Perturbation and variational-perturbation method for the free energy of anharmonic oscillators

K. Vlachos, V. Papatheou, and A. Okopińska

Abstract: The perturbation and the variational-perturbation methods are applied for calculating the partition function of one-dimensional oscillators with anharmonicity x^{2n}. New formally simple expressions for the free energy and for the Rayleigh–Schrödinger energy corrections are derived. It is shown that the variational-perturbation method overcomes all the deficiencies of the conventional perturbation method. The results of fifth-order numerical calculations for the free energy of the quartic, quartic–sextic, and octic anharmonic oscillator are highly accurate in the whole range of temperatures.

PACS Nos.: 03.65.−w, 05.30.−d

Résumé : Nous utilisons la méthode perturbative et la méthode mixte perturbative-variationnelle pour calculer la fonction de partition pour des oscillateurs harmoniques avec un terme anharmonique en x^{2n}. Nous obtenons de nouvelles expressions simples pour l'énergie libre et pour les corrections en énergies de Rayleigh–Schrödinger. Nous montrons que la méthode perturbative-variationnelle permet de surmonter les faiblesses de la méthode perturbative traditionnelle. Les résultats de calculs numériques au 5$^\text{e}$ ordre pour l'énergie libre des oscillateurs d'anharmonicité quartique, quartique-sextique et octique sont très précis sur tout le domaine de température.

[Traduit par la Rédaction]

1. Introduction

The anharmonic potential proves to be very useful to model phenomena in nuclear physics, solid state physics, molecular–atomic physics, and laser theory. Therefore, anharmonic systems have been studied extensively both by analytical and numerical methods. These developments were triggered by the demonstration that the Rayleigh–Schrödinger perturbation series for the simple system of the quartic anharmonic oscillator diverges even for small values of the coupling constants [1]. Many techniques have been developed for determining the energy spectra of various anharmonic oscillators. Highly accurate approximations have been achieved by the use of the Hill determinant [2–6], the Bargmann representation [7, 8], the coupled cluster method [9–11], the variational (optimized) perturbation expansion [12–15], and many others approaches [16–21].

K. Vlachos[1] and V. Papatheou. Department of Physics, University of Patras, 26500 Patras, Greece.
A. Okopińska. Institute of Physics, Świętokrzyska Academy, 25406 Kielce, Poland.

[1] Corresponding author (e-mail: vlachos@physics.upatras.gr).

For an approximate description of the thermal equilibrium, the thermodynamic perturbation theory based on the Schwinger trace formula [22] has been developed [23, 24]. The method has been applied for computing the partition function of various anharmonic oscillators up to third order [25]. It has been shown that the results obtained agree with the exact ones only in a limited range of temperatures, which shrinks with increasing value of the anharmonic couplings. A much better description is obtained, using the slightly modified perturbation theory with a variational frequency parameter introduced in the unperturbed Hamiltonian [26–34]. In this paper, we pursue the study of the perturbation method up to fifth order, presenting the formal formulas for the partition function of anharmonic oscillators with arbitrary polynomial potentials. Using the quartic oscillator example, we discuss two ways of deriving approximations to the free energy: from the partition function (PF) truncated at given order and from the given order formula for the free energy (FE). The fifth-order results of both methods are shown to be similar only for small values of the coupling in a narrow range of temperatures. We show how the formulas for the partition function can be used to derive new formal forms of Rayleigh–Schrödinger (RS) corrections to bound-state energies. Later, we consider the third method of approximating the free energy, based on calculating the partition function as a sum of Boltzmann factors with RS eigenvalues. We show that deficiencies of the perturbation method for the quartic oscillator persist in all of the three formulations: the differences between the results of the PF, FE, and RS methods and the deviations from the exact free energy increase with increasing order calculation. The difficulties are overcome by the variational improvement of perturbation theory. We demonstrate that the variational-perturbation results of the three methods (PF, FE, and RS) of approximating the free energy appear very similar in the broad range of temperatures, the RS approximation being the most accurate. The approximations to the energy eigenvalues become systematically improved in higher orders and the relative errors in the fifth order are between 10^{-2} and 10^{-7}, depending on the temperature and on the value of the coupling constant.

The paper is organized as follows. In Sect. 2, we present the formal perturbation formulas for the partition function of anharmonic oscillators. We discuss the PF and FE methods of approximating the free energy on the quartic oscillator example. In Sect. 3, the formal forms of the RS corrections to bound-state energies are derived and the RS approximations to the free energy are obtained. In Sect. 4, the formulas of optimized perturbation theory are presented and calculations of the free energy up to fifth order are performed for the quartic, quartic–sextic, and octic anharmonic oscillator.

2. Perturbation expansion of the free energy

Let us consider a one-dimensional system with a Hamiltonian given by

$$H = H_0 + \varepsilon V(x) \tag{2.1}$$

where the unperturbed Hamiltonian is that of the harmonic oscillator with frequency ω

$$H_0 = \frac{p^2}{2} + \frac{\omega^2}{2} x^2 \tag{2.2}$$

and the perturbation potential is given by a polynomial

$$V(x) = \sum_{\kappa} d_{\kappa} x^{\kappa} \tag{2.3}$$

with constant coefficients d_{κ}, and κ being even numbers. The parameter ε has been introduced to identify the order of the perturbation and has to be set equal to one at the end.

The partition function of the system can be defined as the trace of density operator, that is

$$Z(\beta) = \text{Tr} \{\exp(-\beta H)\} \tag{2.4}$$

where β is the inverse temperature.

In refs. 25 and 30, it has been shown that the thermodynamic perturbation theory can be formulated in a way that greatly facilitates numerical calculation. The expansion of (2.4) in powers of ε has been represented by a formally simple expression

$$Z(\beta) = Z_0(\beta) \left[1 - \varepsilon\beta V^{\{1\}}(Q) + \varepsilon^2 \frac{\beta^2}{2} V^{\{2\}}(Q) + \sum_{\nu=2}^{\infty} (-1)^{\nu+1} \varepsilon^{\nu+1} \frac{\beta^{\nu+1}}{\nu+1} V^{\{\nu+1\}}(Q) \right] \quad (2.5)$$

where

$$Z_0(\beta) = \mathrm{Tr}\left\{ e^{-\beta H_0} \right\} = \frac{1}{2 \sinh \frac{\beta\omega}{2}} \quad (2.6)$$

is the partition function of the unperturbed system,

$$Q^\kappa(\beta) = \frac{1}{Z_0(\beta)} \mathrm{Tr}\left(x^\kappa e^{-\beta H_0} \right) = (\kappa-1)!! \left(\frac{1}{2\omega} \coth \frac{\beta\omega}{2} \right)^{\kappa/2} \quad (2.7)$$

$$Q^{\kappa_0 \kappa_1}(\beta) = \frac{1}{Z_0(\beta)} \int_0^1 dt_1 \, \mathrm{Tr}\left(x^{\kappa_0} e^{-\beta H_0} e^{\beta t_1 H_0} x^{\kappa_1} e^{-\beta t_1 H_0} \right) \quad (2.8)$$

and

$$Q^{\kappa_0 \kappa_1 \cdots \kappa_\nu}(\beta) = \frac{1}{Z_0(\beta)} \int_0^1 t_1^{\nu-1} dt_1 \int_0^1 t_2^{\nu-2} dt_2 \cdots \int_0^1 dt_\nu \, \mathrm{Tr}\left(x^{\kappa_0} e^{-\beta H_0} \prod_{j=1}^{\nu} e^{\beta \xi_j H_0} x^{\kappa_j} e^{-\beta \xi_j H_0} \right) \quad (2.9)$$

with

$$\xi_j = t_1 t_2 \cdots t_j \quad (2.10)$$

The expressions $V^{\{\nu\}}(Q)$ are defined as follows:

$$V^{\{\nu\}}(Q) = V(Q) * V(Q) * \cdots * V(Q) \quad (2.11)$$

where $*$ symbolizes an unconventional multiplication that obeys the following rules:

$$Q^{\kappa_0 \kappa_1 \cdots \kappa_\mu} * Q^{\lambda_0 \lambda_1 \cdots \lambda_\nu} = Q^{\kappa_0 \kappa_1 \cdots \kappa_\mu \lambda_0 \lambda_1 \cdots \lambda_\nu} \quad (2.12)$$

for example, the expression

$$Q^{24} * Q^{68} = Q^{2468} \quad (2.13)$$

represents the equation

$$\frac{1}{Z_0(\beta)} \int_0^1 dt_1 \, \mathrm{Tr}\left(x^2 e^{-\beta H_0} e^{\beta t_1 H_0} x^4 e^{-\beta t_1 H_0} \right) * \frac{1}{Z_0(\beta)} \int_0^1 dt_1 \, \mathrm{Tr}\left(x^6 e^{-\beta H_0} e^{\beta t_1 H_0} x^8 e^{-\beta t_1 H_0} \right)$$

$$= \frac{1}{Z_0(\beta)} \int_0^1 t_1^2 dt_1 \int_0^1 t_2 dt_2 \int_0^1 dt_3$$

$$\times \left(x^2 e^{-\beta H_0} e^{\beta t_1 H_0} x^4 e^{-\beta t_1 H_0} e^{\beta t_1 t_2 H_0} x^6 e^{-\beta t_1 t_2 H_0} e^{\beta t_1 t_3 t_3 H_0} x^8 e^{-\beta t_1 t_2 t_3 H_0} \right) \quad (2.14)$$

The functions $Q^{\kappa_0\kappa_1}(\beta)$ and $Q^{\kappa_0\kappa_1\kappa_2}(\beta)$ have been shown to be invariant under all permutations of κ_0, κ_1, and κ_2 [30]. Similarly, we can prove the invariance of $Q^{\kappa_0\kappa_1\cdots\kappa_\nu}(\beta)$ functions under clockwise and anticlockwise cyclic permutations of $\kappa_0, \kappa_1, \cdots, \kappa_\nu$. The proof can be done along similar lines to that described in Appendix B of ref. 30 with the use of the relation

$$\mathrm{Tr}\left(x^{\kappa_0}\mathrm{e}^{-\beta H_0}\prod_{j=1}^{\nu}\mathrm{e}^{\beta\xi_j H_0}x^{\kappa_j}\mathrm{e}^{-\beta\xi_j H_0}\right) = \int_{-\infty}^{+\infty}\mathrm{d}x_0\mathrm{d}x_1\cdots\mathrm{d}x_\nu\rho_0(x_0, x_1; \beta(1-\xi_1))$$

$$\rho_0(x_1, x_2; \beta(\xi_1-\xi_2))\cdots\rho_0(x_{\nu-1}, x_\nu; \beta(\xi_{\nu-1}-\xi_\nu))\rho_0(x_\nu, x_0; \beta\xi_\nu) \quad (2.15)$$

where ρ_0 is the density matrix corresponding to the Hamiltonian H_0. For analytical calculation of traces we use the formulas

$$\frac{1}{Z_0(\beta)}\mathrm{Tr}\left(x^{\kappa_0}\mathrm{e}^{-\beta H_0}\prod_{j=1}^{n}\mathrm{e}^{\beta\xi_j H_0}x^{\kappa_j}\mathrm{e}^{-\beta\xi_j H_0}\right)$$

$$= \sqrt{\frac{\omega}{\pi}\tanh\frac{\beta\omega}{2}}\sum_{\kappa_0,\cdots,\kappa_n}\mathrm{d}_{\kappa_0}\cdots\mathrm{d}_{\kappa_n}\left(\frac{\sinh(\beta\omega\xi_1)}{\omega}\right)^{\kappa_1}\cdots\left(\frac{\sinh(\beta\omega\xi_1)}{\omega}\right)^{\kappa_n}$$

$$\times\int_{-\infty}^{\infty}x^{\kappa_0}\mathrm{e}^{-\omega\tanh\frac{\beta\omega}{2}\cdot x^2}\left\{\sum_{s_n=0}^{\kappa_n}\frac{(2\kappa_n)!a_n^{s_n}}{2^{s_n}s_n!(2\kappa_n-2s_n)!}\left(Mx+a_nx_1+\frac{\mathrm{d}}{\mathrm{d}x_1}\right)_{\mathcal{N}}^{2\kappa_n-2s_n}\right.$$

$$\left.\times\cdots\sum_{s_1=0}^{\kappa_1}\frac{(2\kappa_1)!a_1^{s_1}}{2^{s_1}s_1!(2\kappa_1-2s_1)!}\left(Mx+a_1x_1+\frac{\mathrm{d}}{\mathrm{d}x_1}\right)_{\mathcal{N}}^{2\kappa_1-2s_1}\cdot\mathbf{1}\right\}_{x_1=x}\mathrm{d}x \quad (2.16)$$

where

$$M = \frac{\omega}{\sinh(\beta\omega)}, \quad a_i = M\frac{\sinh(\beta\omega(1-\xi_i))}{\sinh(\beta\omega\xi_i)} \tag{2.17}$$

and the symbol $\mathcal{N}$ denotes the normal ordering of operators. The products of the operators in (2.16) are calculated by successive application of the formula given in ref. 35

$$\left(Mx+a_2x_1+\frac{\mathrm{d}}{\mathrm{d}x_1}\right)_{\mathcal{N}}^{n_2}\left(Mx+a_1x_1+\frac{\mathrm{d}}{\mathrm{d}x_1}\right)_{\mathcal{N}}^{n_1}$$

$$= \left[\left(Mx+a_2x_1+\frac{\mathrm{d}}{\mathrm{d}x_1}\right)^{n_2}(Mx+a_1x_1)^{n_1}\right]_{\mathcal{N}} \tag{2.18}$$

With the help of the above relations, the terms of the series for the partition function (2.5) can be determined to the required order.

The free energy $F(\beta) = 1/\beta\ln Z(\beta)$ can be approximated in two ways. One way is to use the finite order truncation, $Z^{[i]}$, of the series for the partition function (2.5), to calculate the ith order approximation to the free energy via the form

$$F_{\mathrm{PF}}^{[i]}(\beta) = -\frac{1}{\beta}\ln Z^{[i]}(\beta) \tag{2.19}$$

On the other hand, the perturbation formula can be obtained directly for the free energy, by expanding

the logarithm with respect to ϵ, that is

$$
\begin{aligned}
F_{\text{FE}} &= -\frac{1}{\beta} \ln \left[\text{Tr} \left(e^{-\beta H} \right) \right] \\
&= -\frac{1}{\beta} \left\{ \ln Z_0 \left(\beta \right) - \epsilon \beta V^{\{1\}} \left(Q \right) + \epsilon^2 \frac{\beta^2}{2} \left[-\left[V^{\{1\}} \left(Q \right) \right]^2 + V^{\{2\}} \left(Q \right) \right] + \cdots \right\}
\end{aligned} \quad (2.20)
$$

The finite-order truncation of the above formula $F_{\text{FE}}^{[i]}$ is equivalent to the perturbation expression for the free energy, which can be derived by diagrammatic techniques of field theory [27], but it proves more efficient in the numerical evaluation of higher order terms.

As an example, we discuss here the perturbation expansion up to fifth order, for the quartic oscillator with the anharmonic potential $V \left(x \right) = \lambda x^4$. In this case, the coefficients $V^{\{\nu\}} \left(Q \right)$ are given by

$$
\begin{aligned}
V^{\{1\}}(Q) &= \lambda Q^4 \\
V^{\{2\}}(Q) &= \lambda^2 Q^{44} \\
V^{\{3\}}(Q) &= \lambda^3 Q^{444} \\
V^{\{4\}}(Q) &= \lambda^4 Q^{4444} \\
V^{\{5\}}(Q) &= \lambda^5 Q^{44444}
\end{aligned} \quad (2.21)
$$

with the expressions for the products of Q given in the Appendix.

In the numerical calculations, we take the harmonic frequency $\omega = 1$ and discuss the dependence on the parameter $\omega = 1$ that measures the relative strength of anharmonicity. The fifth-order perturbation approximations to the free energy, obtained with the use of both the PF definition (2.19) and FE definition (2.20), are compared with the exact results in Fig. 1. The exact free energy has been calculated numerically, using the energy eigenvalues determined by the optimized Rayleigh–Ritz method [36]. First, we observe that the F_{PF} and F_{FE} functions follow the exact free energy, only if the coupling constant λ is quite small, and only in the range of mediocre temperatures. In the case when the coupling constant is large, for example, $\lambda = 0.3$, the PF method cannot be applied, since the partition function $Z^{[5]} \left(\beta \right)$ is always negative, and the free energy F_{PF} cannot be defined. At smaller coupling constant, for example, $\lambda = 0.1$, the partition function is positive only between the two roots ($\beta_1 = 2.5907$ and $\beta_2 = 11.3214$) and the approximation to the free energy $F_{\text{PF}} \left(\beta \right)$ is defined only in this range of temperatures. At still smaller coupling constant, for example, $\lambda = 0.01$, there is only one root of $Z^{[5]} \left(\beta \right)$, on the right of which $F_{\text{PF}} \left(\beta \right)$ is defined, but the deviations from the exact result increase for decreasing temperature ($\beta \to \infty$). The FE method performs better, since the function $F_{\text{FE}} \left(\beta \right)$ is well defined at all temperatures, and proves to be closer to the exact free energy than $F_{\text{PF}} \left(\beta \right)$ in the whole range of temperature. However, even at small values of λ, the function $F_{\text{FE}} \left(\beta \right)$ diverges at high temperatures ($\beta \to 0$), which reflects the asymptotic character of the perturbation expansion, in agreement with the observation that the spectrum is dominated by the anharmonic part of the potential, as the system approaches a classical behavior [37]. At intermediate and low temperatures, the F_{FE} curve follows the exact free energy, but the agreement spoils with increasing value of λ.

3. Rayleigh–Schrödinger energy corrections

It is interesting to observe, following the Fernández idea [37], that the formal expressions for the partition function (2.5) can be conveniently utilized for determination of Rayleigh–Schrödinger corrections to the energy eigenvalues of the system considered, by representing the eigenvalues E_n, as a power series in a parameter ε

$$
E_n = E_n^{[0]} + \sum_{\nu=1}^{\infty} \varepsilon^\nu \Delta_\nu E_n \quad (3.1)
$$

Fig. 1. Inverse temperature (β) dependence of the fifth-order perturbative approximations to the free energy of the quartic anharmonic oscillator, $V(x) = \lambda x^4$, in the case of $\lambda = 0.1$ and $\lambda = 0.3$. The approximations obtained from the partition function expansion (F_{PF}), from the free energy expansion (F_{FE}) and from the sum over states definition of the partition function (F_{RS}), are compared with the exact free energy.
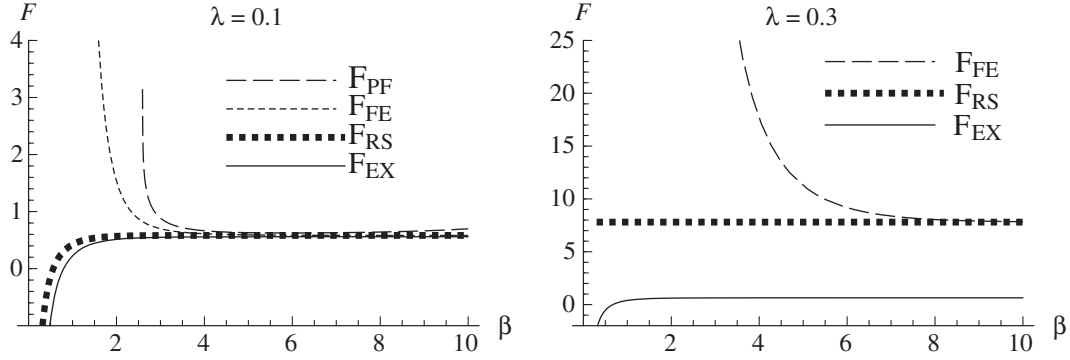
where

$$E_n^{[0]} = \omega \left(n + \frac{1}{2} \right) \tag{3.2}$$

is the nth energy eigenvalue of the unperturbed system H_0, and $\Delta_\nu E_n$, $\nu = 1, 2, 3, \ldots$ are the Rayleigh–Schrödinger corrections, and expanding the partition function into a power series in ε

$$Z(\beta) = \sum_{n=0}^{\infty} \exp(-\beta E_n) = \sum_{n=0}^{\infty} \exp\left[-\beta \left(E_n^{[0]} + \sum_{\nu=1}^{\infty} \varepsilon^\nu \Delta_\nu E_n \right) \right] \tag{3.3}$$

we obtain [38]

$$Z(\beta) = \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} \sum_{\lambda=0}^{\infty} c_\lambda \varepsilon^\lambda \tag{3.4}$$

where

$$c_0 = \left(E_n^{[0]} \right)^k, \qquad c_m = \frac{1}{m E_n^{[0]}} \sum_{\lambda=1}^{m} (\lambda k - m + \lambda) \, c_{m-\lambda} \Delta_\lambda E_n \quad \text{for} \quad m \geq 1 \tag{3.5}$$

Because of the form of (3.1), the coefficients of ε^λ in (3.4) are the series of the linearly independent functions $\{ e^{-\beta\omega n}, \beta e^{-\beta\omega n}, \beta^2 e^{-\beta\omega n}, \cdots \}$ with $n = 0, 1, 2, \ldots$. Equating the above coefficients with the corresponding ones in (2.5) yields the following relations:

$$\sum_{n=0}^{\infty} e^{-\beta\omega n} \Delta_1 E_n = \frac{Q^\kappa(\beta)}{1 - e^{-\beta\omega}} \tag{3.6}$$

$$\sum_{n=0}^{\infty} e^{-\beta\omega n} \left[-\Delta_2 E_n + \frac{\beta}{2} (\Delta_1 E_n)^2 \right] = \frac{\beta}{2} \frac{Q^{\kappa\kappa}(\beta)}{1 - e^{-\beta\omega}} \tag{3.7}$$

$$\sum_{n=0}^{\infty} e^{-\beta\omega n} \left[\Delta_3 E_n - \beta (\Delta_1 E_n)(\Delta_2 E_n) + \frac{\beta^2}{6} (\Delta_1 E_n)^3 \right] = \frac{\beta^2}{3} \frac{Q^{\kappa\kappa\kappa}(\beta)}{1 - e^{-\beta\omega}} \tag{3.8}$$

Expanding the second term of these equations with respect to the linearly independent set $\{e^{-\beta\omega n}\}$, and comparing the coefficients of like powers of $e^{-\beta\omega}$, the perturbation corrections for each energy eigenvalue can be determined. With the above coefficients denoted as

$$L^{\kappa_1\kappa_2\cdots\kappa_\nu}(\omega, n) = \text{Series Coefficient}\left[\frac{\beta^{\nu-1}}{\nu}\frac{Q^{\kappa_1\kappa_2\cdots\kappa_\nu}(\beta)}{1 - e^{-\beta\omega}}, e^{-\beta\omega n}\right] \tag{3.9}$$

the energy corrections, determined from the relations (2.7)–(2.9) and (3.6)–(3.8), can be represented by formally simple expressions

$$\Delta_1 E_n = V^{\{1\}}(L), \qquad \Delta_2 E_n = V^{\{2\}}(L), \cdots, \Delta_\kappa E_n = V^{\{\kappa\}}(L) \tag{3.10}$$

where the L-functions have the same properties as the Q-functions. The above expressions allow an easy derivation of the perturbation corrections to the energy eigenvalues for an arbitrary anharmonic potential of the polynomial form.

The first energy correction is easily determined from (2.7) for an arbitrary κ in an analytic form

$$\Delta_1 E_n = \lambda L^\kappa(\omega, n) = \lambda\frac{(\kappa - 1)!!}{2^{\kappa/2}\omega^{\kappa/2}}\sum_{i=0}^{k/2}\frac{\left(\frac{\kappa}{2} + n - i\right)!}{i!\left(\frac{\kappa}{2} - i\right)!(n - i)!} \tag{3.11}$$

Next corrections can be determined using algebraic programming. In the case of the quartic anharmonic oscillator ($\kappa = 4$) we have

$$\Delta_1 E_n = \lambda L^4$$
$$\Delta_2 E_n = -\lambda^2 L^{44}$$
$$\Delta_3 E_n = \lambda^3 L^{444} \tag{3.12}$$
$$\Delta_4 E_n = -\lambda^4 L^{4444}$$
$$\Delta_5 E_n = \lambda^5 L^{44444}$$

with the L-coefficients presented in the Appendix.

The approximations to the free energy can be obtained via

$$F_{\text{RS}}^{[i]}(\beta) = -\frac{1}{\beta}\ln Z_{\text{RS}}^{[i]}(\beta) \tag{3.13}$$

where the partition function $Z_{\text{RS}}^{[i]}(\beta)$ is calculated as a sum over the states (3.3) with the Rayleigh–Schrödinger approximations to the energy eigenvalues, $E_n^{[i]} = E_n^{[0]} + \sum_{k=1}^{i}\Delta_k E_n$. The RS approximation to the partition function $Z_{\text{RS}}^{[i]}(\beta)$ is always positive, thereby the free energy (3.13) is defined for any value of temperature. In Fig. 1, the $F_{\text{RS}}^{[5]}(\beta)$ function is shown in comparison with $F_{\text{PF}}^{[5]}(\beta)$, $F_{\text{FE}}^{[5]}(\beta)$ and the exact free energy. We observe that the F_{RS} approximation performs better than F_{PF} and F_{FE} in the whole range of λ and β. However, one has to admit that such a good agreement is obtained only in odd orders of the perturbation method. In even orders, the RS energy eigenvalues become negative at sufficiently large coupling constant, and the value, at which this happens, decreases with increasing calculation order. Another symptom of the breakdown of perturbation theory is the fact that the three perturbation expansions (2.19), (2.20), and (3.13), truncated at the same order, provide very different results (F_{PF}, F_{FE}, and F_{RS}). One has to stress that none of the methods is able to provide reliable approximations to the free energy, even in the case of very small anharmonicity.

4. Optimized perturbation theory

This is not too well-known that a powerful approximation method, called variational or optimized perturbation theory, can be obtained by a simple modification of perturbation approach [12–15]. The Hamiltonian of the system considered

$$H = \frac{p^2}{2} + \frac{1}{2}x^2 + v(x) \tag{4.1}$$

is modified by adding and subtracting the term $\omega^2 x^2/2$ and an unconventional splitting

$$H = H_0(\omega) + \varepsilon V(x) \tag{4.2}$$

where the unperturbed part has a form of the harmonic oscillator with an arbitrary frequency parameter ω

$$H_0(\omega) = \frac{p^2}{2} + \frac{\omega^2}{2}x^2 \tag{4.3}$$

and the perturbation part is also ω-dependent

$$V(x) = \frac{1 - \omega^2}{2}x^2 + v(x) \tag{4.4}$$

Approximations are obtained by truncating the series for the quantity of interest at a given order in ε, and setting $\varepsilon = 1$. Since the modified perturbation term (4.4) has a polynomial form of (2.3), the formulas for the partition function and the energy eigenvalues can be derived in the same way as discussed in Sect. 3. For the quartic anharmonic oscillator, the successive coefficients $V^{\{v\}}(Q)$ are obtained in the form

$$V^{\{1\}}(Q) = \frac{1 - \omega^2}{2}Q^2 + \lambda Q^4 \tag{4.5}$$

$$V^{\{2\}}(Q) = \left(\frac{1 - \omega^2}{2}Q^2 + \lambda Q^4 \right)^{\{2\}} = \frac{\left(1 - \omega^2\right)^2}{4}Q^{22} + \lambda \left(1 - \omega^2\right) Q^{42} + \lambda^2 Q^{44} \tag{4.6}$$

$$V^{\{3\}}(Q) = \left(\frac{1 - \omega^2}{2}Q^2 + \lambda Q^4 \right)^{\{3\}} = \frac{\left(1 - \omega^2\right)^3}{8}Q^{222} + 3\lambda \frac{\left(1 - \omega^2\right)^2}{4}Q^{422}$$
$$+ 3\lambda^2 \frac{1 - \omega^2}{2}Q^{442} + \lambda^3 Q^{444} \tag{4.7}$$

$$V^{\{4\}}(Q) = \left(\frac{1 - \omega^2}{2}Q^2 + \lambda Q^4 \right)^{\{4\}} = \frac{\left(1 - \omega^2\right)^4}{16}Q^{2222} + 4\lambda \frac{\left(1 - \omega^2\right)^3}{8}Q^{4222} + \lambda^2 \frac{\left(1 - \omega^2\right)^2}{4}$$
$$\times \left(4Q^{4422} + 2Q^{4242} \right) + 4\lambda^3 \frac{1 - \omega^2}{2}Q^{4442} + \lambda^4 Q^{4444} \tag{4.8}$$

$$V^{\{5\}}(Q) = \left(\frac{1 - \omega^2}{2}Q^2 + \lambda Q^4 \right)^{\{5\}} = \frac{\left(1 - \omega^2\right)^5}{32}Q^{22222} + 5\lambda \frac{\left(1 - \omega^2\right)^4}{16}Q^{42222}$$
$$+ 5\lambda^2 \frac{\left(1 - \omega^2\right)^3}{8} \left(Q^{44222} + Q^{42422} \right) + 5\lambda^3 \frac{\left(1 - \omega^2\right)^2}{4} \left(Q^{44422} + Q^{44242} \right)$$
$$+ 5\lambda^4 \frac{1 - \omega^2}{2}Q^{44442} + \lambda^5 Q^{44444} \tag{4.9}$$

Fig. 2. Inverse temperature (β) dependence of the fifth-order variational-perturbative approximations to the free energy of the quartic anharmonic oscillator, $V(x) = \lambda x^4$, in the case of $\lambda = 0.1$ and $\lambda = 0.3$. The approximations obtained from the partition function expansion (F_{PF}), from the free energy expansion (F_{FE}) and from the sum over states definition of the partition function (F_{RS}), are compared with the exact free energy.**(Author, caption correct?)**
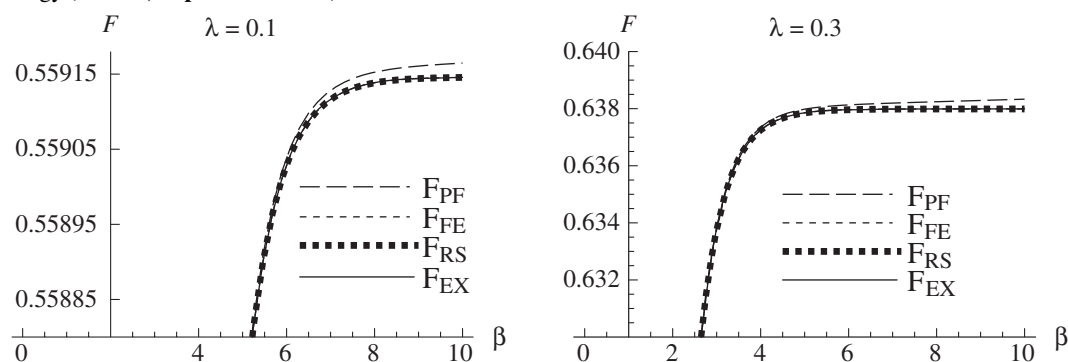
The formulae for $\Delta_\nu E_n$ are given by (4.5)–(4.9) with the $Q^{k_1 k_2 \cdots k_\nu}$-functions replaced by the $L^{k_1 k_2 \cdots k_\nu}$-coefficients, respectively. All the necessary products of Q and L are presented in the Appendix.

At any finite order, the approximate expressions depend on the arbitrary parameter ω, in contrast to the exact result, which does not depend on this parameter. The freedom of choosing the value of ω is used to advantage in formulating the variational-perturbation theory [12–15]. According to Stevenson's principle of minimal sensitivity (PMS) [39], the value of ω is chosen so that the approximate expression is insensitive to small variations of this parameter, i.e., the dependence on ω is as flat as possible. The variational-perturbation methodology has been successfully applied for calculating the energy eigenvalues to high orders [12, 13]. The first-order expressions have been obtained for the partition function [26]. The free energy, not very well described in the first order [28, 29], has been shown to improve noticeably in the second and third order [27, 33]. Here, we extend the calculation of the free energy to the fifth order, considering the three methods of deriving the approximate result, namely, calculating $F_{PF}(\beta)$, $F_{FE}(\beta)$, and $F_{RS}(\beta)$, as they are defined in (2.19), (2.20), and (3.13), respectively. One should note that the variational-perturbation expression for $F_{FE}(\beta)$ agrees with those derived with diagrammatic techniques up to the third [27] and fourth order [34]. Approximations to $F_{FE}(\beta)$ are also discussed in ref. 40, where the perturbation expansion of the imaginary-time evolution amplitude was derived in a recursive way. The coefficients of the recursion formulas were used to obtain the variational-perturbation results up to fifth order for the quartic oscillator; however, the explicit formulas for the free energy were not obtained. In our approach, the formulas for $F_{PF}(\beta)$ and $F_{FE}(\beta)$ up to fifth order can be easily derived with the use of (4.1)–(4.9). In each order calculation, the application of the minimal sensitivity condition to the $F_{PF}(\beta)$ and $F_{FE}(\beta)$, determines the arbitrary frequency ω as a function of the temperature. In the RS method, the optimized value of ω is temperature independent but fixed for each energy level independently. The RS method seems to be more complicated, as the summation over many optimized states has to be performed for determining the partition function, but the optimization conditions are easier to analyze, because the polynomial equations can be solved with the Mathematica command *NSolve* instead of *FindRoot* that is necessary in the PF and FE methods.

In Fig. 2, the fifth-order results of the above calculations are plotted in comparison with the exact free energy of the quartic oscillator. A comparison with the results of the conventional perturbation theory (Fig. 1) shows that the optimization procedure has significantly improved the accuracy in the whole range of temperature, both for small and for large values of the parameter λ. Also the discrepancies between the results of the PF, FE, and RS methods have been greatly diminished, which can be attributed

Table 1. The five successive variational-perturbation approximations $F^{[1]}$, $F^{[2]}$, $F^{[3]}$, $F^{[4]}$, $F^{[5]}$, to the free energy of quartic, quartic–sextic, and octic anharmonic oscillators, as calculated from the PF, FE, and RS methods at various values of the coupling constant λ.

Quartic	$\lambda = 1$				$\lambda = 1000$			
β	0.01	0.1	1	10	0.01	0.1	1	10
$F_{PF}^{[1]}$	−304.729	−12.8758	0.698309	0.832822	−132.833	5.55002	7.16351	7.21579
$F_{FE}^{[1]}$	−306.817	−13.0631	0.677890	0.812500	−135.068	5.22948	6.82795	6.82795
$F_{RS}^{[1]}$	−311.976	−13.4945	0.667282	0.812500	−140.159	5.05194	6.82795	6.82795
$F_{PF}^{[2]}$	−308.577	−13.2303	0.668282	0.815787	−136.810	5.13230	6.96789	7.24651
$F_{FE}^{[2]}$	−310.512	−13.3926	0.659344	0.804190	−138.887	4.94572	6.70400	6.70400
$F_{RS}^{[2]}$	−311.280	−13.4629	0.657256	0.804190	−139.788	4.90215	6.70400	6.70400
$F_{PF}^{[3]}$	−310.214	−13.3665	0.661660	0.811481	−138.554	4.99051	6.85562	7.07671
$F_{FE}^{[3]}$	−311.182	−13.4470	0.657601	0.803914	−139.587	4.90722	6.69703	6.69703
$F_{RS}^{[3]}$	−311.293	−13.4559	0.657106	0.803914	−139.694	4.89789	6.69703	6.69703
$F_{PF}^{[4]}$	−310.819	−13.4189	0.658579	0.807329	−139.191	4.93534	6.79762	7.11167
$F_{FE}^{[4]}$	−311.390	−13.4644	0.658579	0.803756	−139.805	4.89439	6.6939	6.69390
$F_{RS}^{[4]}$	−311.292	−13.4565	0.657073	0.803756	−139.700	4.89744	6.69390	6.69390
$F_{PF}^{[5]}$	−311.077	−13.4394	0.657793	0.806438	−139.469	4.91505	6.76247	7.00198
$F_{FE}^{[5]}$	−311.415	−13.4663	0.656912	0.803762	−139.832	4.89329	6.69397	6.69397
$F_{RS}^{[5]}$	−311.291	−13.4566	0.657097	0.803762	−139.702	4.89794	6.69397	6.69397
F_{EXACT}	−311.291	−13.4565	0.657105	0.803771	−139.699	4.89816	6.69422	6.69422

Quartic–sextic	$\lambda_1 = 1, \lambda_2 = 1$				$\lambda_1 = 1, \lambda_2 = 10$			
β	0.01	0.1	1	10	0.01	0.1	1	10
$F_{PF}^{[1]}$	−258.013	−9.89832	0.936651	1.020520	−222.026	−6.50083	1.47954	1.54319
$F_{FE}^{[1]}$	−261.724	−10.2345	0.891213	0.963747	−225.959	−6.89758	1.38494	1.40218
$F_{RS}^{[1]}$	−273.506	−11.1321	0.876347	0.963747	−238.664	−7.86784	1.37753	1.40218
$F_{PF}^{[2]}$	−260.880	−10.2130	0.891952	1.011910	−224.66	−6.79348	1.41563	1.57529
$F_{FE}^{[2]}$	−267.141	−10.7299	0.855942	0.939982	−231.519	−7.42854	1.32818	1.34951
$F_{RS}^{[2]}$	−272.051	−11.1332	0.848199	0.939982	−237.238	−7.95890	1.32186	1.34951
$F_{PF}^{[3]}$	−266.544	−10.6640	0.868163	0.992276	−230.957	−7.35447	1.36782	1.51698
$F_{FE}^{[3]}$	−270.416	−10.9765	0.848772	0.937867	−235.237	−7.74398	1.31639	1.34118
$F_{RS}^{[3]}$	−272.049	−11.1062	0.845906	0.937867	−237.103	−7.93549	1.31339	1.34118
$F_{PF}^{[4]}$	−267.536	−10.7603	0.859244	0.998444	−231.938	−7.45378	1.35382	1.57313
$F_{FE}^{[4]}$	−271.680	−11.0766	0.844958	0.935953	−236.634	−7.86645	1.30961	1.33536
$F_{RS}^{[4]}$	−272.097	−11.0945	0.844340	0.935953	−237.190	−7.90724	1.30763	1.33536
$F_{PF}^{[5]}$	−269.459	−10.9055	0.853101	0.985871	−234.131	−7.64473	1.33779	1.52845
$F_{FE}^{[5]}$	−272.215	−11.1111	0.844348	0.935844	−237.290	−7.91780	1.30810	1.33447
$F_{RS}^{[5]}$	−272.065	−11.0971	0.844332	0.935844	−237.175	−7.90735	1.30668	1.33447
F_{EXACT}	−272.072	−11.0969	0.844240	0.935566	−237.169	−7.90511	1.30552	1.33295
$F_{PF}^{[1]}$	−235.701	−8.9292	0.899074	0.997290	−169.417	−1.98262	2.61935	2.76327
$F_{FE}^{[1]}$	−240.791	−9.4319	0.821229	0.889691	−174.581	−2.56974	2.32060	2.32124
$F_{RS}^{[1]}$	−260.918	−11.0606	0.790936	0.889691	−194.214	−3.80197	2.31942	2.32124

Table 1. (*concluded*).

Octic	$\lambda = 1$				$\lambda = 200$			
β	0.01	0.1	1	10	0.01	0.1	1	10
$F_{\mathrm{PF}}^{[2]}$	−229.774(3)	−8.371(3)	0.889320	1.078530	−163.503(3)	−1.69417	2.70361	3.09564
$F_{\mathrm{FE}}^{[2]}$	−243.318	−9.7176	0.780272	0.856656	−177.164	−2.92164	2.21277	2.21271
$F_{\mathrm{RS}}^{[2]}$	−258.751	−11.1909	0.745475	0.856656	−193.208	−4.15904	2.21004	2.21271
$F_{\mathrm{PF}}^{[3]}$	−244.417	−9.7702	0.816753	1.032820	−178.213	−2.88536	2.52759	2.95025
$F_{\mathrm{FE}}^{[3]}$	−251.942	−10.4792	0.745999	0.842822	−185.799	−3.62704	2.15405	2.15485
$F_{\mathrm{RS}}^{[3]}$	−258.433	−11.1960	0.729874	0.842822	−192.499	−4.25475	2.15203	2.15485
$F_{\mathrm{PF}}^{[4]}$	−243.160	−9.6745	0.826264	1.138220	−176.970	−2.81629	2.65263	3.39989
$F_{\mathrm{FE}}^{[4]}$	−253.227	−10.6084	0.739421	0.838340	−187.103	−3.76666	2.14085	2.14085
$F_{\mathrm{RS}}^{[4]}$	−258.733	−11.0811	0.723901	0.838340	−192.236	−4.19546	2.13785	2.14085
$F_{\mathrm{PF}}^{[5]}$	−248.620	−10.1685	0.792115	1.090350	−182.444	−3.29461	2.52499	3.24850
$F_{\mathrm{FE}}^{[5]}$	−256.227	−10.8695	0.728728	0.833459	−190.097	−3.99758	2.12001	2.12063
$F_{\mathrm{RS}}^{[5]}$	−258.733	−11.0935	0.718932	0.833459	−192.647	−4.23124	2.11767	2.12063
F_{EXACT}	−258.639	−11.0750	0.709342	0.820685	−192.481	−4.16669	2.07037	2.07309

to the fact that the optimization procedure improves the convergence properties of the approximation scheme. One can see that the convergence of the above scheme for $F_{\mathrm{FE}}(\beta)$ is much quicker that those obtained in the variational expansion of Lu et al. [34], where $\omega(\beta)$ has been fixed so as to minimize the first-order expression for the free energy, and used as an optimal frequency in higher order calculations. In our scheme, the minimal sensitivity condition is applied to each order approximation for $F_{\mathrm{FE}}(\beta)$, and the optimal frequency $\omega(\beta)$ changes from order to order.

We performed a similar calculation for the quartic–sextic anharmonic potential

$$v(x) = \lambda_1 x^4 + \lambda_2 x^6 \tag{4.10}$$

and for the octic potential

$$v(x) = \lambda x^8 \tag{4.11}$$

Numerical results of the PF, FE, and RS methods for the free energy of the oscillators above are listed in Table 1 at various temperatures. For determination of the optimal ω, the condition for vanishing for the first derivative of the F-functions in odd-order approximations, and of the second derivative in even-order approximations, except in a few cases, is indicated by (3) in Table 1, where the third derivative has been used. One can observe how successive order approximations of the PF, FE, and RS method approach the exact free energy. In all orders, the FE and RS methods give much better results than those obtained using the PF method. The function $F_{\mathrm{PF}}(\beta)$ shows a wrong asymptotic behavior for small temperatures, namely, it diverges for $\beta > \beta_0$, where β_0 corresponds to the minimum of internal energy, according to the criterion of decreasing internal energy [30]. At low temperatures ($\beta \to \infty$), the functions $F_{\mathrm{FE}}(\beta)$ and $F_{\mathrm{RS}}(\beta)$ have exactly the same form, approaching the variational-perturbation approximation to the ground-state energy. At high temperatures ($\beta \to 0$), the function $F_{\mathrm{FE}}(\beta)$ diverges to negative infinity for even-order approximations and to positive infinity for odd-order approximations, the RS method proves to agree better with the exact free energy, which can be attributed to the fact that optimization of the frequency parameter in this method is performed independently for individual energy levels. This is particularly clearly visible for the octic anharmonic oscillator in Fig. 3.

Fig. 3. The first five successive variational-perturbation approximations to the free energy of the octic anharmonic oscillator, $V(x) = \lambda x^8$, compared with the exact free energy, in the case of $\lambda = 1000$.
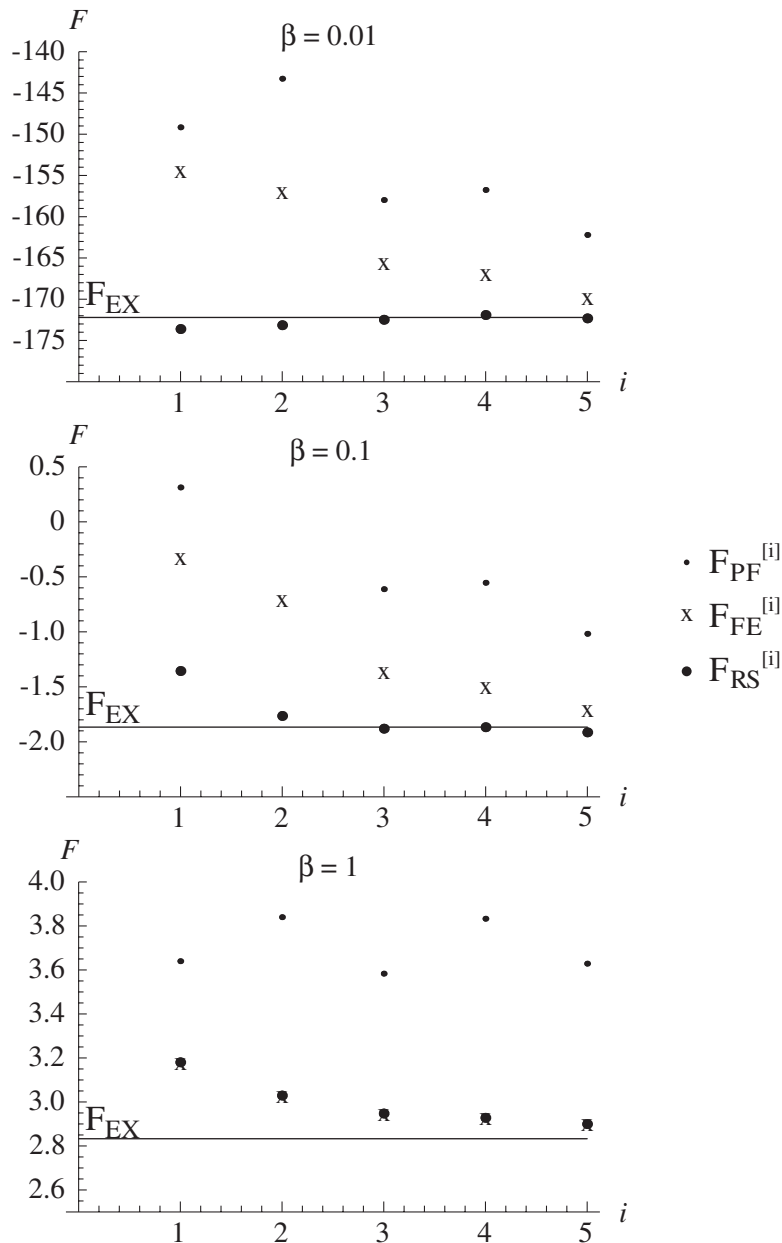
5. Conclusion

In this paper, we derive the perturbation expansion of the partition function for a general class of oscillators with a polynomial anharmonic potential, providing a formally simple formula for an arbitrary order term. Similar formulas have also been obtained for the optimized perturbation expansion with a frequency variational parameter. The above expansions for the partition function have been used

to obtain the formal formulas for energy levels and the free energy in perturbation and variational-perturbation theory. We discussed the three methods of calculating the free energy: from the partition function expansion (PF), from the free energy expansion (FE), and from the sum over states definition of the partition function (RS).

Numerical results have been discussed up to fifth order of the perturbation and variational-perturbation theory, in the case of quartic, quartic–sextic, and octic anharmonic oscillators. The divergent character of perturbation theory shows up in calculating the free energy, since the PF, FE, and RS methods yield very different results that deviate from the exact results, especially strongly at high temperatures. The deficiencies of the perturbation theory are overcome in the variational-perturbation approach, which provides highly accurate approximations to the free energy of the oscillators considered. The fifth-order results of the FE and RS methods are similar to each other and agree well with the exact free energy in the broad range of temperatures. The PF method is much worse and should be avoided, the choice has to be made thus between the RS and FE methods. Although the results of the RS method are the most accurate in the whole range of temperature, the FE method is more elegant, since summation over states is avoided, and only one function of a compact form has to be analyzed to determine the optimal frequency. The fact that the optimal frequencies change from order to order is crucial for convergence of both approximation schemes.

The operator method of deriving the perturbation expansion elaborated in this paper can be very useful in studying the extensions to multidimensional problems. The main advantage of the method is that the perturbation formulas, for both the energy eigenvalues and the free energy, can be determined to any order without necessity of summation over intermediary states, which circumvents possible degeneracy complications. This makes the task of determining the accurate energy spectrum and the study of thermal properties of multidimensional systems feasible within the variational-perturbation theory. We shall discuss this issue in a separate publication.

References

1. C.M. Bender and T.T. Wu. Phys. Rev. **184**, 1231 (1969).
2. S.N. Biswas, K. Datta, R.P. Saxena, P.K. Srivastava, and V.S. Varma. J. Math. Phys. **14**, 1190 (1973).
3. K. Banerjee and S.P. Bhatnagar. Phys. Rev. D, **18**, 4767 (1978).
4. K. Banerjee and S.P. Bhatnagar. Phys. Rev. D, **18**, 4767 (1978).
5. R.N. Chaudhuri and M. Mondal. Phys. Rev. A, **40**, 6080 (1989).
6. R.N. Chaudhuri and M. Mondal. Phys. Rev. A, **43**, 3241 (1991).
7. F.T. Hioe and E.W. Montroll. J. Math. Phys. **16**, 1945 (1975).
8. F.T. Hioe, D. Macmillen, and E.W. Montroll. Phys. Rep. **43**, 305 (1978).
9. H. Chen-Shiung and J.L. Chern. Phys. Rev. D, **29**, 643 (1984).
10. U.B. Kaulfuss and M. Altenbokum. Phys. Rev. D, **33**, 3658 (1986).
11. R.F. Bishop and M.F. Flynn. Phys. Rev. A, **38**, 2211 (1988).
12. W.E. Caswell. Ann. Phys. **123**, 153 (1979).
13. J. Killingbeck. J. Phys. A, **14**, 1005 (1981).
14. A. Okopińska. Phys. Rev. D, **35**, 1835 (1987).
15. W. Janke and H. Kleinert. Phys. Rev. Lett. **75**, 2787 (1995).
16. R. Jáuregui and J. Récamier. Phys. Rev. A, **46**, 2240 (1992).
17. F.M. Fernández and J.F. Ogilvie. Phys. Lett. **178A**, 11 (1993).
18. M.R.M. Witwit. J. Math. Phys. **36**, 187 (1995).
19. M.R.M. Witwit. J. Math. Chem. **22**, 11 (1997).
20. H. Meißner and E.O. Steinborn. Phys. Rev. A, **56**, 1189 (1997).
21. M.H. Macfarlane. Ann. Phys. **271**, 159 (1999).
22. J. Schwinger. Phys. Rev. **82**, 664 (1951).
23. G.V. Chester. Phys. Rev. **93**, 664 (1951).
24. A.W. Saenz and R.C. O'Rourke. Rev. Mod. Phys. **27**, 386 (1955).
25. K. Vlachos. Phys. Lett. **141A**, 65 (1989).

26. W. Witschel. Phys. Lett. **77A**, 107 (1980).
27. A. Okopińska. Phys. Rev. D, **36**, 2415 (1987).
28. H. Büttner and N. Flytzanis. Phys. Rev. A, **36**, 3443 (1987).
29. S. Srivastastava and Vishwamittar. Phys. Rev. A, **44**, 8006 (1991).
30. K. Vlachos. Phys. Rev. A, **47**, 838 (1993).
31. H. Kleinert. Phys. Lett. **173A**, 332 (1993).
32. H. Kleinert and H. Meyer. Phys. Lett. **173A**, 332 (1994).
33. K. Vlachos and A. Okopińska. Phys. Lett. **186A**, 375 (1994).
34. W.F. Lu, S.K. You, J. Bak, C.K. Kim, and K. Nahm. J. Phys. A, **35**, 21 (2002).
35. R.M. Wilcox. J. Math. Phys. **8**, 962 (1966).
36. A. Okopińska. Phys. Rev. D, **36**, 1273 (1987).
37. F.M. Fernández. Am. J. Phys. **71**,(11) 1136 (2003).
38. I.S. Gradshteyn and I.M. Ryzhik. Tables of integrals, series, and products. *Edited by* Yu.V. Geronimus and M.Yu. Tseytlin. Academic Press, New York and London. 1965. p. 14.
39. P.M. Stevenson. Phys. Rev. D, **23**, 2916 (1981).
40. F. Weissbach, A. Pelster, and B. Hamprecht. Phys. Rev. E, **66**, 036129 (2002).

Appendix A.

The Q–functions that appear in (2.20) and (4.5)–(4.9) in terms of the variable $y = e^{-\beta\omega}$ have the form

$$Q^{22} = \frac{1}{4(1-y)^2\beta\omega^3}\left[2\left(1-y^2\right) + \left(1+6y+y^2\right)\beta\omega\right] \tag{A1}$$

$$Q^{42} = \frac{3(1+y)}{8(1-y)^3\beta\omega^4}\left[4\left(1-y^2\right) + \left(1+10y+y^2\right)\beta\omega\right] \tag{A2}$$

$$Q^{44} = \frac{3}{16(1-y)^4\beta\omega^5}\left[4\left(1-y^2\right)\left(7+20y+7y^2\right)\right.$$
$$\left. + 3\left(1+20y+54y^2+20y^3+y^4\right)\beta\omega\right] \tag{A3}$$

$$Q^{222} = \frac{1}{16(1-y)^3\beta^2\omega^5}\left[12(1-y)(1-y)^2 + 6(1-y)\left(1+6y+y^2\right)\beta\omega\right.$$
$$\left. + \left(1+23y+23y^2+y^3\right)\beta^2\omega^2\right] \tag{A4}$$

$$Q^{422} = \frac{3}{32(1-y)^4\beta^2\omega^6}\left[32\left(1-y^2\right)^2 + 10\left(1-y^2\right)\left(1+10y+y^2\right)\beta\omega\right.$$
$$\left. + \left(1+40y+110y^2+40y^3+y^4\right)\beta^2\omega^2\right] \tag{A5}$$

$$Q^{442} = \frac{3}{64(1-y)^5\beta^2\omega^7}\left[40(1-y)^2\left(7+27y+27y^2+7y^3\right)\right.$$
$$+ (1-y)\left(13+250y+594y^2+250y^3+13y^4\right)\beta\omega$$
$$\left. + 3\left(1+69y+410y^2+410y^3+69y^4+y^5\right)\beta^2\omega^2\right] \tag{A6}$$

$$Q^{444} = \frac{27}{128\,(1-y)^6\,\beta^2\omega^8}\Big[8\left(1-y^2\right)^2\left(37+176y+37y^2\right)$$
$$- 4\left(1-y^2\right)\left(7+226y+894y^2+226y^4+7y^4\right)\beta\omega$$
$$+ \left(1+10y+y^2\right)\left(1+108y+262y^2+108y^3+y^4\right)\beta^2\omega^2\Big] \quad \text{(A7)}$$

$$Q^{2222} = \frac{1}{96\,(1-y)^4\,\beta^3\omega^7}\Big[120\,(1+y)\,(1-y)^3+60\,(1-y)^2\left(1+6y+y^2\right)\beta\omega$$
$$+ 12\left(1-y^2\right)\left(1+22y+y^2\right)\beta^2\omega^2$$
$$+ \left(1+76y+230y^2+76y^3+y^4\right)\beta^3\omega^3\Big] \quad \text{(A8)}$$

$$Q^{4222} = \frac{1}{64\,(1-y)^5\,\beta^3\omega^8}\Big[384\,(1-y)\left(1-y^2\right)^2+132\,(1-y)\left(1-y^2\right)\left(1+10y+y^2\right)\beta\omega$$
$$+ 18\,(1-y)\left(1+40y+110y^2+40y^3+y^4\right)\beta^2\omega^2$$
$$+ (1+y)\left(1+128y+702y^2+128y^3+y^4\right)\beta^3\omega^3\Big] \quad \text{(A9)}$$

$$Q^{4422} = \frac{3}{256\,(1-y)^6\,\beta^3\omega^9}\Big[\left(1-y^2\right)\left(527+462y-1642y^2+462y^3+527y^4\right)$$
$$+ 4\left(154+2507y+581y^2-7324y^3+581y^4+2507y^5+154y^6\right)\beta\omega$$
$$+ 2\left(1-y^2\right)\left(29+1912y+8758y^2+1912y^3+29y^4\right)\beta^2\omega^2$$
$$+ 2\left(1+218y+2671y^2+5740y^3+2671y^4+218y^5+y^6\right)\beta^3\omega^3\Big] \quad \text{(A10)}$$

$$Q^{4242} = \frac{3}{128\,(1-y)^6\,\beta^3\omega^9}\Big[5\left(1-y^2\right)\left(257+210y-1270y^2+210y^3+257y^4\right)$$
$$+ 12\left(24+447y+291y^2-1244y^3+291y^4+447y^5+24y^6\right)\beta\omega$$
$$+ 24\left(1-y^2\right)\left(1+68y+342y^2+68y^3+y^4\right)\beta^2\omega^2$$
$$+ \left(1+218y+2671y^2+5740y^3+2671y^4+218y^5+y^6\right)\beta^3\omega^3\Big] \quad \text{(A11)}$$

$$Q^{4442} = \frac{9}{256\,(1-y)^7\,\beta^3\omega^{10}}\Big[128\,(1-y)\left(1-y^2\right)^2\left(37+176y+37y^2\right)$$
$$+ 16\,(1-y)\left(1-y^2\right)\left(43+1314y+4546y^2+1314y^3+43y^4\right)\beta\omega$$
$$+ 8\,(1-y)\left(5+565y+5863y^2+12094y^3+5863y^4+565y^5+5y^6\right)\beta^2\omega^2$$
$$+ (1+y)\left(1+366y+7647y^2+24292y^3+7647y^4+366y^5+y^6\right)\beta^3\omega^3\Big] \quad \text{(A12)}$$

$$Q^{4444} = \frac{3\lambda^4}{512\,(1-y)^8\,\beta^3\omega^{11}} \left[80\,(1-y)\left(1-y^2\right)\left(2059 + 20286y + 40822y^2 + 20286y^3 \right.\right.$$
$$\left. + 2059y^4\right) + 48\,(1-y)^2\left(271 + 14178y + 109209y^2 + 205164y^3 + 109209y^4 \right.$$
$$\left. + 14178y^5 + 271y^6\right)\beta\omega + 72\left(1-y^2\right)\left(7 + 1312y + 22529y^2 + 66544y^3 \right.$$
$$\left. + 22529y^4 + 1312y^5 + 7y^6\right)\beta^2\omega^2 + 9\left(1 + 616y + 22972y^2 + 155992y^3 \right.$$
$$\left.\left. + 285958y^4 + +155992y^5 + 22972y^6 + 616y^7 + y^8\right)\beta^3\omega^3 \right] \quad \text{(A13)}$$

$$Q^{22222} = \frac{1}{768\,(1-y)^5\,\beta^4\omega^9}\left[1680\,(1-y)^4\,(1+y) + 840\,(1-y)^3\left(1 + 6y + y^2\right)\beta\omega \right.$$
$$+ 180\,(1-y)^2\,(1+y)\left(1 + 22y + y^2\right)\beta^2\omega^2$$
$$+ 20\,(1-y)\left(1 + 76y + 230y^2 + 76y^3 + y^4\right)\beta^3\omega^3$$
$$\left. + (1+y)\left(1 + 236y + 1446y^2 + 236y^3 + y^4\right)\beta^4\omega^4 \right] \quad \text{(A14)}$$

$$Q^{42222} = \frac{1}{512\,(1-y)^6\,\beta^4\omega^{10}}\left[6144\,(1-y)^2\left(1-y^2\right)^2 + 2232\,(1-y)^2\left(1-y^2\right) \right.$$
$$\times\left(1 + 10y + y^2\right)\beta\omega + 348\,(1-y)^2\left(1 + 40y + 110y^2 + 40y^3 + y^4\right)\beta^2\omega^2$$
$$+ 28\left(1-y^2\right)\left(1 + 128y + 702y^2 + 128y^3 + y^4\right)\beta^3\omega^3$$
$$\left. + \left(1 + 398y + 5311y^2 + 11620y^3 + 5311y^4 + 398y^5 + y^6\right)\beta^4\omega^4 \right] \quad \text{(A15)}$$

$$Q^{44222} = \frac{1}{1024\,(1-y)^7\,\beta^4\omega^{11}}\left[90\,(1-y)\left(1-y^2\right)\left(797 + 714y - 2014y^2 + 714y^3 + 797y^4\right) \right.$$
$$+ 9\,(1-y)\left(2121 + 33508y + 5999y^2 - 87736y^3 + 5999y^4 + 33508y^5 + 2121y^6\right)\beta\omega$$
$$+ 36\,(1+y)\left(62 + 3807y + 8899y^2 - 27496y^3 + 8899y^4 + 3807y^5 + 62y^6\right)\beta^2\omega^2$$
$$+ 16\,(1-y)\left(8 + 1699y + 19708y^2 + 41650y^3 + 19708y^4 + 1699y^5 + 8y^6\right)\beta^3\omega^3$$
$$\left. + 3\,(1+y)\left(1 + 666y + 15087y^2 + 49132y^3 + 15087y^4 + 666y^5 + y^6\right)\beta^4\omega^4 \right] \quad \text{(A16)}$$

$$Q^{42422} = \frac{3}{1024\,(1-y)^7\,\beta^4\omega^{11}}\left[90\,(1-y)\left(1-y^2\right)\left(257 + 210y - 1270y^2 + 210y^3 + 257y^4\right) \right.$$
$$+ (1-y)\left(5893 + 106964y + 50387y^2 - 313048y^3 + 50387y^4 + 106964y^5 + 5893y^6\right)\beta\omega$$
$$+ 12\,(1+y)\left(52 + 3477y + 10539y^2 - 26176y^3 + 10539y^4 + 3477y^5 + 52y^6\right)\beta^2\omega^2$$
$$+ 36\,(1-y)\left(1 + 218y + 2671y^2 + 5740y^3 + 2671y^4 + 218y^5 + y^6\right)\beta^3\omega^3$$
$$\left. + (1+y)\left(1 + 666y + 15087y^2 + 49132y^3 + 15087y^4 + 666y^5 + y^6\right)\beta^4\omega^4 \right] \quad \text{(A17)}$$

$$Q^{44422} = \frac{1}{2048\,(1-y)^8\,\beta^4\omega^{12}}\left[10\left(1-y^2\right)^2\left(86827 + 238626y - 472154y^2 + 238626y^3\right.\right.$$
$$\left.+\,86827y^4\right) + 15\left(1-y^2\right)\left(10777 + 278628y + 306303y^2 - 1316856y^3\right.$$
$$\left.+306303y^4 + 278628y^5 + 10777y^6\right)\beta\omega + 108\left(124 + 12829y + 94991y^2\right.$$
$$\left.+4291y^3 - 255830y^4 + 4291y^5 + 94991y^6 + 12829y^7 + 124y^8\right)\beta^2\omega^2$$
$$+\,12\left(1-y^2\right)\left(43 + 15138y + 293141y^2 + 90207y^3 + 293141y^4 + 15138y^5\right.$$
$$\left.+43y^6\right)\beta^3\omega^3 + 9\left(1 + 1116y + 44836y^2 + 311716y^3 + 574902y^4 + 311716y^5\right.$$
$$\left.\left.+44836y^6 + 1116y^7 + y^8\right)\beta^4\omega^4\right] \quad (A18)$$

$$Q^{42442} = \frac{1}{2048\,(1-y)^8\,\beta^4\omega^{12}}\left[10\left(1-y^2\right)^2\left(83669 + 231390y - 808870y^2 + 231390y^3\right.\right.$$
$$\left.+83669y^4\right) + 15\left(1-y^2\right)\left(9767 + 295068y + 491073y^2 - 1466376y^3\right.$$
$$\left.+491073y^4 + 295068y^5 + 9767y^6\right)\beta\omega + 36\left(292 + 32697y + 278003y^2\right.$$
$$\left.+75303y^3 - 678510y^4 + 75303y^5 + 278003y^6 + 32697y^7 + 292y^8\right)\beta^2\omega^2$$
$$+\,24\left(1-y^2\right)\left(19 + 6804y + 136373y^2 + 425928y^3 + 136373y^4 + 6804y^5\right.$$
$$\left.+19y^6\right)\beta^3\omega^3 + 9\left(1 + 1116y + 44836y^2 + 311716y^3 + 574902y^4 + 311716y^5\right.$$
$$\left.\left.+44836y^6 + 1116y^7 + y^8\right)\beta^4\omega^4\right] \quad (A19)$$

$$Q^{44442} = \frac{3}{4096\,(1-y)^9\,\beta^4\omega^{13}}\left[1760\left(1-y^3\right)\left(1-y^2\right)\left(2059 + 20286y + 40822y^2 + 20286y^3\right.\right.$$
$$\left.+\,2059y^4\right) + 80\,(1-y)^3\left(5311 + 259820y + 1817153y^2 + 3317480y^3\right.$$
$$\left.+\,1817153y^4 + 259820y^5 + 5311y^6\right)\beta\omega + 480\,(1-y)\left(1-y^2\right)\left(46 + 8121y\right.$$
$$\left.+126450y^2 + 355950y^3 + 126450y^4 + 8121y^5 + 46y^6\right)\beta^2\omega^2 + 72\,(1-y)$$
$$\times\left(9 + 5294y + 182296y^2 + 1197746y^3 + 2175230y^4 + 1197746y^5\right.$$
$$\left.+\,182296y^6 + 5294y^7 + 9y^8\right)\beta^3\omega^3 + 9\,(1+y)\left(1 + 1864y + 122236y^2\right.$$
$$\left.\left.+\,1268344y^3 + 3021190y^4 + 1268344y^5 + 122236y^6 + 1864y^7 + y^8\right)\beta^4\omega^4\right] \quad (A20)$$

$$Q^{44444} = \frac{9}{8192\,(1-y)^{10}\,\beta^4\omega^{14}} \Bigg[480\,(1-y)^2\left(1-y^2\right)^2 \left(33953 + 483478y + 1299778y^2 \right.$$
$$\left. + 483478y^3 + 33953y^4\right) + 80\,(1-y)^2\left(1-y^2\right)\left(13403 + 1033948y \right.$$
$$\left. + 11090101y^2 + 25920136y^3 + 11090101y^4 + 1033948y^5 + 13403y^6\right)\beta\omega +$$
$$+ 480\,(1-y)^2\left(80 + 23155y + 626726y^2 + 3710541y^3 + 6537876y^4 + \right.$$
$$\left. + 3710541y^5 + 626726y^6 + 23155y^7 + 80y^8\right)\beta^2\omega^2$$
$$+ 120\left(1-y^2\right)\left(7 + 6798y + 375152y^2 + 3632658y^3 + 8421330y^4 \right.$$
$$\left. + 3632658y^5 + 375152y^6 + 6798y^7 + 7y^8\right)\beta^3\omega^3$$
$$+ 9\left(1 + 3114y + 336973y^2 + 5853112y^3 + 28340146y^4 + 47054908y^5 \right.$$
$$\left. + 28340146y^6 + 5853112y^7 + 336973y^8 + 3114y^9 + y^{10}\right)\beta^4\omega^4 \Bigg] \quad \text{(A21)}$$

The L coefficients that appear in (3.11) have the form

$$N_0 = 1 + 2n \tag{A22}$$

$$L^2 = \frac{1}{2\omega}N_0, \quad L^{22} = \frac{1}{2\omega^2}L^2, \quad L^{222} = \frac{1}{2\omega^4}L^2, \quad L^{2222} = \frac{5}{8\omega^6}L^2, \quad L^{22222} = \frac{7}{8\omega^8}L^2 \tag{A23}$$

$$L^4 = \frac{3}{8\omega^2}\left(1 + N_0^2\right), \quad L^{42} = \frac{1}{\omega^2}L^4, \quad L^{422} = \frac{4}{3\omega^4}L^4, \quad L^{4222} = \frac{2}{\omega^6}L^4, \quad L^{42222} = \frac{16}{5\omega^8}L^4 \tag{A24}$$

$$L^{44} = \frac{1}{32\omega^5}\left(67N_0 + 17N_0^3\right), \qquad L^{442} = \frac{5}{3\omega^2}L^{44}, \qquad 4L^{4422} + 2L^{2424} = \frac{35}{2\omega^4}L^{44},$$
$$L^{44222} + L^{42422} = \frac{21}{2\omega^6}L^{44} \tag{A25}$$

$$L^{444} = \frac{3}{16^2\omega^8}\left(513 + 1138N_0^2 + 125N_0^4\right), \quad L^{4442} = \frac{2}{\omega^2}L^{444}, \quad L^{44422} + L^{44242} = \frac{8}{\omega^4}L^{444} \tag{A26}$$

$$L^{4444} = \frac{1}{2^{11}\omega^{11}}\left(305141N_0 + 178330N_0^3 + 10689N_0^5\right), \qquad L^{44442} = \frac{55}{\omega^2}L^{4444} \tag{A27}$$

$$L^{44444} = \frac{3}{2^{12}\omega^{14}}\left(971046 + 3105983N_0^2 + 783020N_0^4 + 29183N_0^6\right) \tag{A28}$$