Calculation of the Partition Function of a Double Minimum Oscillator from a Modified Variation Perturbation Method

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The partition function of a double minimum oscillator is evaluated by means of variation perturbation theory. For low temperatures, the method cannot be applied in the usual way. Even for a symmetric double minimum potential $V_{\mathrm{DM}}(x)$, the shift of the harmonic reference oscillator is not always zero as expected, but its minimum is near one of the minima of $V_{\mathrm{DM}}(x)$ at low temperatures. The partition function thus calculated is only half the correct value. For sufficiently high temperature, the method works normally. The anomaly in the low temperature region is investigated in detail, and a modification of the variation perturbation method is suggested which eliminates most of the problems.

Key words: partition function, double minimum oscillator, inversion modes, variation perturbation theory, Pitzer–Gwinn method.

Introduction

The theoretical description of inversion modes is still an actual topic in spectroscopy [1, 2]. Inversion modes do not only occur in the well known examples of organic amines and of ammonia itself [3, 4], but also in the molecule ion H_3O^+ postulated in chemistry textbooks since a long time, which has been identified recently as free molecule in the gas phase by high resolution infrared spectroscopy [5].

The partition function (PF) of anharmonic oscillators can be evaluated by various approaches, e. g., the thermal Hartree method [6], the thermal cluster cumulant method [7, 8], path integral methods [9, 10, 11, 12] and the thermodynamic variation pertubation approach [13, 14]. In this work, the latter method is employed, which has been used in two preceeding papers [13, 14] to calculate the vibrational partition function of diatomic molecules. At the present stage of development, the variation perturbation method is applicable only to polynomial potentials, thus neglecting dissociation. The goal of those papers was therefore not so much to evaluate an accurate vibrational PF for diatomic molecules, but to test the accuracy and validity of the method, which is to be extended to polyatomic molecules. The polynomial potential used for the diatomics in [13] and [14] is of the same functional form as the normal mode description of the polyatomic molecules.

In this paper, the variation perturbation method will be applied to a double minimum potential, which is used in theoretical spectroscopy to describe inversion vibrations. A simple polynomial expression of a symmetric double minimum potential is of the form

$$V(x) = -Ax^2 + Bx^4 + C, \ A, B > 0, \tag{1}$$

where the parameter C can be chosen in such a way that the two minima are at $V = 0$. A double minimum potential differs qualitatively from the single–minimum potentials of diatomic molecules, thus its behaviour in the variation perturbation theory may differ from that of the potentials treated earlier.

1. The variation perturbation method

The thermodynamic variation perturbation method developed by Witschel and coworkers in the eighties [15, 16, 17] has been recently worked out numerically for diatomic molecules using quartic [13, 18] and sextic [14, 19] polynomial potentials. A comprehensive treatment of the computational details can be found in [14]. Therefore, in the present work the method is only sketched briefly.

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The thermodynamic variation perturbation method for the evaluation of partition functions is based on the Schwinger–type perturbation expansion of the partition function q of a Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_1$ [20]. Up to second order, the expansion is given by

$$
\begin{aligned}
q &= \mathrm{Tr}\left\{\exp\left[-\beta\left(\hat{H}_0 + \hat{H}_1\right)\right]\right\} \\
&= q_0 - q_1 + q_2 \mp \ldots,
\end{aligned}
$$

where

$$
\begin{aligned}
q_0 &= \mathrm{Tr}\left\{\exp\left(-\beta \hat{H}_0\right)\right\}, \\
q_1 &= \beta \mathrm{Tr}\left\{\exp\left(-\beta \hat{H}_0\right) \hat{H}_1\right\}, \\
q_2 &= \frac{\beta^2}{2}\mathrm{Tr}\left\{\int_0^1 \mathrm{d}s_1 \exp\left(-\beta \hat{H}_0\right) \exp\left(s_1 \beta \hat{H}_0\right)\right. \\
&\qquad \left. \hat{H}_1 \exp\left(-s_1 \beta \hat{H}_0\right) \hat{H}_1\right\}.
\end{aligned}
\tag{2}
$$

In order to obtain optimal convergence of (2), $\hat{H}$ has to be split in a way that $\hat{H}_1$ is "small" compared to $\hat{H}_0$. Contrary to $\hat{H}_1$, $\hat{H}_0$ occurs in the exponential functions of the expansion (2). The evaluation of matrix elements of transcendental functions of operators, which are off–diagonal in the basis used causes severe problems. Moreover, if the matrix elements of the exponential function $\exp\left\{-\beta\left(\hat{H}_0 + \hat{H}_1\right)\right\}$ of the off–diagonal operator $\hat{H}_0 + \hat{H}_1$ could be calculated easily, the partition function could be computed in a straightforward manner from a direct summation of the trace on the left hand side of (2) instead of using the complicated Schwinger expansion on the right hand side of this equation. Therefore, no off–diagonal term must occur in $\hat{H}_0$. Here, a splitting called "DIAG" is chosen, in which all diagonal terms are included in $\hat{H}_0$ in order to maximize it, whereas all the off–diagonal terms are collected in $\hat{H}_1$.

An exact lower bound (LB) of q is given by [21]

$$
\begin{aligned}
\mathrm{LB} &= \mathrm{Tr}\left\{e^{-\beta \hat{H}_0} e^{-\beta \langle \hat{H}_1 \rangle_0}\right\} \leq q, \\
\langle \hat{H}_1 \rangle_0 &= \frac{\mathrm{Tr}\left\{\exp\left(-\beta \hat{H}_0\right) \hat{H}_1\right\}}{\mathrm{Tr}\left\{\exp\left(-\beta \hat{H}_0\right)\right\}}.
\end{aligned}
\tag{3}
$$

In this case the splitting of $\hat{H} = \hat{H}_0 + \hat{H}_1$ is arbitrary, because the bound is an exact one. Using the splitting DIAG, we obtain for the lower bound and the first two orders q_0 and q_1 of the perturbation expansion (2)

$$
\mathrm{LB} = \mathrm{Tr}\left\{\exp\left(-\beta \hat{H}_0\right)\right\}, \; q_0 = \mathrm{LB}, \; q_1 = 0. \tag{4}
$$

By maximizing the lower bound LB, also the zeroth order q_0 of the expansion (2) is maximized, whereas the first order term q_1 vanishes because $\hat{H}_1$ is purely off–diagonal. Thus, the convergence of the perturbation expansion (2) is optimized by the subsequent variation step (3), (4). Numerical investigations indicate that the variation perturbation method is an asymptotic expansion for small anharmonicities [13, 19].

In order to obtain the variation parameters, a reference frequency Ω and a shift $-\Delta$ are introduced into $\hat{H} = \hat{T} + V(x)$.

$$
\begin{aligned}
\hat{H} = \underbrace{\frac{\hat{p}^2}{2\mu}}_{\hat{T}} &+ \frac{\mu\Omega^2}{2}(x+\Delta)^2 - \frac{\mu\Omega^2}{2}(x+\Delta)^2 \\
&+ \underbrace{\frac{\mu\omega^2}{2}x^2 + \sum_{j=3}^{N} k_j x^j}_{V(x)}.
\end{aligned}
\tag{5}
$$

μ: Reduced mass, $\hat{T}$: Operator of kinetic energy, x, $\hat{p}$: Coordinate and momentum, $V(x)$: Potential, k_j: Force constants, N is even.
A new coordinate X is introduced:

$$
X = x + \Delta, \; \left[\hat{X}, \hat{p}\right] = \left[\hat{x}, \hat{p}\right] = i\hbar. \tag{6}
$$

In the new variables,

$$
\hat{H} = \underbrace{\frac{\hat{p}^2}{2\mu} + \frac{\mu\Omega^2}{2}\hat{X}^2}_{\text{reference oscillator}} + \sum_{j=0}^{N} K_j \hat{X}^j \tag{7}
$$

is obtained for the Hamiltonian of a particle in a polynomial potential of degree N. The new constants K_j depend on μ, the force constants k_j in $V(x)$, and the variation parameters Ω and Δ [14]. Using the annihilation operator $\hat{a}$ and the creation operator $\hat{a}^\dagger$ of the harmonic reference oscillator,

$$
\hat{p} = i\sqrt{\frac{\mu\hbar\Omega}{2}}\left(\hat{a}^\dagger - \hat{a}\right), \; \hat{X} = \sqrt{\frac{\hbar}{2\mu\Omega}}\left(\hat{a}^\dagger + \hat{a}\right), \tag{8}
$$

the diagonal and the off–diagonal terms of $\hat{H}$ can be separated easily. In the diagonal part only pure numbers or powers of the number operator $\hat{n} = \hat{a}^\dagger\hat{a}$ occur. The traces in (2) and (3) are evaluated in the

Table 1. Various approaches to the PF of a double minimum oscillator ω_ϵ = 4401.21 cm^{-1}, $\xi_0 = \pm 5.576$, $\lambda_2 = -0.25$, $\lambda_4 = 0.00402045$.

ϵ^{-1}	δ	α	q_{WK}	q_e	$\tilde{q}_{\mathrm{DM}}^{\mathrm{sc.}}$	q_0	Σq_2	Σq_4
7.896D-2	–5.375	17.266	–1.375	3.201D-4	3.186D-4	1.511D-4	1.593D-4	1.600D-4
1.579D-1	–5.375	8.633	–0.515	2.531D-2	2.526D-2	1.230D-2	1.263D-2	1.265D-2
3.159D-1	–5.369	4.312	0.087	0.229	0.228	0.1124	0.1142	0.1143
7.893D-1	–5.276	1.695	1.034	1.048	1.037	0.5064	0.5184	0.5212
1.579	–4.983	0.799	2.417	2.419	2.398	1.139	1.201	1.232
2.053	–4.704	0.579	3.226	3.227	3.273	1.529	1.660	1.752
2.445	–4.177	0.427	3.880	3.881	4.010	1.876	2.169	2.463
2.525	0.000	0.205	4.009	4.009	3.912	2.955	3.912	4.045
3.003	0.000	0.187	4.762	4.763	4.681	3.696	4.681	4.808

The Wigner–Kirkwood expansion is a semiclassical expansion valid for sufficiently high temperatures only. Therefore, negative or very small values of q_{WK} (11) are found for the three lowest temperatures. q_0 (4), $\Sigma q_2 = q_0 + q_2$, and $\Sigma q_4 = q_0 + q_2 + q_3 + q_4$ (2) were calculated with the splitting DIAG and no constraint on the variation parameters α or δ (9). The temperature is given in the dimensionless form $\epsilon^{-1} = (kT)/(\hbar\omega)$. $\tilde{q}_{\mathrm{DM}}^{\mathrm{sc.}}$ is the scaled partition function (18), the exact value of the PF is q_e.

basis of the reference oscillator. The method works as follows:

1. For every temperature T, LB (3) is maximized by choosing optimal values of $\Omega(T)$ and $\Delta(T)$.
2. The perturbation expansion (2) is evaluated in the basis of the reference oscillator with $\Omega(T)$ and $\Delta(T)$.

For convenience, dimensionless force constants λ_j and parameters ϵ, α, and δ are introduced.

$$\delta = \left(\frac{2\mu\omega}{\hbar}\right)^{1/2}\Delta, \quad \lambda_j = \left(\frac{\hbar}{2\mu\omega}\right)^{j/2}\frac{1}{\hbar\omega}k_j, \qquad (9)$$
$$\epsilon = \beta\hbar\omega, \qquad \alpha = \beta\hbar\Omega.$$

2. Other methods for the calculation of the partition function

The lowest eigenvalues of $\hat{H}$ can be obtained from the diagonalization of a large matrix [14]. In this work, harmonic oscillator wave functions were used as basis. Recently, also eigenfunctions of a particle in a box of appropriate width have been applied sucessfully [22]. For sufficiently low temperatures, the exact partition function q_e can be calculated by summing up the eigenvalues E_n:

$$q_e = \sum_n g_n\, e^{-\beta E_n} \qquad (10)$$

The eigenvalue E_n is g_n–fold degenerate.

The Wigner–Kirkwood expansion q_{WK} is a semiclassical expansion in powers of $\hbar$ [23], which is a good approximation to the PF for high temperatures.

$$q_{\mathrm{WK}} = q_{\mathrm{cl}}\left(1 + \hbar^2\overline{\chi}_2 + \dots\right),$$
$$q_{\mathrm{cl}} = \left(\frac{\mu}{2\pi\beta\hbar^2}\right)^{1/2}\int_{-\infty}^{+\infty} e^{-\beta V(x)}\,\mathrm{d}x, \qquad (11)$$
$$\overline{\chi}_2 = -\frac{\beta^2}{24\mu}\,\frac{\int_{-\infty}^{+\infty}\frac{\mathrm{d}^2V(x)}{\mathrm{d}x^2}e^{-\beta V(x)}\,\mathrm{d}x}{\int_{-\infty}^{+\infty}e^{-\beta V(x)}\,\mathrm{d}x}.$$

It can be seen from the numerical results in Table 1 that the ranges of validity of q_ϵ and of q_{WK} overlap, if a sufficiently large number of eigenvalues is used for the calculation of q_ϵ. Therefore, the exact solution for q is known for all T and the variation perturbation method can be tested against these results.

3. The double minimum potential

A double minimum potential of the form

$$V_{\mathrm{DM}}(x) = -\frac{\mu\omega^2}{2}x^2 + k_4x^4 + \frac{1}{k_4}\left(\frac{\mu\omega^2}{4}\right)^2 \qquad (12)$$

has its minima at $x_0 = \pm\sqrt{\mu\omega^2/(4k_4)}$, $V_{\mathrm{DM}}(x_0) = 0$. x_0 can be expressed as a dimensionless length ξ_0 defined according to δ (9) as $\xi_0 = \sqrt{2m\omega/\hbar}\,x_0 = \pm 1/\sqrt{8\lambda_4}$. The variation perturbation method should give a shift of $\delta = 0$, because $V_{\mathrm{DM}}(x)$ is an even function $V_{\mathrm{DM}}(x) = V_{\mathrm{DM}}(-x)$. Using the operators (8) and the parameters (9), diagonal terms $\beta\hat{H}_0$,

$$\beta\hat{H}_0 = \left(6\epsilon\frac{\epsilon^2}{\alpha^2}\lambda_4\right)\hat{n}^2 + \left[\frac{\alpha}{2}\left(1-\frac{\epsilon^2}{\alpha^2}\right)+6\epsilon\frac{\epsilon^2}{\alpha^2}\lambda_4\right]\hat{n} + \left[3\epsilon\frac{\epsilon^2}{\alpha^2}\lambda_4+\frac{\alpha}{4}\left(1-\frac{\epsilon^2}{\alpha^2}\right)+\frac{\epsilon}{64\lambda_4}\right], \tag{13}$$

and off-diagonal terms $\beta\hat{H}_1$,

$$\beta\hat{H}_1 = \left(\epsilon\frac{\epsilon^2}{\alpha^2}\lambda_4\right)(\hat{a}^\dagger)^4 + \left[2\lambda_4\epsilon\frac{\epsilon^2}{\alpha^2}(2\hat{n}-1)-\frac{\alpha}{4}\left(\frac{\epsilon^2}{\alpha^2}+1\right)\right](\hat{a}^\dagger)^2 + \left[2\lambda_4\epsilon\frac{\epsilon^2}{\alpha^2}(2\hat{n}+3)-\frac{\alpha}{4}\left(\frac{\epsilon^2}{\alpha^2}+1\right)\right]\hat{a}^2 + \left(\epsilon\frac{\epsilon^2}{\alpha^2}\lambda_4\right)\hat{a}^4, \tag{14}$$

are obtained. In (13) and (14), δ is explicitly set to zero. If, however, a numerical calculation with no constraints on δ is carried out at low temperatures, δ is not found to be zero as expected from the symmetry of the potential (12) but δ is around $\pm\xi_0$, i. e., the minimum of the reference oscillator is near one of the minima of $V_{\mathrm{DM}}(x)$.

Numerical results for a double minimum oscillator with $\lambda_4 = 4.02045 \cdot 10^{-3}$, $\omega_e = 4401.21$ cm^{-1}, and $\xi_0 = \pm 5.576$ are shown in Figure 1. Up to a certain temperature T_c, which depends slightly on the initial conditions of the minimization of LB, the second order partition function $\Sigma q_2(T) = q_0 + q_2$ from the variation perturbation method is about one halb of the exact partition function $q_e(T)$ and $\delta(T) \approx \pm\xi_0$. Above T_c, $\Sigma q_2(T)$ is near the exact value and $\delta(T) = 0$. The numerical value of T is not significant, because the value of T_c depends on the actual choice of ω and λ_4 (9) in the potential $V_{\mathrm{DM}}(x)$ (12). Therefore, the results are given as functions of the dimensionless temperature $\epsilon^{-1} = (kT)/(\hbar\omega)$ (9) in the figures.

If δ is constrained to zero for low temperatures, the partition function $\Sigma q_2(T)$ is too small by several orders of magnitude. The lowest basis functions of a reference oscillator with $\delta = 0$ have large values only near $x = 0$. Thus, only contributions near the maximum of the double minimum potential are considered. On the other hand, the region of the minima where the main contributions of the exact wave functions of the double minimum oscillator come from, are nearly neglected. Therefore, the PF for low T and $\delta = 0$ is much too small.

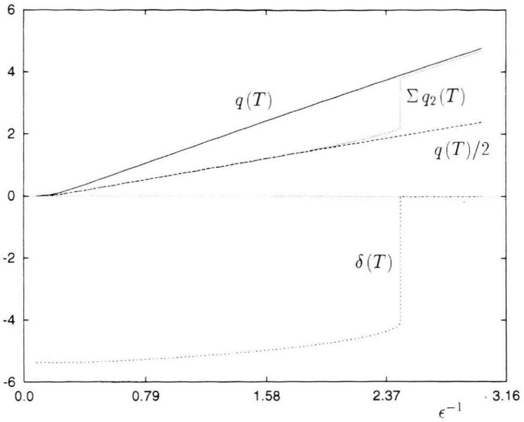

Fig. 1. The PF of the double minimum oscillator from the variation perturbation method. Given are the exact partition function $q(T)$ and $q(T)/2$. The PF from the variation perturbation method up to the second order with unconstrained shift is denoted by $\Sigma q_2(T)$, the corresponding dimensionless shift is $\delta(T)$. Below a certain temperature T_c, $\delta(T)$ is near one of the minima of the potential and $\Sigma q_2(T) \approx q(T)/2$. Above T_c, $\delta(T)$ jumps to zero and $\Sigma q_2(T)$ is correct within the accuracy of the method. The temperature is given in a dimensionless form as $\epsilon^{-1} = (kT)/(\hbar\omega)$.

In order to test the behaviour of the variation perturbation method with temperature, the lower bound is maximized by variation of the reference frequency Ω with fixed Δ. LB is shown in Fig. 2 as function of δ for four different temperatures. The same potential as in Fig. 1 is considered. For low temperatures (e. g. $\epsilon^{-1} = 0.158$), only two maxima of LB occur near the minima of $V_{\mathrm{DM}}(x)$, for higher temperatures (e. g. $\epsilon^{-1} = 0.316$ and $\epsilon^{-1} = 1.58$) a third maximum at $\delta = 0$ appears and grows with increasing temperature. For very high T (e. g. $\epsilon^{-1} = 3.00$), only the maximum in the middle remains. The results show that the (single minimum) harmonic reference oscillator cannot probe both minima of $V_{\mathrm{DM}}(x)$ at the same time, thus only ca. half of the space is considered for low temperatures and only one half of the correct partition functon is found. For high temperatures, however, $V_{\mathrm{DM}}(x)$ is a quartic oscillator with a small x^2–perturbation and is therefore easily described by the harmonic reference oscillator.

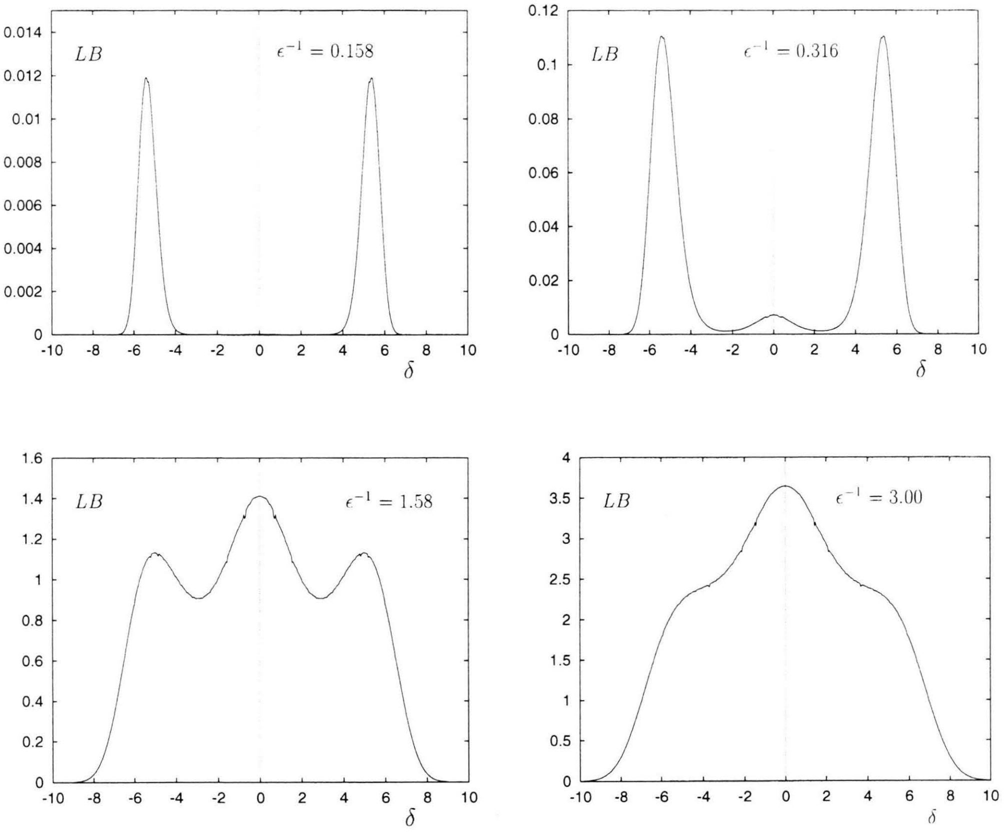

Fig. 2. The lower bound (4) from a variation of the reference frequency with constrained shift δ as function of the parameter δ for various temperatures.

4. A modified variation perturbation approach

In this section, a modified variation perturbation approach suitable for $V_{\mathrm{DM}}(x)$ (12) will be given. If the PF q_{DM} of the even potential $V_{\mathrm{DM}}(x)$ could be written as integral of some function f $(V_{\mathrm{DM}}(x))$ of the potential, the following relation would hold:

$$q_{\mathrm{DM}} = \int_{-\infty}^{+\infty} \mathrm{f}\ (V_{\mathrm{DM}}(x))\ \mathrm{d}x = 2 \underbrace{\int_{0}^{+\infty} \mathrm{f}\ (V_{\mathrm{DM}}(x))\ \mathrm{d}x}_{\tilde{q}_{\mathrm{DM}}}, \tag{15}$$

i. e. for negative and for positive x, a contribution $\tilde{q}_{\mathrm{DM}} = q_{\mathrm{DM}}/2$ is found.

The thermal average $\langle \hat{O}(x) \rangle$ of an operator $\hat{O}(x)$, which depends only on x, can be calculated from the integral

$$\langle \hat{O}(x) \rangle = \int_{-\infty}^{+\infty} O(x) W(x)\, \mathrm{d}x \tag{16}$$

with the coordinate probability distribution $W(x)$. For a harmonic oscillator with a frequency Ω', a closed expression for $W(x)$ exists [23]:

$$W(x) = \sqrt{\frac{\mu\Omega'}{\pi\hbar} \tanh\left(\frac{\beta\hbar\Omega'}{2}\right)} \cdot \exp\left\{-\frac{\mu\Omega'}{\hbar} \tanh\left(\frac{\beta\hbar\Omega'}{2}\right) x^2\right\}, \tag{17}$$

$$\int_{-\infty}^{\infty} W(x)\, \mathrm{d}x = 1.$$

Equation (16) can be applied to the first two terms q_0^{HAR} and q_1^{HAR} of the perturbation expansion (2), if the Hamiltonian $\hat{H}$ is not split in diagonal and off–diagonal terms ("DIAG") according to (13) and (14), but into a purely harmonic part $\hat{H}_0$ and an anharmonic part $\hat{H}_1$, which is a polynomial of x only (splitting "HARMON"). The superscript "HAR" in q_0^{HAR} and q_1^{HAR} corresponds to the splitting HARMON. The calculation cannot be extended beyond q_1^{HAR} in this simple way, because momentum contributions occur due to the commutation relations between $\hat{H}_1$ and $\exp(-\beta \hat{H}_0)$. Furthermore, the convergence of the variation perturbation method is considerably better with the splitting DIAG than with HARMON [14, 18]. Therefore, $\tilde{q}_{\mathrm{DM}}$ cannot be calculated with sufficient accuracy from the variation perturbation method with the splitting HARMON.

The unmodified variation perturbation method with the reference oscillator in one of the two minima (e. g. the one with $x > 0$) gets most of its contribution to the partition function $q_{\mathrm{DM}}^{\mathrm{VP}} = \Sigma q_2$ from the part of $V_{\mathrm{DM}}(x)$ with $x > 0$. Only a small part of $q_{\mathrm{DM}}^{\mathrm{VP}}$ comes from contributions with the other sign of x. In the modified approach, $\tilde{q}_{\mathrm{DM}}^{\mathrm{VP}}$ (18) will be scaled in a Pitzer–Gwinn-like approach [24] in such a way that the contribution of the "wrong sign" of x is nearly compensated, giving a corrected partition function $\tilde{q}_{\mathrm{DM}}^{\mathrm{sc.}}$, which approximately reproduces q_{DM}.

In the following text $\delta \leq 0$ is supposed, i. e. the minimum of the reference oscillator is at positive x. I–th order contributions to the PF from an integration over all x are denoted by q_i^{HAR}, whereas terms from an integration only over the positive x are denoted by $\tilde{q}_i^{\mathrm{HAR}}$. A scaled approximation $\tilde{q}_{\mathrm{DM}}^{\mathrm{sc.}}$ can be defined by

$$\tilde{q}_{\mathrm{DM}}^{\mathrm{sc.}} = 2 q_{\mathrm{DM}}^{\mathrm{VP}} \frac{\tilde{q}_0^{\mathrm{HAR}} + \tilde{q}_1^{\mathrm{HAR}}}{q_0^{\mathrm{HAR}} + q_1^{\mathrm{HAR}}}. \tag{18}$$

The limits of integration can be chosen freely for q_i^{HAR} and $\tilde{q}_i^{\mathrm{HAR}}$, but not for $q_{\mathrm{DM}}^{\mathrm{VP}}$, which is not evaluated by integration. In (18) it is supposed that the relative contribution due to the region with the wrong sign of x is approximately the same for $q_{\mathrm{DM}}^{\mathrm{VP}}$ and for $(q_0^{\mathrm{HAR}} + q_1^{\mathrm{HAR}})$. This behaviour can be expected, because $q_{\mathrm{DM}}^{\mathrm{VP}}$ and $(q_0^{\mathrm{HAR}} + q_1^{\mathrm{HAR}})$ are both calculated from a similar approach, namely the variation perturbation method, though with different order (two and one, respectively) and with different splittings of the Hamiltonian (DIAG and HARMON). The definition (18) does not only hold for low temperatures with $q_{\mathrm{DM}}^{\mathrm{VP}} \approx q/2$, but also for the high temperature region with $\Delta = 0$. Here, both the reference oscillator and $\hat{H}_1(X)$ are even functions of x and an integral over all positive x is half of an integral over all x, i. e. $q_0^{\mathrm{HAR}} + q_1^{\mathrm{HAR}} = 2\,(\tilde{q}_0^{\mathrm{HAR}} + \tilde{q}_1^{\mathrm{HAR}})$.

Using the dimensionless length

$$y = \sqrt{\frac{2\mu\omega}{\hbar}}\, X, \tag{19}$$

we obtain for the Hamiltonian $\hat{H}_1^{\mathrm{HAR}}$ of the perturbation with the splitting HARMON:

$$\begin{aligned} \beta \hat{H}_1^{\mathrm{HAR}}(y) = {} & \epsilon \left(\frac{\epsilon}{\alpha}\right)^2 \lambda_4 y^4 - 4\epsilon \left(\frac{\epsilon}{\alpha}\right)^{3/2} \lambda_4 \delta y^3 \\ & + \left[-\frac{\epsilon}{4}\left(\frac{\epsilon}{\alpha}\right) - \frac{\alpha}{4} + 6\epsilon \left(\frac{\epsilon}{\alpha}\right) \lambda_4 \delta^2\right] y^2 \\ & + \left[\frac{\epsilon}{2}\left(\frac{\epsilon}{\alpha}\right)^{1/2} \delta - 4\epsilon \left(\frac{\epsilon}{\alpha}\right)^{1/2} \lambda_4 \delta^3\right] y \\ & + \left[-\frac{\epsilon}{4}\delta^4 + \epsilon \lambda_4 \delta^4 + \frac{\epsilon}{64\lambda_4}\right]. \end{aligned} \tag{20}$$

$\tilde{q}_0^{\mathrm{HAR}}$ and $\tilde{q}_1^{\mathrm{HAR}}$ are given by

$$\tilde{q}_0^{\mathrm{HAR}} = q_0^{\mathrm{HAR}} \int_{x=0}^{\infty} W(X)\,\mathrm{d}X, \tag{21}$$

$$\tilde{q}_1^{\mathrm{HAR}} = -q_0^{\mathrm{HAR}} \int_{x=0}^{\infty} W(X) \beta H_1^{\mathrm{HAR}}(X)\,\mathrm{d}X. \tag{22}$$

With dimensionless variables and parameters we get

$$\begin{aligned} \tilde{q}_0^{\mathrm{HAR}} = {} & \frac{1}{4\sinh(\alpha/2)} \left(\frac{1}{\pi \sinh\alpha}\right)^{1/2} \\ & \cdot \int_{\sqrt{\alpha/\epsilon}\,\delta}^{\infty} \exp\left[-\frac{1}{2}\tanh\left(\frac{\alpha}{2}\right) y^2\right] \mathrm{d}y \end{aligned} \tag{23}$$

and

$$\begin{aligned} \tilde{q}_1^{\mathrm{HAR}} = {} & -\frac{1}{4\sinh(\alpha/2)} \left(\frac{1}{\pi \sinh\alpha}\right)^{1/2} \\ & \cdot \int_{\sqrt{\alpha/\epsilon}\,\delta}^{\infty} \exp\left[-\frac{1}{2}\tanh\left(\frac{\alpha}{2}\right) y^2\right] \beta H_1(y)\,\mathrm{d}y. \end{aligned} \tag{24}$$

With the integrals $J_n(t; a)$ [19]

$$J_n(t; a) = \int_{-t}^{\infty} x^n e^{-ax^2}\,\mathrm{d}x, \tag{25}$$

expressed in terms of the complementary error function $\mathrm{erfc}(x)$ [25],

$$J_0(t;a) = \frac{1}{2}\sqrt{\frac{\pi}{a}}\,\mathrm{erfc}(-\sqrt{a}\,t),\; J_1(t;a) = \frac{1}{2a}\,e^{-at^2},$$
$$J_2(t;a) = \sqrt{\frac{1}{a^3}}\left[\frac{\sqrt{\pi}}{4}\mathrm{erfc}\left(-\sqrt{a}\,t\right) - \frac{\sqrt{a}\,t}{2}\,e^{-at^2}\right],$$
$$J_3(t;a) = \frac{1+at^2}{2a^2}\,e^{-at^2}, \tag{26}$$
$$J_4(t;a) = \sqrt{\frac{1}{a^5}}\left[\frac{3}{8}\sqrt{\pi}\mathrm{erfc}\left(-\sqrt{a}t\right) - \frac{1}{2}\left(\frac{3}{2}\sqrt{a}t + a^{3/2}t^3\right)e^{-at^2}\right],$$

we get

$$\frac{\tilde{q}_0^{\mathrm{HAR}} + \tilde{q}_1^{\mathrm{HAR}}}{q_0^{\mathrm{HAR}} + q_1^{\mathrm{HAR}}} = \frac{J_0\left(\sqrt{\frac{\alpha}{\epsilon}}|\delta|\,;a\right) - \sum_{i=0}^{4} b_i J_i\left(\sqrt{\frac{\alpha}{\epsilon}}|\delta|\,;a\right)}{J_0^{\infty} - \sum_{i=0}^{2} b_{2i} J_{2i}^{\infty}} \tag{27}$$

with $a = 1/2\ \tanh(\alpha/2)$ and $J_n^{\infty} = \lim_{t\to\infty} J_n(t;a)$. The b_i are defined by $\beta\hat{H}_1(y) = \sum_{i=0}^{4} b_i y^i$. The parameters α and δ in the scaling factor (27) are taken from the variation of LB (4) in the splitting DIAG.

The numerical results for $\tilde{q}_{\mathrm{DM}}^{\mathrm{sc.}}$ together with $q_{\mathrm{DM}}^{\mathrm{VP}}$, $2\,q_{\mathrm{DM}}^{\mathrm{VP}}$, and the exact partition function q are shown in Figure 3. For temperatures slightly below T_c, $\tilde{q}_{\mathrm{DM}}^{\mathrm{sc.}}$ is slightly ($\approx$ 3%) larger than the exact value q, at T_c $\tilde{q}_{\mathrm{DM}}^{\mathrm{sc.}}$ jumps down a little bit below ($\approx$ 2%) q. Contrary to $\tilde{q}_{\mathrm{DM}}^{\mathrm{sc.}}$, $2\,q_{\mathrm{DM}}^{\mathrm{VP}}$ is up to $\approx$ 12% larger than q. The scaling according to (18) is no perfect method due to the jump of $q_{\mathrm{DM}}^{\mathrm{VP}}$ at T_c. Nevertheless, the error below T_c is not much larger than the deviation above T_c. The latter error is not affected by the scaling, but is caused by the uncertainty of the variation perturbation method with the double minimum potential. The error in the case of the double minimum potential is larger than for a single minimum potential with comparable force constants, because $V_{\mathrm{DM}}(x)$ deviates much more from the harmonic reference oscillator than a harmonic oscillator with anharmonic perturbations, making the double minimum oscillator with its negative k_2 in fact more anharmonic than the value of λ_4 indicates. It is known that higher anharmonicities can be handled in the variation perturbation theory using a higher order of the perturbation expansion [14]. In fact, the deviations ($\approx$ 0.9%) of the fourth order approximation $\Sigma q_4(T) = q_0 + q_2 + q_3 + q_4$ in the splitting DIAG are less than half of the second order error in the high temperature region $T > T_c$. Below T_c, however, a scaling according to (18) is much less effective, because then a fourth order $\Sigma q_4(T)$ in the splitting DIAG would be scaled with a first order ($q_0^{\mathrm{HAR}}(T) + q_1^{\mathrm{HAR}}(T)$) in the splitting HARMON, whereas the orders of DIAG and HARMON differ only by one in $\tilde{q}_{\mathrm{DM}}^{\mathrm{sc.}}$. Numerical values of the various approximations to q are given in Table 1.

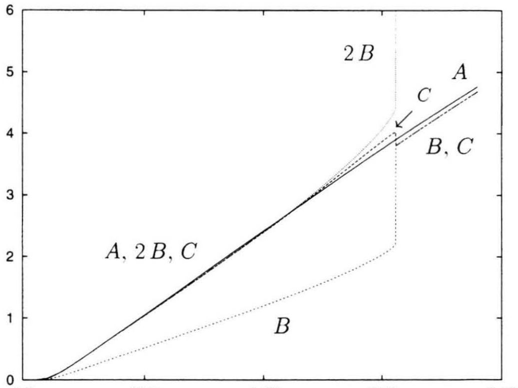

Fig. 3. The PF of the double minimum oscillator from the modified variation perturbation approach. Shown are the exact partition function q (A), the second order result $q_{\mathrm{DM}}^{\mathrm{VP}}$ of the variation perturbation method in the splitting DIAG (B), $2\,q_{\mathrm{DM}}^{\mathrm{VP}}$ (2B), and the scaled partition function $\tilde{q}_{\mathrm{DM}}^{\mathrm{sc.}}$ (C).

5. Conclusion

The PF of a symmetric double minimum oscillator has been calculated from the variation perturbation method. In the low temperature region, the method does not behave as expected: For a reference oscillator with both frequency Ω and shift Δ unconstrained, Δ is not found to be zero in the variation step of LB as expected from the symmetry of the potential, but the minimum of the reference oscillator is near one of the minima of $V_{\mathrm{DM}}(x)$. The PF calculated is only ca. half of the exact value. Above a certain temperature T_c, $\Delta = 0$ is found and the PF is reproduced correctly within the accuracy of the method.

It has been shown that the low temperature behaviour is due to the fact that a harmonic reference oscillator is a valid approximation only to potentials which also have a single minimum or for which the deviation from the overall shape of a single minimum potential is only a small perturbation. For small T, where only the lowest levels of the double minimum oscillator are concerned, $V_{\mathrm{DM}}(x)$ is described by two minima, whereas for high temperature $V_{\mathrm{DM}}(x)$ can be seen as quartic oscillator with a perturbation.

The problem could be overcome, if the PF could be calculated by integration over x. In this case, the contributions of positive and negative x could be separated and the PF is given by twice the integral over, i.e., the positive region. With the variation perturbation theory, however, the evaluation of the PF by integration is feasible only up to the first order of the expansion in the splitting HARMON. This low order together with a splitting, which yields in corresponding orders of theory results of less accuracy than the usual splitting DIAG does not allow sufficient accuracy for the direct calculation of the PF by integration. Therefore, the results of first order HARMON are used to scale the results of second order DIAG yielding an estimate to the PF, which does not deviate from the exact value by more than 3% over the whole temperature range considered.

It has been shown that variation perturbation theory cannot be applied in a straightforward way to a double minimum potential. For the calculation of the PF of a polyatomic molecule, therefore, modes with more than one minimum have to be considered separately. This can be performed either by the method described in Sect. 4 or by a combination of q_e and q_{WK} (11) as outlined in Section 2. The latter method gives very accurate values of the PF, whereas the former one fits better into the variation perturbation approach to polyatomic molecules. Depending on the actual shape of the molecular potential considered, a different method of scaling might be necessary.

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