6}$$

According to Abramowitz and Stegun (1965, p 692), the modified Bessel function $K_{1/4}(\zeta)$ can be expressed in terms of the parabolic cylinder function $D_{-1/2}(\zeta')$ according to

$$U(0, x) = \pi^{-1/2} (x/2)^{1/2} K_{1/4}(x^2/4), \quad U(a, x) = D_{-a-1/2}(x). \tag{4.7}$$

This formulation has the advantage that the extended tables of $U(a, x)$ given by Abramowitz and Stegun (1965, p 702) and the recursion-derivation formulae for the parabolic cylinder function can be used. As the upper bound including variation of the frequency is a very good high-temperature approximation, the thermodynamic functions H, E, S, C_v can be easily derived from equation (4.5). We do not give the final formulae as they can be written down immediately, but are very lengthy. We give the entropy without variation of the frequency for high temperatures in table 5.

Finally, it should be remarked that the result can also be found from a direct integration of the diagonal harmonic oscillator density matrix $\rho(x, x; \beta)$. The transformation technique seems to be more appropriate for coupled anharmonic oscillators.

4.2. Generalisation to coupled anharmonic oscillators

This result can be easily generalised to coupled anharmonic oscillators of the type H5, which after a transformation to normal coordinates reads

$$\hat{H}_0 = \sum_i \hat{H}_{0i} \quad \text{with} \quad \hat{H}_{0i} = \frac{1}{2}\hbar\omega_i(\hat{P}_i^2 + \hat{Q}_i^2), \tag{4.8}$$

$$\hat{H}_1 = \left(\sum_k \lambda_k \hat{Q}_k \right)^4.$$

The same integral transforms and trace technique are applied. After the second Laplace transform, the argument of the exponential is linear in Q_k , so that the traces can be calculated separately according to equation (4.4).

As this Hamiltonian has not found application in physics as yet, we only give the result without variation of the frequency. The anharmonic part H_1 ,

$$\hat{H}_1 = (\lambda_1 \hat{Q}_1 + \lambda_2 \hat{Q}_2)^4, \tag{4.9}$$

gives, with the abbreviation $F_k = \beta^{1/4} \lambda_k$, the upper bound

$$\begin{aligned} Z_{\text{UB}} &= \text{Tr}\{\exp[-\beta(\hat{H}_0^{(1)} + \hat{H}_0^{(2)})] \exp[-(F_1 \hat{Q}_1 + F_2 \hat{Q}_2)^4]\} \\ &= \pi^{-1} \int_{-\infty}^{+\infty} dx e^{-x^2} \int_{-\infty}^{+\infty} dy e^{-y^2} \text{Tr}\{\exp[-\beta(\hat{H}_0^{(1)} + \hat{H}_0^{(2)})] \\ &\quad \times \exp[-2iy \sqrt{2ix} (F_1 \hat{Q}_1 + F_2 \hat{Q}_2)]\}. \end{aligned} \quad (4.10)$$

Using equation (4.2), this is

$$Z_{\text{UB}} = \pi^{-1} \int_{-\infty}^{+\infty} dx e^{-x^2} \int_{-\infty}^{+\infty} dy e^{-y^2} Z_0 \exp(-2ixy^2 A) \quad (4.11)$$

with

$$Z_0 = Z_0^{(1)} Z_0^{(2)}, \quad (4.12)$$

$$A = R^{(1)} F_1^2 + R^{(2)} F_2^2. \quad (4.13)$$

The back-transformations are identical to the one-dimensional case, leading to

$$Z_{\text{UB}} = Z_0 (2\pi^{1/2} A)^{-1} \exp[(8A^2)^{-1}] K_{1/4}[(8A^2)^{-1}]. \quad (4.14)$$

4.2.1. Type H2. The Hamiltonian H2 is used in the ordinary coordinate representation. For a special choice of λ_{12} it was used as a model system for irregularity by Pomphrey (1974). We derive the upper bound for $\lambda_{12} > 0$, using the diagonal harmonic oscillator density matrix

$$\rho(q, q; \beta) = a \exp(-b\hat{q}^2), \quad (4.15)$$

$$a = \left(\frac{m\omega}{2\pi\hbar \sinh\beta\hbar\omega} \right)^{1/2}, \quad b = \frac{m\omega^2}{\hbar} \tanh(\beta\hbar\omega/2), \quad (4.16)$$

and consider the upper bound

$$Z_{\text{UB}} = \text{Tr}\{\exp[-\beta(\hat{H}_{01} + \hat{H}_{02})] \exp(-\beta\lambda_{12}\hat{q}_1^2\hat{q}_2^2)\} \quad (4.17)$$

as thermal average, calculated with $\rho(q, q; \beta)$:

$$\begin{aligned} Z_{\text{UB}} &= a_1 a_2 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dq_1 dq_2 \exp(-b_1 q_1^2 - b_2 q_2^2 - \beta\lambda_{12} q_1^2 q_2^2) \\ &= a_1 a_2 \int_{-\infty}^{+\infty} dq_1 \exp(-b_1 q_1^2) (b_2 + \beta\lambda_{12} q_1^2)^{-1/2}. \end{aligned} \quad (4.18)$$

This integral is known (A3). It leads to

$$\begin{aligned} Z_{\text{UB}} &= a_1 a_2 (\beta\lambda_{12})^{-1/2} \exp(-b_3^2 b_1/2) K_0(b_3^2 b_1/2), \\ b_3^2 &= b_2 (\beta\lambda_{12})^{-1}. \end{aligned} \quad (4.19)$$

Thermodynamic functions as high-temperature approximations can be calculated using the derivation–recursion relations for modified Bessel functions.

4.2.2. Types H3 and H4. For both types the upper bound can be calculated by the transformation technique (Bohmann 1979). Unfortunately the final back-transformation cannot be performed analytically. After a substitution in terms of polar coordinates it remains to solve a simple integral numerically. As the calculations are

more complicated and as it is necessary to compare the numerical results to the important work of Hioe and Montroll on coupled anharmonic oscillators, we postpone these calculations to a later paper. It should be mentioned that expansion of the coupling terms $\lambda_{12}x_1x_2$ and $\lambda_{12}x_1^2x_2^2$ in a power series and application of $\rho(x, x; \beta)$ as in the preceding case leads to oscillating divergent series, which, however, may be summable according to the techniques discussed by Bender and Orszag (1978).

5. Thermodynamic perturbation theory for the QA

It has already been mentioned that in contrast to the Rayleigh–Schrödinger theory of the QA-eigenvalues (Simon 1970, Graffi and Grecchi 1978) nothing is known on the high-order behaviour of the thermodynamic perturbation theory. A disadvantage in a previous formulation was that the formulae contain non-ordered products of boson creation and annihilation operators, leading to complicated operator ordering expressions. Using the Bloch theorem, it is easy to give generating functions for arbitrary powers of the coordinate (or momentum) in the perturbation theory. They are free of non-commuting operators and present the simple but tedious algebraic-combinatorial problem of comparing the coefficients of equal powers of an ordering parameter. We plan a systematic investigation of the higher-order terms with respect to convergence and summability with the techniques given by Bender and Orszag (1978). We show the first- and second-order terms as an example. We have

$$\text{Tr}\{\exp[-\beta(\hat{H}_0 + \hat{H}_1)]\} = P(0) + P(1) + P(2) + \dots \tag{5.1}$$

$P(1)$ presents no difficulties and will be written down subsequently, whereas in $P(2)$ the ordering integration appears for the first time.

$$P(2) = \frac{1}{2}(\lambda \hbar \omega \beta)^2 \text{Tr}\left(\int_0^1 ds_1 \exp[-\beta \hat{H}_0(1 - s_1)] \hat{Q}_4 \exp(-\beta \hat{H}_0 s_1) \hat{Q}^4\right). \tag{5.2}$$

Using the occupation number representation

$$\hat{Q} = 2^{-1/2}(\hat{a}^+ + \hat{a}) \quad \text{with} \quad [\hat{a}, \hat{a}^+]_- = 1 \tag{5.3}$$

and the Hausdorff transformation (equation (2.9)), we have

$$P(2) = (\lambda^2 \epsilon^2 / 32) \text{Tr}\left(\int_0^1 ds_1 \exp(-\beta \hat{H}_0) [\hat{a}^+ \exp(\beta \hbar \omega s_1) + \hat{a} \exp(-\beta \hbar \omega s_1)]^4 (\hat{a}^+ + \hat{a})^4\right). \tag{5.4}$$

Instead of performing normal ordering, one writes the generating function $G(2)$ as

$$G(2) = \text{Tr}\{\exp(-\beta \hat{H}_0) \exp[k_1(\hat{a}^+ \alpha_1^* + \hat{a} \alpha_1)] \exp[k_2(\hat{a}^+ + \hat{a})]\} \tag{5.5}$$

where k_1, k_2 are ordering parameters and

$$\alpha_1^* = \exp(+\beta \hbar \omega s_1), \quad \alpha_1 = \exp(-\beta \hbar \omega s_1).$$

Application of the Baker–Campbell–Hausdorff formula leads exactly to the form of the characteristic function (equation (2.4)):

$$\begin{aligned} G(2) &= \text{Tr}\{\exp[(k_1 \alpha_1^* + k_2) \hat{a}^+ + (k_1 \alpha_1 + k_2) \hat{a}] \exp(-\beta \hat{H}_0) \exp[k_1 k_2 (\alpha_1 - \alpha_1^*) / 2]\} \\ &= Z_0 \exp[R(k_1 \alpha_1^* + k_2)(k_1 \alpha_1 + k_2) / 2] \exp[k_1 k_2 (\alpha_1 - \alpha_1^*) / 2]. \end{aligned} \tag{5.6}$$

Expansion and comparison leads to

$$P(0) = Z_0, \quad P(1) = -3\epsilon\lambda R^2 Z_0/4, \quad (5.7)$$

$$P(2) = Z_0[(\epsilon\lambda)^2/32]\{9R^4 + 18R^2[(R-1)^2 Y(2\omega) + 2(R^2-1) \\ + (R+1)^2 Y(-2\omega)] + \frac{3}{2}[(R-1)^4 Y(4\omega) + (R+1)^4 Y(-4\omega) \\ + 4(R+1)(R-1)^3 Y(2\omega) + 4(R-1)(R+1)^3 Y(-2\omega) + 6(R^2-1)^2]\}. \quad (5.8)$$

We give the results for second-order perturbation theory in comparison to variational results with

$$Y(z) = [\exp(\beta \hbar z) - 1]/\beta \hbar z. \quad (5.9)$$

Higher-order terms have a similar symmetric structure like $P(2)$ but the calculation of the coefficients is tedious. Preliminarily it should be noted that for very high temperatures corresponding to small β the series seem to diverge, as the third-order term is much larger than the second. For intermediate temperatures and not too large anharmonicity, the third-order term is smaller than $P(2)$. No final conclusion can be drawn as yet. As, to second order, it can be shown explicitly that the Schwinger expansion corresponds to Rayleigh-Schrödinger perturbation theory, it may be possible to apply similar summation techniques.

6. The entropy function for the quartic anharmonic oscillator

Good approximations for the partition function Z are interesting from a theoretical point of view, but from a practical point of view it is necessary to know bounds to the thermodynamic functions S, C_p, \dots . Though these quantities can be expressed in terms of the first and second derivatives of the free energy $F = -(1/\beta) \ln Z$ with respect to β , derivatives of the bounds to Z do not lead necessarily to bounds to S, C_p, \dots . For example, the bounds to Z can show severe oscillations so that their derivatives do not resemble the behaviour of the derivatives of Z . Direct inequalities for these thermodynamic functions applicable to systems with perturbations are not known. However, for the special case of convex functions, it was shown by Ruelle (1963) and Fisher (1965) how bounds to the first derivative can be obtained from bounds to the original function. In the derivation of bounds to the entropy function of the quartic anharmonic oscillator we follow the way outlined by Fisher.

The entropy function in a dimensionless form can be expressed in terms of the free energy functions as

$$s(\beta) = (1/k_B)S = \beta^2 \partial F / \partial \beta. \quad (6.1)$$

As the following relation holds,

$$\partial^2 F / \partial \beta^2 \leq 0, \quad (6.2)$$

$F(\beta)$ is a convex function in the sense of Fisher, and the upper and lower bounds to $s(\beta)$ at a point $\beta = \beta_0$ can be taken immediately from his article:

$$s(\beta_0) \geq s_{LB}(\beta_0) = \beta_0^2 [F_{LB}(\beta_1) - F_{UB}(\beta_0)] / (\beta_1 - \beta_0), \quad \beta_1 > \beta_0, \quad (6.3)$$

$$s(\beta_0) \leq s_{UB}(\beta_0) = \beta_0^2 [F_{UB}(\beta_0) - F_{LB}(\beta_2)] / (\beta_0 - \beta_2), \quad \beta_2 < \beta_0, \quad (6.4)$$

where F_{UB} and F_{LB} are given by

$$F_{UB}(\beta) = -(1/\beta) \ln Z_{LB}(\beta), \tag{6.5}$$

$$F_{LB}(\beta) = -(1/\beta) \ln Z_{UB}(\beta). \tag{6.6}$$

By variation of β_1 and β_2 respectively, upper and lower bounds to the entropy function can be calculated. Unfortunately, these variations have to be performed numerically so that the bounds cannot be given in analytical form.

Approximations to the entropy function can be obtained from approximations to the partition function. With $F = -(1/\beta) \ln Z$ it follows from equation (5.1) that

$$s = \ln Z - \beta(1/Z)\partial Z/\partial\beta. \tag{6.7}$$

For intermediate and high temperatures the exact upper bound to Z is shown in the following numerical calculations to be a good approximation to the PF, becoming better and better with increasing temperature. By differentiation of the upper bound and insertion in the preceding equation we obtain an approximate analytical result for S_I :

$$\begin{aligned} S_I = \ln Z_{UB} + \frac{1}{2}\beta\hbar\omega^*R^* + \epsilon\gamma(R^*/2 - \beta\hbar\omega^*Z_0^{*2})/(1 + \epsilon\gamma R^*) \\ + [\frac{3}{4} + \zeta - \zeta K_{5/4}(\zeta)/K_{1/4}(\zeta)][2\epsilon\gamma(2\beta\hbar\omega^*Z_0^{*2} - R^*)/(1 + \epsilon\gamma R^*) \\ + (R^* - 4\beta\hbar\omega^*Z_0^{*2})/R^*]. \end{aligned}$$

To evaluate this equation one has to look for a minimum of Z_{UB} with respect to ω^* by numerical variation. This ω^* -value is inserted in the preceding equation. For simplicity we took $\omega^* = \omega$ and for Z_{UB} a form which could be manipulated more easily by substituting the Bessel function by the parabolic cylinder function according to equation (4.7).

We used for the parabolic cylinder functions the tables given by Abramowitz and Stegun and five-point Lagrange interpolation. It also follows that $H, E, C_v \dots$ can be calculated in analytical form using Z_{UB} with and without variation of the frequency.

7. Numerical results and discussion

7.1. Results for the PF

First we want to point out the way we did the numerical calculations. The lower as well as the upper bound for both the quartic anharmonic oscillators and the two quartic coupled oscillators are analytical functions of the variation parameters ω^* and ω_1^*, ω_2^* respectively. Because of the complex structure of these functions, maxima of the lower bounds and minima of the upper bounds with respect to the variation parameters cannot be given in closed form. Therefore, we varied the frequencies numerically, looking for improved values of the bounds. Though we cannot claim these improved bounds to be the optimal ones, the gap between the still exact bounds becomes narrower by this procedure. For one-dimensional cases the transcendental equation for ω^* can be solved by iteration, but for coupled oscillators we get coupled transcendental equations making the calculations complicated.

Results of the numerical evaluation of different approximations to the partition function of the quartic anharmonic oscillator are shown in tables 1 and 2 in terms of a reduced inverse temperature $\epsilon = \beta\hbar\omega$ and of the anharmonicity constant λ . One sees that the bounds are improved considerably by the variation of the frequency. The

agreement with the numerical partition function from the Hioe and Montroll eigenvalues is quite good even for large anharmonicity. The values calculated from the corrected formula for the free energy given by Schwarz (1976) are reasonable only for high temperatures and large anharmonicities. From the results of table 1 it follows that for small and intermediate anharmonicity and for intermediate and high temperatures the arithmetic mean of the upper and lower bounds is a good approximation to the partition function. As the lower bound can be calculated also for asymmetric anharmonicity and for coupled oscillators, we suggest the lower bound as a fair approximation for calculations of level densities of complex oscillator systems.

We calculated the PF of the QA also by second-order perturbation theory and compared the result with the upper and lower bounds, and, where possible, also to the numerical PF from the Hioe-Montroll eigenvalues. As we expected from previous calculations of the molecular PF (Witschel *et al* 1977), thermodynamic perturbation theory is very useful for intermediate temperatures and not too strong anharmonicity. For intermediate anharmonicity and high temperatures the results fall out of the exact bounds, leading to meaningless numbers which are wrong by a factor of 10^2 .

Results for the system of two coupled quartic anharmonic oscillators defined by equation (3.8) are known neither from analytical nor from numerical calculations. Therefore, the results of table 3 for large and of table 4 for small anharmonicity and

Table 1. Comparison of different bounds to the PF of the QA. Z_{LB} = lower bound; Z_{LB}^{Δ} = lower bound with variation of the frequency; Z_n = numerical PF from the Hioe-Montroll eigenvalues; Z_s = approximate PF by Schwarz (misprint corrected); Z_{UB}^{Δ} = upper bound including variation of the frequency; Z_{UB} = upper bound; $\epsilon = \beta \hbar \omega$, λ = anharmonicity constant.

ϵ	λ	Z_{LB}	Z_{LB}^{Δ}	Z_n	Z_s	Z_{UB}^{Δ}	Z_{UB}
0.2	0.01	4.292 1	4.505 0	—	—	4.529 5	4.530 3
0.2	0.1	1.102 7	3.393 3	—	—	3.472 8	3.479 2
0.2	0.5	0.002 6	2.488 9	2.573 1	1.101 0	2.577 9	2.593 0
0.2	1.0	0.000 001	2.137 2	2.215 3	1.192 0	2.222 5	2.242 5
0.2	10.0	* * *	1.218 8	1.266 4	1.071 2	1.282 7	1.323 9
0.6	0.01	1.557 1	1.570 0	—	—	1.572 3	1.572 8
0.6	0.1	0.966 2	1.295 8	—	—	1.316 0	1.324 3
0.6	0.5	0.115 9	0.982 9	1.007 3	0.642 6	1.015 5	1.041 2
0.6	1.0	0.008 2	0.843 5	0.866 1	0.614 6	0.878 5	0.915 1
0.6	10.0	* * *	0.436 0	0.448 5	0.345 1	0.498 7	0.556 8
1.0	0.01	0.926 4	0.929 7	—	—	0.930 5	0.931 0
1.0	0.1	0.675 3	0.790 8	—	—	0.801 4	0.810 1
1.0	0.5	0.165 7	0.600 2	0.612 5	0.147 0	0.621 9	0.652 7
1.0	1.0	0.028 6	0.507 7	0.518 8	0.179 9	0.532 9	0.578 3
1.0	10.0	* * *	0.220 2	0.226 9	0.243 1	0.299 7	0.357 6
2.0	0.01	0.414 6	0.415 2	—	—	0.415 5	0.415 8
2.0	0.1	0.328 5	0.356 1	—	—	0.361 3	0.370 0
2.0	0.5	0.116 8	0.254 5	0.259 6	0.062 95	0.269 2	0.303 8
2.0	1.0	0.032 0	0.200 5	0.205 0	0.073 52	0.226 4	0.271 0
2.0	10.0	* * *	0.046 8	0.049 3	0.119 2	0.127 3	0.169 9
5.0	0.01	0.079 52	0.079 61	—	—	0.079 72	0.079 98
5.0	0.1	0.056 22	0.060 85	—	—	0.063 40	0.069 10
5.0	0.5	0.012 04	0.029 95	0.031 19	—	0.042 66	0.055 36
5.0	1.0	0.001 75	0.017 21	0.018 06	—	0.035 87	0.048 96
5.0	10.0	* * *	0.000 47	0.000 54	—	0.020 17	0.030 16

Table 2. Comparison of the PF of the QA by perturbation theory with bounds and numerical results. Z_{TP} = PF in second-order thermodynamic perturbation theory; the other symbols are the same as in table 1.

ϵ	λ	Z_{LB}^{Δ}	Z_n	Z_{TP}	Z_{UB}^{Δ}
0.2	0.005	4.701 0	—	4.779 5	4.712 9
0.2	0.01	4.505 0	—	4.896 8	4.529 5
0.2	0.05	3.781 0	—	17.696	3.846 5
0.2	0.2	2.995 5	3.082 3	253.48	3.082 9
0.4	0.005	2.400 8	—	2.408 6	2.403 2
0.4	0.01	2.336 0	—	2.375 5	2.342 1
0.4	0.05	2.047 8	—	3.611 4	2.072 4
0.4	0.2	1.671 3	1.711 6	32.006	1.712 8
1.0	0.005	0.943 7	—	0.944 1	0.944 0
1.0	0.001	0.929 7	—	0.931 6	0.930 5
1.0	0.05	0.851 2	—	0.936 1	0.857 3
1.0	0.2	0.715 5	0.728 6	2.606 2	0.731 1
2.0	0.005	0.420 2	—	0.420 2	0.420 2
2.0	0.01	0.415 2	—	0.415 4	0.415 5
2.0	0.05	0.383 8	—	0.394 4	0.386 3
2.0	0.2	0.318 1	0.323 8	0.588 4	0.327 1
5.0	0.005	0.081 09	—	0.081 10	0.081 12
5.0	0.01	0.079 61	—	0.079 64	0.079 72
5.0	0.05	0.069 81	—	0.071 26	0.071 02
5.0	0.2	0.048 63	0.050 31	0.091 54	0.053 64

Table 3. Comparison of different methods for the partition function of two quartic coupled oscillators (equation (3.8)); strong coupling case: $\omega_2 = 0.75\omega_1$, $\lambda_1 = \lambda_2 = (0.064\hbar\omega_1)^{1/4}$, $\epsilon_1 \equiv \beta \hbar \omega_1$; Z_{LB} = lower bound; Z_{LB}^{Δ} = lower bound with variation of the frequencies ω_1^* , ω_2^* ; Z_{TP} = second-order thermodynamic perturbation theory; Z_{UB}^{Δ} = upper bound with variation of the frequencies ω_1^* , ω_2^* ; Z_{UB} = upper bound.

ϵ_1	Z_{LB}	Z_{LB}^{Δ}	Z_{TP}	Z_{UB}^{Δ}	Z_{UB}
0.5	0.607	2.68	131.0	3.44	3.45
1.0	0.385	0.745	8.64	0.899	0.905
1.5	0.209	0.320	1.89	0.382	0.386
2.0	0.116	0.162	0.673	0.195	0.198
2.5	0.066 5	0.088 8	0.306	0.109	0.111
3.0	0.038 7	0.050 6	0.161	0.063 7	0.065 3

Table 4. Comparison of different methods for the partition function of quartic coupled anharmonic oscillators (equation (3.8)); weak coupling case: $\omega_2 = 0.75\omega_1$, $\lambda_1 = \lambda_2 = (0.004\hbar\omega_1)^{1/4}$; notation as in table 3.

ϵ_1	Z_{LB}	Z_{LB}^{Δ}	Z_{TP}	Z_{UB}^{Δ}	Z_{UB}
0.5	4.586	4.702	5.077	4.797	4.799
1.0	1.161	1.170	1.192	1.181	1.181
1.5	0.484 9	0.487 0	0.491 3	0.490 3	0.490 4
2.0	0.246 1	0.246 1	0.248 2	0.248 1	0.248 3
2.5	0.137 5	0.137 5	0.138 4	0.138 7	0.138 7
3.0	0.081 12	0.081 12	0.081 57	0.081 73	0.081 84

coupling are interesting. For large anharmonicity we found in table 3 that perturbation theory is meaningless in this case. The gap between upper and lower bounds is of the order of 20%, which after forming the arithmetic mean may lead to a suitable approximation for the calculation of coupling corrections to the level densities of such systems. The Hioe–Montroll method for finding the eigenvalues of anharmonic oscillators presented difficulties to us because of the asymmetric terms $\propto Q_i Q_j^3$ which are as yet not solved. We therefore consider for the moment variational methods as a rough workable technique for treating such systems. For small anharmonicity and coupling and for intermediate temperatures, table 4 shows that thermodynamic perturbation theory will be a good approximation to the partition function. For $\epsilon_1 < 2$ and for the constants' give, the perturbation results fall out of the bounds, but are down to $\epsilon_1 = 0.5$ of the right magnitude.

7.2. Calculation of the entropy

Using the Ruelle–Fisher technique, we calculated exact bounds to the entropy from exact bounds to the PF including variation of the frequency and compared these results with numerical data from the Hioe–Montroll eigenvalues and the approximate formula of Schwarz (1976). In contrast to the bad agreement of the PF, even if a printing error is corrected, the agreement for the entropy is surprisingly good. We also calculated S_I from the unvaried upper bound. Comparison shows the very good agreement with the numerical entropy in table 5. It would not be reasonable to calculate a 'lower bound-entropy' by differentiation and insertion into equation (3.5) as, in contrast to the upper bound, the lower bound will be nowhere approached exactly for a certain temperature.

Table 5. Comparison of different methods for the entropy function of the QA. S_{LB} = lower bound, S_{UB} = upper bound by Fisher–Ruelle technique; S_I = entropy function from the analytical expression for Z_{UB} ; S_{HM} = numerical entropy function from Hioe–Montroll eigenvalues for $\lambda \geq 0.2$; S_S = approximate entropy function from Schwarz's article for $\lambda \geq 0.2$; ϵ, λ the same as in table 1.

ϵ	λ	S_{LB}	S_I	S_{HM}	S_S	S_{UB}
0.1	0.1	2.083	2.645	—	—	3.271
0.1	0.2	1.906	2.496	2.497	2.555	3.161
0.1	0.5	1.679	2.289	2.290	2.326	2.987
0.5	0.1	0.987	1.353	—	—	1.768
0.5	0.2	0.808	1.232	1.234	1.348	1.733
0.5	0.5	0.567	1.052	1.060	1.119	1.660
1.0	0.1	0.492	0.799	—	—	1.166
1.0	0.2	0.324	0.699	0.703	0.828	1.183
1.0	0.5	0.108	0.540	0.558	0.599	1.192

7.3. Conclusion and discussion

We summarise the results in a few points.

Trace inequalities can be used for the calculation of exact upper and lower bounds to the PF and the entropy including variation of the frequency, and, for asymmetric potentials, variations of the distance. They can be used to check approximate methods

and are, therefore, a statistical counterpart to the variational bounds to eigenvalues given by Bazley and Fox (1961) and by Reid (1965).

We generalised the technique to coupled anharmonic oscillators of the quartic type and gave numerical results for a special Hamiltonian H_5 , postponing the results for other types to a later paper.

Finally, it should be remarked that the exact upper bound is a good approximation to the PF which is approached at high temperatures. As we could give Z_{UB} in terms of special functions, it was possible to derive the thermodynamic functions again in terms of special functions. Thus, it is possible to derive level densities for some types of quartic–quadratic Hamiltonians in analytic form.

Acknowledgment

We gratefully acknowledge written remarks by Professors Byers-Brown, Helleman, Mills, Uhlmann, Wehrl, and financial support by the ‘Fonds der Chemischen Industrie’.

Appendix. Sketch of formulae used in the text

From the Laplace type integral

$$\int_0^\infty t^{\nu-1} \exp(-at^2 - st) dt = (2a)^{-\nu/2} \Gamma(\nu) \exp(s^2/8a) D_{-\nu}[s(2a)^{-1/2}] \quad (\text{A1})$$

follows, after the substitution $t = z^{2k}$, the integral of the preceding text

$$\int_0^\infty z^{2\nu-1} \exp(-az^4 - sz^2) dz = \frac{1}{2} (2a)^{-\nu/2} \Gamma(\nu) \exp(s^2/8a) D_{-\nu}[s(2a)^{-1/2}]. \quad (\text{A2})$$

$$\int_0^\infty \frac{e^{-\lambda x^2}}{(x^2 + a^2)^{1/2}} dx = \frac{1}{2} \exp(a^2 \lambda / 2) K_0(a^2 \lambda / 2), \quad \lambda > 0, a^2 > 0, \quad (\text{A3})$$

where K_0 is a modified Bessel function.

For the calculation of thermodynamic functions some differentiation–recursion formulae are necessary:

$$-2K'_\nu(z) = K_{\nu-1}(z) + K_{\nu+1}(z), \quad -2(\nu/z)K_\nu(z) = K_{\nu-1}(z) - K_{\nu+1}(z), \quad (\text{A4})$$

$$D'_\nu(z) + \frac{1}{2}zD_\nu(z) - \nu D_{\nu-1}(z) = 0, \quad D'_\nu(z) - \frac{1}{2}zD_\nu(z) + D_{\nu+1}(z) = 0. \quad (\text{A5})$$

Parabolic cylinder functions are tabulated (Abramowitz and Stegun 1965, p 702) in terms of $U(a, x)$, which are related to the $D_{-\nu}(x)$ notation by

$$U(a, x) = D_{-a-1/2}(x).$$

Five-point Lagrange interpolation is sufficient to get five-figure accuracy everywhere.

References

- Abramowitz M and Stegun I A 1965 *Handbook of Mathematical Functions* (New York: Dover)
 Bazley N W and Fox D W 1961 *Phys. Rev.* **124** 483–92
 Beck H 1976 *J. Phys. C: Solid St. Phys.* **9** 33–49

- Bender C M and Orszag S A 1978 *Advanced Mathematical Methods for Scientists and Engineers* (New York: McGraw-Hill)
- Bohmann J 1979 *Doctorial Dissertation, Universität Ulm*
— 1980 to be published
- Bohmann J and Witschel W 1978 *J. Chem. Soc. Faraday II* **74** 2235–45
- Breitenecker M and Grümh H R 1972 *Commun. Math. Phys.* **26** 276–7
- Falk H 1970 *Am. J. Phys.* **38** 859–69
- Feynman R P 1972 *Statistical Mechanics* (Reading: Benjamin) pp 55–7
- Fisher M E 1965 *J. Chem. Phys.* **42** 3852–6
- Girardeau M and Mazo R M 1973 in *Advances Chem. Phys.* ed I Prigogine and S A Rice **24** 187–255
- Gradshteyn I S and Ryzhik I M 1965 *Tables of Integrals, Series and Products* (New York: Academic Press)
- Graffi S and Grecchi V 1978 *J. Math. Phys.* **19** 1002–6
- Hioe F T 1976 *Phys. Rev. B* **16** 4112–20
— 1977 *Phys. Rev. D* **15** 488–96
— 1978 *J. Chem. Phys.* **69** 204–13
- Hioe F T, MacMillen D and Montroll E W 1978 *Phys. Rep.* **43** 305–35
- Hioe F T and Montroll E W 1975 *J. Math. Phys.* **16** 1945–55
- Jorish V S and Zitserman V Yu 1975 *Chem. Phys. Lett.* **34** 378–80
— 1976 *Chem. Phys. Lett.* **41** 274–7
- Leschke H 1979 *Lecture Notes in Physics 106: Feynman Path Integrals* **106** 435–43
- Lieb E 1973a *Adv. Math.* **11** 267–88
— 1973b *Commun. Math. Phys.* **31** 327–40
- Lieb E and Ruskai M B 1973a *Phys. Rev. Lett.* **30** 434
— 1973b *J. Math. Phys.* **14** 1938
- Mathews P M and Seshadri M S 1975 *Int. J. Theor. Phys.* **13** 279–89
- Messiah A 1964 *Quantum Mechanics* vol I (Amsterdam: North-Holland)
- Miller W H 1971 *J. Chem. Phys.* **55** 3146–9
- Pant M M and Mitra S K 1979 *Chem. Phys. Lett.* **62** 495–8
- Papadopoulos G J 1969 *J. Phys. A: Math., Nucl. Gen.* **2** 172–80
- Percival I C and Pomphrey N 1976 *Molec. Phys.* **31** 97–114
- Pomphrey N 1974 *J. Phys. B: Atom. Molec. Phys.* **7** 1909–15
- Powell G E and Percival I 1979 *J. Phys. A: Math. Gen.* **12** 2053–71
- Reid C 1965 *J. Chem. Phys.* **43** S186–89
- Ruelle D 1963 *Helv. Phys. Acta* **36** 789–99
- Saenz A W and O'Rourke R C 1955 *Rev. Mod. Phys.* **27** 381–98
- Schwarz M 1976 *J. Statist. Phys.* **15** 255–61
- Simon B 1970 *Ann. Phys.* **58** 76–136
- Wehrl A 1978 *Rev. Mod. Phys.* **50** 221–60
- Witschel W, Großwendt B and Bohmann J 1977 *FTB Mitteilungen* **87** 3–15