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Padé approximant method for the statistical thermodynamics of a quantum system: II. Quartic anharmonic oscillator

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Abstract. A method of successive approximation involving two-point Padé approximants developed in a previous paper is applied to the quartic oscillator and to the anharmonic oscillator with quartic anharmonicity. The input data are the first three energy levels and the coefficients in a high-temperature series derived from the first three terms of the Wigner–Kirkwood series. The method gives an approximate expression for the partition function which is then differentiated to find the internal energy and the heat capacity. Good results are obtained at all temperatures and for a wide range of anharmonicities.

1. Introduction

This paper is concerned with the equilibrium thermodynamics of a quantum system with the Hamiltonian

$$H = p^2/2m + V(x) \tag{1.1}$$

where

$$V(x) = \tfrac{1}{2}m\omega^2 x^2 + \mu x^4 \tag{1.2}$$

with $\mu > 0$.

The energy eigenvalues E_n of this system have been extensively investigated, the most comprehensive study being that of Hioe and Montroll (1975) (see also Hioe *et al* 1978). They develop numerical methods for obtaining very accurate eigenvalues, and also give formulae for approximating E_n in various (λ, n) regions. ($\lambda = \mu\hbar/m^2\omega^3$.) These eigenvalues can then be used to calculate the various thermodynamic properties of the system. This procedure works well at low temperatures (low T) where only a few eigenvalues are needed, but is less satisfactory at high temperatures (high T) where many terms must be included in order to achieve reasonable accuracy.

An early investigation is that of Schwartz (1976), who used the Hioe–Montroll eigenvalues to calculate numerically the heat capacity (results given graphically only), and to develop low-T and high-T approximations which, however, have only very restricted validity (Witschel and Bohmann 1980).

Pant and Mitra (1979) used an interpolation formula to approximate the energy eigenvalues for all n and $\lambda \geq 0$, and then used these values to calculate the heat capacity. The accuracy of their approximation depends on λ and n, and although they show

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how systematically to improve the interpolation formula, this destroys the simplicity of the method.

A somewhat different approach was taken by Witschel and Bohmann (1980). They used variational methods to derive upper and lower bounds to the partition function, and also calculated terms in a perturbation expansion up to second order in λ. Again, these techniques work quite well in some regions, but fail badly in others. In a subsequent paper (Witschel 1981) these bounds are supplemented by the first Wigner–Kirkwood (WK) correction term, which gives good high-temperature results.

In the present work, we apply a method of successive approximation involving two-point Padé approximants (Gibson 1984. This paper will subsequently be referred to as I). This enables us to calculate accurate values of the partition function for all temperatures and for all values of $\lambda \geqslant 0.01$. The input for this method is the first three energy levels, and a high-T expansion which is derived from the first three terms of the WK series. The approximate partition function is given in analytic form, and can be differentiated to find the internal energy and heat capacity. The whole calculation parallels that given for the harmonic oscillator in I.

Before treating the anharmonic oscillator with potential (1.2), we do the corresponding calculations for the pure quartic oscillator with potential

$$V(x) = \mu x^4. \tag{1.3}$$

This case is simpler in that there is only one parameter involved, and only one set of eigenvalues is needed. Previous work on the thermodynamics of this system includes that of Miller (1971), Schwartz (1976), Witschel and Bohmann (1980), and Witschel (1980).

2. Quartic oscillator

2.1. Partition function

For the quartic oscillator with potential (1.3) the partition function is

$$Q = \sum_{n=0}^{\infty} \mathrm{e}^{-\tau\varepsilon_n} \tag{2.1}$$

where $\tau = \beta(\hbar^2\mu^{1/2}/m)^{2/3}$. Accurate values of ε_n are given by Hioe and Montroll (1975). At low T, we approximate Q by the first three terms of this series:

$$Q \sim \mathrm{e}^{-\tau\varepsilon_0} + \mathrm{e}^{-\tau\varepsilon_1} + \mathrm{e}^{-\tau\varepsilon_2} + \ldots, \qquad \tau \to \infty \tag{2.2}$$

where

$$\varepsilon_0 = 0.667\,986\,259, \qquad \varepsilon_1 = 2.393\,644\,02, \qquad \varepsilon_2 = 4.696\,795\,39.$$

At high T the WK series is applicable. The classical limit plus the first two correction terms are (see appendix 1 for details)

$$Q = \alpha_0\tau^{-3/4} + \alpha_1\tau^{3/4} + \alpha_2\tau^{9/4} + \mathrm{O}(\tau^{15/4}), \qquad \tau \to 0 \tag{2.3}$$

where

$$\alpha_0 = \Gamma(\tfrac{1}{4})/2(2\pi)^{1/2}, \qquad \alpha_1 = -\Gamma(\tfrac{3}{4})/4(2\pi)^{1/2}, \qquad \alpha_2 = 11\Gamma(\tfrac{1}{4})/960(2\pi)^{1/2}.$$

After making the change of variable $u = \tau^{1/4}$ we can implement the approximation

scheme of I, using successively 1, 2 and 3 terms from each of (2.2) and (2.3). Let

$$[N/N]=\frac{p_0+p_1u+\ldots+p_Nu^N}{1+q_1u+\ldots+q_Nu^N} \tag{2.4}$$

be the Nth diagonal Padé approximant (see the appendix of I). The results are

$$Q\simeq e^{-\varepsilon_0u^4}(\alpha_0/u^3+[3/3]), \tag{2.5}$$

$$Q\simeq e^{-\varepsilon_0u^4}+e^{-\varepsilon_1u^4}(\alpha_0/u^3+[6/6]), \tag{2.6}$$

$$Q\simeq e^{-\varepsilon_0u^4}+e^{-\varepsilon_1u^4}+e^{-\varepsilon_2u^4}(\alpha_0/u^3+[9/9]). \tag{2.7}$$

The coefficients for these three Padé approximants are given in table 1.

Table 1. Coefficients for the Padé approximants in equations (2.5), (2.6) and (2.7).

	[3/3]		[6/6]		[9/9]	
n	p_n	q_n	p_n	q_n	p_n	q_n
0	0.0	1.0	−1.0	1.0	−2.0	1.0
1	0.483 091	0.483 091	2.367 576	−0.636 482	1.864 889	0.765 928
2	0.233 377	0.233 377	−1.113 463	0.011 653	0.230 354	1.185 653
3	1.382 734	1.382 734	−0.076 145	−0.025 900	0.079 869	1.912 635
4			−0.846 352	−0.846 352	0.599 496	−0.264 167
5			0.851 811	0.851 811	0.315 669	0.884 599
6			0.069 476	0.069 476	0.441 453	0.465 886
7					−0.537 381	−0.537 381
8					1.262 858	1.262 858
9					0.033 784	0.033 784

All the poles of these approximants lie outside the region of analyticity of Q (which is $|\arg u|<\pi/8$). We have also calculated a number of other approximants using different combinations of terms from (2.2) and (2.3) and found that the situation is qualitatively similar to that of the rigid rotator (§ 4 of I): the inclusion of too many high-T terms causes poles to appear in $|\arg u|<\pi/8$; the inclusion of too few leads to slow convergence in the intermediate-to-large temperature range. The approximations (2.5)–(2.7) lie between these two cases.

Some values calculated from each of these approximations are shown in table 2. The exact values are calculated from (2.1), using values for ε_n given by Hioe and Montroll (1975). For $n\leqslant 10$ we use the nine-figure values listed in table IV of that paper (note the misprint in ε_0—it should be 0.667...), and for $n\geqslant 11$ we use the WKB-type approximation (Hioe and Montroll 1975)

$$\varepsilon_n\simeq 1.376\,507\,40[n+\tfrac{1}{2}+0.026\,50/(n+\tfrac{1}{2})]^{4/3}, \tag{2.8}$$

which is accurate to at least eight significant figures in this region.

A comparison of table 2 with the corresponding table for the simple harmonic oscillator (table 1 of I) shows that convergence is similar, though a bit slower in the present case. However, the third approximation (2.7) is giving four-figure accuracy, and this is satisfactory.

Table 2. Comparison of different approximations to the partition function for the quartic oscillator. I, II and III are from equations (2.5), (2.6) and (2.7) respectively. EXACT is from (2.1) using the eigenvalues of Hioe and Montroll (1975). $(-n)$ means the corresponding entry is to be multiplied by 10^{-n}.

τ^{-1}	I	II	III	EXACT
0.1	1.296 39 (−3)	1.255 95 (−3)	1.255 95 (−3)	1.255 95 (−3)
0.5	3.138 04 (−1)	2.736 68 (−1)	2.713 19 (−1)	2.713 21 (−1)
1.0	7.181 13 (−1)	6.331 95 (−1)	6.137 51 (−1)	6.138 50 (−1)
2.0	1.287 81	1.168 89	1.146 49	1.146 76
5.0	2.515 45	2.389 10	2.381 96	2.382 06
10.0	4.151 68	4.047 26	4.045 21	4.045 24

2.2. Thermodynamic quantities

As pointed out in § 2.2 of I, we can find thermodynamic quantities either by differentiating the partition function, or by developing further series and fitting Padé approximants to them. Our experience with the harmonic oscillator indicates that the differentiation method works well, and as it is the easiest to implement we use it here also. Thus we have calculated the internal energy and heat capacity using our approximations for Q, (2.5)–(2.7), in equations (2.11) and (2.12) of I. Analytic differentiation becomes cumbersome for the higher approximations so we have differentiated numerically, a procedure which is fast and accurate for this type of function.

Table 3 shows values of $\varepsilon = (\hbar^2 \mu^{1/2}/m)^{-2/3} E$ and C_V/k calculated using (2.7). These are compared with the exact values calculated from

$$\varepsilon = \frac{1}{Q} \sum_{n=0}^{\infty} \varepsilon_n \, \mathrm{e}^{-\tau \varepsilon_n} \tag{2.9}$$

and

$$C_V/k = \frac{1}{Q} \sum_{n=0}^{\infty} (\tau \varepsilon_n)^2 \, \mathrm{e}^{-\tau \varepsilon_n} - (\tau \varepsilon)^2, \tag{2.10}$$

using the Hioe–Montroll eigenvalues ε_n, as discussed in § 2.1 above. The agreement

Table 3. Internal energy ε and heat capacity C_V/k for the quartic oscillator. The approximate values are from differentiating (2.7). The exact values are from (2.9) and (2.10).

	ε		C_V/k	
τ^{-1}	APPROX.	EXACT	APPROX.	EXACT
0.1	0.667 986	0.667 986	9.538 34 (−6)	9.538 34 (−6)
0.5	0.722 222	0.722 246	0.373 995	0.374 352
1.0	0.991 841	0.992 193	0.631 836	0.632 006
2.0	1.674 80	1.674 43	0.709 678	0.708 939
5.0	3.862 97	3.862 40	0.738 896	0.739 026
10.0	7.580 09	7.579 91	0.746 004	0.746 041
100.0	75.025 4	75.025 4	0.749 873	0.749 873

is satisfactory—the approximant values are very accurate in the low-T and high-T regions, and no more than 0.1% in error at medium temperatures.

Thus we have established that our approximation scheme works well for the quartic oscillator, and we now apply it to the more complicated case of the anharmonic oscillator.

3. Anharmonic oscillator

The partition function for the anharmonic oscillator with potential (1.2) is

$$Q = \sum_{n=0}^{\infty} e^{-tE_n} \tag{3.1}$$

where $t = \beta\hbar\omega$ and E_n is now measured in units of $\hbar\omega$. A complication is that the E_n's are no longer constants, but depend on the potential strength through the parameter $\lambda = \mu\hbar/m^2\omega^3$.

At low T, Q is represented by the leading terms of (3.1). At high T we again use the WK series, and the first three terms are given in appendix 1. However, unlike the quartic oscillator case, these no longer yield single terms but rather infinite series in powers of $t^{1/2}$. These series are truncated and combined to give the following high-T expansion (see appendix 1 for details):

$$Q = \theta_0 u^{-3} + \theta_1 u^{-1} + \theta_2 u + \ldots + \theta_8 u^{13} + O(u^{15}), \qquad u \to 0 \tag{3.2}$$

where $u = t^{1/4}$, and the θ_n's are functions of λ given explicitly by equations (A1.13)–(A1.21) of appendix 1. It is important to note that (3.2) is not the WK series, but rather a rearrangement of it. The WK series gives an expansion for Q in powers of $\hbar^2$, with coefficients that are functions of β (see equations (A1.1)–(A1.4)). We have expanded these coefficients in powers of $\beta^{1/2}$, and then collected terms so that we have a series in powers of $\beta^{1/2}$ with coefficients that are functions of $\hbar$.

At this stage the problem essentially parallels that of the quartic oscillator, with the added complication that the energy levels E_n and the coefficients θ_n are functions of λ. Thus the Padé fitting must be done for each value of λ—however, this is not too serious a drawback since the whole procedure is readily programmed for computer and can be re-run for each λ value.

We have calculated a number of approximations to Q, and found that the behaviour is similar to that found for the quartic oscillator. Again, one has to maintain a balance between low-T and high-T terms in order to keep poles out of the region $|\arg u| < \pi/8$. We do not give details of all these approximations, but instead concentrate on the third, which uses the first three energy levels and all the coefficients, θ_0 to θ_8, of (3.2). The detailed equations are given in appendix 2. The highest order approximant which can be formed is [9/9]. However, this has a defect (pole–zero pair) on the positive real axis, the exact position depending on the value of λ. Although the numerical values at points away from this defect are very good, we prefer to use the [8/8] approximant formed from a_0 to a_{12} and b_0 to b_3 of appendix 2. This has no singularities in $|\arg u| < \pi/8$ and is thus reliable for all real u. In this approximation Q is given by

$$Q \simeq e^{-E_0 u^4} + e^{-E_1 u^4} + e^{-E_2 u^4}\left(\frac{\theta_0}{u^3} + \frac{\theta_1}{u} + [8/8]\right). \tag{3.3}$$

Table 4 lists the values of the coefficients in [8/8] for $\lambda = 0.01$, 1.0 and 50.0 and table 5 shows values of Q, $E/\hbar\omega$ and C_V/k for $\lambda = 0.01$, 1.0 and 50.0.

Table 4. Coefficients for the Padé approximant in equation (3.3) for various values of λ.

	$\lambda = 0.01$		$\lambda = 1.0$		$\lambda = 50.0$	
n	p_n	q_n	p_n	q_n	p_n	q_n
0	−2.0	1.0	−2.0	1.0	−2.0	1.0
1	10.726 288	1.172 850	1.928 799	0.919 744	2.388 578	1.176 952
2	9.181 599	3.074 943	0.558 472	1.453 694	0.561 663	2.510 007
3	10.937 514	3.564 254	0.131 786	2.293 556	0.403 372	5.530 977
4	11.522 496	2.987 952	0.921 132	0.103 303	2.536 610	−0.140 564
5	6.067 855	3.056 494	0.202 202	1.323 277	0.453 326	5.761 979
6	2.132 229	0.949 284	0.768 983	0.805 236	4.883 461	4.903 865
7	1.417 199	0.306 077	−0.090 532	−0.296 618	−3.011 433	−3.139 069
8	0.287 493	0.287 493	1.686 229	1.686 229	19.636 563	19.636 563

The approximate values are calculated from (3.3) and its derivatives. The exact values are obtained by using the energy eigenvalues E_n in (3.1) for Q, and in equations analogous to (2.9) and (2.10) for $E/\hbar\omega$ and C_V/k. The method used for calculating E_n depends on λ and n. For $\lambda = 50.0$ and 1.0, we use the accurate values for $n \leqslant 8$ and, for $n > 8$, the WKB-type formula (Hioe and Montroll 1975)

$$E_n \simeq C\lambda^{1/3}[n+\tfrac{1}{2}+\delta/(n+\tfrac{1}{2})]^{4/3} + a\lambda^{-1/3}[n+\tfrac{1}{2}+\delta/(n+\tfrac{1}{2})]^{2/3} + b\lambda^{-1}, \tag{3.4}$$

where $C = 1.376\,507\,40$, $a = 0.268\,055\,493$, $b = -0.011\,674\,983$ and $\delta = 0.026\,50$. The accuracy of (3.4) depends both on n and on λ: it is more accurate for large λ, but even for λ as small as 0.1 it still gives five-figure accuracy for $n = 8$. However, for $\lambda = 0.01$ (3.4) is no longer accurate enough (even for quite large n), and there is no other simple formula valid in this region. We therefore calculated the first 50 energy levels, accurate to at least six decimal places, using the method of Banerjee *et al* (1978). These are sufficient to give Q, $E/\hbar\omega$ and C_V/k to six figures for $t^{-1} \leqslant 0.3$; at higher temperatures the accuracy is reduced, and in table 5 we give only the number of decimal places we consider to be valid.

It is seen from table 5 that agreement between approximate and exact results is excellent for $\lambda = 50.0$ and 1.0, and still good for $\lambda = 0.01$. We would expect our scheme to become increasingly inaccurate as λ becomes very small, since the region of validity of both the high-T and the low-T series is diminished. This can be seen by examining the λ-dependence of θ_n and E_n: as λ decreases, the θ_n's become larger (see equations (A1.13)–(A1.21)), and the terms in (3.2) fall off more slowly. Correspondingly, the E_n's become smaller and more closely spaced, so that more terms are needed in (3.1) to achieve the same accuracy. In particular, the θ_n's diverge as $\lambda \to 0$, and the harmonic oscillator results are not recovered in this limit. This divergence can be traced to the expansion we have made in evaluating the WK coefficients (see appendix 1)—expanding e^{-ax^2} in (A1.8) and integrating term by term is invalid when $\lambda = 0$.

Table 5. Partition function Q, internal energy $E/\hbar\omega$ and heat capacity C_V/k for the anharmonic oscillator for various values of λ. The approximate values are based on (3.3). The exact values use either accurate eigenvalues E_n or asymptotic approximations to them, as explained in the text.

	Q		$E/\hbar\omega$		C_V/k	
t^{-1}	APPROX.	EXACT	APPROX.	EXACT	APPROX.	EXACT
			$\lambda = 0.01$			
0.1	6.266 56 (−3)	6.266 56 (−3)	0.507 291	0.507 291	3.614 75 (−3)	3.614 80 (−3)
0.5	0.414 997	0.415 286	0.655 145	0.656 028	0.693 460	0.696 061
1.0	0.928 970	0.930 299	1.064 09	1.063 82	0.882 235	0.877 922
2.0	1.881 90	1.883 23	1.970 26	1.967 87	0.913 064	0.912 754
5.0	4.528 68	4.529 08	4.677 31	4.676 1	0.890 176	0.890 5
10.0	8.569 78	8.569 9	9.051 40	9.051	0.862 353	0.862
100.0	62.027 1		81.973 9		0.791 248	
			$\lambda = 1.0$			
0.1	3.230 49 (−4)	3.230 49 (−4)	0.803 771	0.803 771	1.489 99 (−6)	1.489 99 (−6)
0.5	0.204 597	0.204 599	0.844 005	0.844 034	0.311 266	0.311 726
1.0	0.518 220	0.518 350	1.097 35	1.098 00	0.626 161	0.627 051
2.0	1.022 00	1.022 49	1.793 28	1.792 88	0.730 481	0.728 867
5.0	2.214 69	2.214 96	4.041 26	4.039 85	0.756 530	0.756 774
10.0	3.840 62	3.840 69	7.833 41	7.832 86	0.759 043	0.759 141
100.0	22.486 5	22.486 5	75.853 8	75.853 8	0.754 095	0.754 095
			$\lambda = 50.0$			
0.1	1.392 85 (−11)	1.392 85 (−11)	2.499 71	2.499 71	—	—
0.5	6.741 89 (−3)	6.741 89 (−3)	2.499 73	2.499 73	4.407 26 (−4)	4.407 26 (−4)
1.0	8.224 33 (−2)	8.224 33 (−2)	2.510 19	2.510 19	6.719 03 (−2)	6.719 34 (−2)
2.0	0.298 296	0.298 302	2.756 99	2.757 28	0.413 527	0.414 435
5.0	0.809 822	0.810 183	4.551 12	4.552 70	0.679 784	0.678 451
10.0	1.461 59	1.462 06	8.100 16	8.095 58	0.725 635	0.725 129
100.0	8.569 65	8.569 65	75.298 6	75.298 4	0.749 698	0.749 702

This non-commutivity of the limits $\lambda \to 0$ and $T \to \infty$ is also apparent in figure 1, where we graph the heat capacity as a function of temperature for $\lambda = 0$, 0.01, 1.0 and 50.0. (The values are either exact or approximate; the difference does not show on a graph of this scale.) As $T \to \infty$, $C_V/k \to 0.75$, except for the case $\lambda = 0$ where the limit is 1. Thus, although the $\lambda = 0$ and $\lambda = 0.01$ curves are close at low T, they separate as T increases. As already pointed out by other authors (Hioe and Montroll 1975, Schwartz 1976) this is related to the fact that, even for very small anharmonicity, the quartic term still dominates for sufficiently large mean displacement of the oscillator from its equilibrium position. Since the contribution to thermodynamic quantities from such states becomes increasingly important at high T, the limiting behaviour is that of a quartic oscillator.

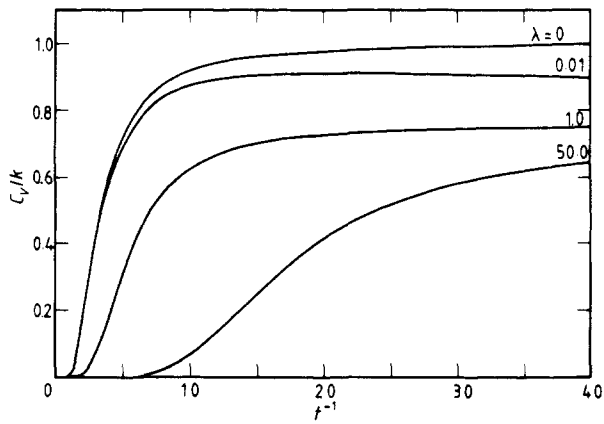

Figure 1. Heat capacity for the anharmonic oscillator as a function of temperature, for $\lambda = 0$, 0.01, 1.0 and 50.0.

4. Conclusion

We have shown that the method of successive approximation developed in I is applicable to the quartic oscillator and to the anharmonic oscillator for a wide range of values of λ. Since the method uses only low-T and high-T information, it completely side-steps the problem of calculating a large number of high energy levels, or of using approximations for them. This is particularly useful in the case of the anharmonic oscillator with λ small, since here there is no simple asymptotic formula for E_n when n is large. But even in the other cases the Padé approximant method is still a simpler and more economical way of investigating the medium-to-high-temperature behaviour.

The scheme is also straightforward mathematically. The most tedious part is calculating the coefficients in the high-T series for Q. The remainder consists of solving a set of linear equations to find the Padé coefficients, and subsequent (numerical) differentiation if E and C_V are required.

It is envisaged that the method has application to more complex systems, where the calculation of many energy eigenvalues is either difficult or impossible with current methods. Examples are the double well anharmonic oscillator (Witschel 1981) and systems of coupled oscillators (Witschel and Bohmann 1980, Hioe *et al* 1978).

Appendix 1. Wigner–Kirkwood expansion

The WK expansion (Wigner 1932, Kirkwood 1933) has the form

$$Q = Q^{C} + \frac{\hbar^2\beta}{2m} Q_{I} + \left(\frac{\hbar^2\beta}{2m}\right)^2 Q_{II} + \ldots . \tag{A1.1}$$

In the one-dimensional case the leading terms are (e.g. Hill 1968):

$$Q^{C} = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\beta V}\, dx, \tag{A1.2}$$

$$Q_{I} = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2} \left(\frac{-1}{12}\right) \int_{-\infty}^{\infty} e^{-\beta V} (\beta V')^2\, dx, \tag{A1.3}$$

$$Q_{II} = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2} \frac{1}{1440} \int_{-\infty}^{\infty} e^{-\beta V} [(\beta V')^4 - 8(\beta V')^2 \beta V'' + 12(\beta V'')^2]. \tag{A1.4}$$

For the quartic oscillator potential (1.3) the integrals in (A1.2)–(A1.4) are straightforward, and we get:

$$Q^{C} = [\Gamma(\tfrac{1}{4})/2(2\pi)^{1/2}]\tau^{-3/4}, \tag{A1.5}$$

$$(\hbar^2\beta/2m) Q_{I} = -[\Gamma(\tfrac{3}{4})/4(2\pi)^{1/2}]\tau^{3/4}, \tag{A1.6}$$

$$(\hbar^2\beta/2m)^2 Q_{II} = [11\Gamma(\tfrac{1}{4})/960(2\pi)^{1/2}]\tau^{9/4}, \tag{A1.7}$$

where $\tau = \beta(\hbar^2\mu^{1/2}/m)^{2/3}$. It can be seen on dimensional grounds that the next term, $(\hbar^2\beta/2m)^3 Q_{III}$, must be proportional to $\tau^{15/4}$. Thus we have established (2.3).

For the anharmonic oscillator potential (1.2) we strike integrals of the type

$$I_n = \int_{-\infty}^{\infty} x^n\, e^{-ax^2}\, e^{-bx^4}\, dx. \tag{A1.8}$$

These can be evaluated in terms of parabolic cylinder functions (Witschel 1981), but for our purposes it is better to expand the first exponential and integrate term by term. This procedure leads to:

$$Q^{C} = \frac{1}{2(2\pi)^{1/2}} \frac{1}{t^{3/4}\lambda^{1/4}} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left(\frac{t}{4\lambda}\right)^{n/2} \Gamma\left(\frac{2n+1}{4}\right), \tag{A1.9}$$

$$\frac{\hbar^2\beta}{2m} Q_{I} = -\frac{1}{3(2\pi)^{1/2}} t^{3/4}\lambda^{1/4} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left(\frac{t}{4\lambda}\right)^{n/2} \times \left[\Gamma\left(\frac{2n+7}{4}\right) + \Gamma\left(\frac{2n+5}{4}\right)\left(\frac{t}{4\lambda}\right)^{1/2} + \tfrac{1}{4}\Gamma\left(\frac{2n+3}{4}\right)\left(\frac{t}{4\lambda}\right)\right], \tag{A1.10}$$

$$\left(\frac{\hbar^2\beta}{2m}\right)^2 Q_{II} = \frac{1}{720(2\pi)^{1/2}} t^{9/4}\lambda^{3/4} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left(\frac{t}{4\lambda}\right)^{n/2} \times \left\{\left[16\Gamma\left(\frac{2n+13}{4}\right) - 96\Gamma\left(\frac{2n+9}{4}\right) + 108\Gamma\left(\frac{2n+5}{4}\right)\right] + \left[32\Gamma\left(\frac{2n+11}{4}\right) - 112\Gamma\left(\frac{2n+7}{4}\right) + 36\Gamma\left(\frac{2n+3}{4}\right)\right]\left(\frac{t}{4\lambda}\right)^{1/2}\right.$$

$$+\left[24\Gamma\left(\frac{2n+9}{4}\right)-40\Gamma\left(\frac{2n+5}{4}\right)+3\Gamma\left(\frac{2n+1}{4}\right)\right]\left(\frac{t}{4\lambda}\right)$$
$$+\left[8\Gamma\left(\frac{2n+7}{4}\right)-4\Gamma\left(\frac{2n+3}{4}\right)\right]\left(\frac{t}{4\lambda}\right)^{3/2}+\Gamma\left(\frac{2n+5}{4}\right)\left(\frac{t}{4\lambda}\right)^{2}\Bigg\}. \quad \text{(A1.11)}$$

(A1.10) has previously been obtained by Witschel (1981). It is again clear that the next term in (A1.1) is $O(t^{15/4})$ so we need only keep terms up to $t^{13/4}$ in (A1.9)–(A1.11). Adding the truncated series and collecting terms gives

$$Q=\sum_{n=0}^{8}\theta_n t^{(2n-3)/4}+O(t^{15/4}). \quad \text{(A1.12)}$$

If we introduce $\xi=\Gamma(\frac{1}{4})/(2\pi)^{1/2}$ and $\eta=\Gamma(\frac{3}{4})/(2\pi)^{1/2}$, these coefficients are:

$$\theta_0=(\xi/2)\lambda^{-1/4}, \qquad \theta_1=-(\eta/4)\lambda^{-3/4}, \qquad \theta_2=(\xi/64)\lambda^{-5/4}, \quad \text{(A1.13, 14, 15)}$$

$$\theta_3=-(\eta/128)(1+32\lambda^2)\lambda^{-7/4}, \qquad \theta_4=(\xi/12288)(5+128\lambda^2)\lambda^{-9/4}, \quad \text{(A1.16, 17)}$$

$$\theta_5=-(\eta/122880)(21+1600\lambda^2)\lambda^{-11/4}, \quad \text{(A1.18)}$$

$$\theta_6=(\xi/5898240)(45+5760\lambda^2+67584\lambda^4)\lambda^{-13/4}, \quad \text{(A1.19)}$$

$$\theta_7=-(\eta/11796480)(33+6240\lambda^2+153600\lambda^4)\lambda^{-15/4}, \quad \text{(A1.20)}$$

$$\theta_8=(\xi/5284823044)(585+152320\lambda^2+9920512\lambda^4)\lambda^{-17/4}. \quad \text{(A1.21)}$$

Appendix 2. Third approximation for anharmonic oscillator

For the third approximation we define

$$Q_3=e^{tE_2}(Q-e^{-tE_0}-e^{-tE_1}). \quad \text{(A2.1)}$$

Setting $t=u^4$, expanding the exponentials and using (3.2) for Q leads to

$$Q_3-\theta_0u^{-3}-\theta_1u^{-1}=\tilde{Q}_3 \quad \text{(A2.2)}$$

where

$$\tilde{Q}_3=\sum_{n=0}^{14}a_nu^n+O(u^{15}), \qquad u\to 0, \quad \text{(A2.3)}$$

$$\tilde{Q}_3=\sum_{n=0}^{3}b_nu^{-n}+O[\exp(-E_{3,2}u^4)], \qquad u\to\infty. \quad \text{(A2.4)}$$

The coefficients are:

$$a_0=-2, \qquad a_1=\theta_2+E_2\theta_0, \qquad a_2=0, \quad \text{(A2.5, 6, 7)}$$

$$a_3=\theta_3+E_2\theta_1, \qquad a_4=-(E_{2,0}+E_{2,1}), \quad \text{(A2.8, 9)}$$

$$a_5=\theta_4+E_2\theta_2+\tfrac{1}{2}E_2^2\theta_0, \qquad a_6=0, \quad \text{(A2.10, 11)}$$

$$a_7=\theta_5+E_2\theta_3+\tfrac{1}{2}E_2^2\theta_1, \qquad a_8=-\tfrac{1}{2}(E_{2,0}^2+E_{2,1}^2), \quad \text{(A2.12, 13)}$$

$$a_9=\theta_6+E_2\theta_4+\tfrac{1}{2}E_2^2\theta_2+\tfrac{1}{6}E_2^3\theta_0, \qquad a_{10}=0, \quad \text{(A2.14, 15)}$$

$$a_{11}=\theta_7+E_2\theta_5+\tfrac{1}{2}E_2^2\theta_3+\tfrac{1}{6}E_2^3\theta_1, \quad \text{(A2.16)}$$

$$a_{12} = -\tfrac{1}{6}(E^3_{2,0} + E^3_{2,1}), \tag{A2.17}$$

$$a_{13} = \theta_8 + E_2\theta_6 + \tfrac{1}{2}E_2^2\theta_4 + \tfrac{1}{6}E_2^3\theta_2 + \tfrac{1}{24}E_2^4\theta_0, \tag{A2.18}$$

$$a_{14} = 0, \qquad b_0 = 1, \qquad b_1 = -\theta_1, \tag{A2.19, 20, 21}$$

$$b_2 = 0, \qquad b_3 = -\theta_0. \tag{A2.22, 23}$$

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