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Padé approximant method for the statistical thermodynamics of a quantum system: I. General formulation and simple examples

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Abstract. The method of two-point Padé approximants is used to interpolate between the low-temperature and high-temperature behaviour of the thermodynamic partition function of a quantum system. The system is assumed to have low-lying discrete energy levels which dominate the low-temperature behaviour. A method of successive approximation is introduced, which allows more information from both regions to be included at each step. Other thermodynamic quantities can be calculated either by an extension of the method, or by differentiating the approximations found for the partition function.

The method is applied to three simple systems (the harmonic oscillator, the rigid rotator, and the particle in a box) and shown to give good results for all temperatures.

1. Introduction

A quantity of fundamental importance in statistical mechanics is the thermodynamic partition function

$$Q = \mathrm{Tr}\, \mathrm{e}^{-\beta H}. \tag{1.1}$$

Here, H is the Hamiltonian of the system and $\beta = 1/kT$. In terms of the energy eigenvalues E_n this becomes

$$Q = \sum_n g_n \, \mathrm{e}^{-\beta E_n}, \tag{1.2}$$

where g_n is the degeneracy of the nth level. Once Q has been found the other equilibrium thermodynamic functions of the system can be derived by application of the standard formulae of statistical mechanics (Huang 1963).

Q has been found in closed form in only a few special cases. Thus much effort has been expended on developing approximation techniques. Usually these work well only for certain systems, or in limiting situations. Two such limits are those of low temperature (low T) and high temperature (high T). The low-T limit is particularly simple for a quantum system which possesses low-lying discrete energy levels which are reasonably well separated. In this case, the first few terms of (1.2) give the dominant behaviour, and the problem is reduced to that of finding the energy of the ground state and of the first few excited states. In the high-T region, the dominant behaviour is that of the corresponding classical system. Quantum mechanical effects are then added as corrections to this behaviour. (For references to recent work on semiclassical methods see Korsch (1979).)

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Our approach is to try to bridge the gap between these two regions by making simultaneous use of the information available from each. The technique employed is that of two-point Padé approximants, in which a rational function is made to reproduce, to specified orders, series expansions about zero and about infinity (see the appendix). This method has recently been applied to the third virial coefficient for quantum hard spheres (Gibson 1980, 1981). In the present case, straightforward application of the Padé method is not possible because Q does not have an expansion in powers of T as $T \to 0$. However, we have developed a method of successive approximation which allows at each stage a two-point Padé approximant to be fitted. At the first stage the input is the ground-state energy plus high-T data which may be as little as the classical limit of Q. At each successive approximation we add one more energy level, and one (or more) high-T quantum correction terms. The details for the partition function are given in § 2.1, and in § 2.2 we extend the method to cover other thermodynamic quantities.

To illustrate the method we apply it to three simple, though rather different, systems: the harmonic oscillator, the rigid rotator and the particle in a hard-wall box (cf Stratt and Miller 1977, Korsch 1979). Since the aim of these examples is elucidation, we restrict ourselves to one particle in one dimension. Also, we do not consider the effect of quantum statistics—that is, our formulae are valid for Boltzmann statistics only.

2. Successive approximation method

2.1. Partition function

We consider a quantum mechanical system which has discrete energy levels $E_0, E_1, E_2, \ldots$ ordered so that $E_0 < E_1 < E_2 \ldots$. We assume that the first few energy levels are reasonably well separated, so that at low T (large β) the dominant contribution to the partition function comes from the first few terms:

$$Q \sim g_0 \, e^{-\beta E_0} + g_1 \, e^{-\beta E_1} + g_2 \, e^{-\beta E_2} + \ldots, \qquad \beta \to \infty. \tag{2.1}$$

In writing (2.1) we are not excluding the possibility that the system also has a continuous energy spectrum, but rather we are specifying that it does have discrete states which dominate the low-T behaviour.

At high T (small β), the exact form of Q depends on the nature of the system, the interactions present, the boundary conditions, etc, but in general an expansion exists of the form

$$Q \sim \beta^{\nu}(a_0 + \alpha_1 \beta^{\mu} + \alpha_2 \beta^{2\mu} + \ldots), \qquad \beta \to 0, \tag{2.2}$$

where $\nu, \mu > 0$ are constants, and $\alpha_0, \alpha_1, \alpha_2, \ldots$ are independent of temperature. For a system of particles interacting through a potential which is differentiable an arbitrary number of times, the Wigner–Kirkwood (WK) expansion applies (Wigner 1932, Kirkwood 1933, Hill 1968, Fujiwara *et al* 1982). The coefficients in this expansion are functions of β, and these must be expanded to get a series of type (2.2). If in addition the potential has bounded derivatives to all orders the series is simply in powers of β, and the coefficients can be obtained directly (Perelomov 1976, Onofri 1978, Hasslacher and Neveu 1979, Wilk *et al* 1981). In other cases (for example, if discontinuous potentials are present) special techniques have to be used.

We now wish to fit a Padé approximant to Q, using the leading terms of (2.1) and (2.2). This cannot be done directly because (2.1) does not have an expansion in powers of β^{-1}. We therefore use the following approximation procedure. For the first approximation we define

$$Q_1 = e^{\beta E_0} Q. \tag{2.3}$$

Then

$$Q_1 = g_0 + O(e^{-\beta E_{1,0}}), \qquad \beta \to \infty, \tag{2.4}$$

where $E_{i,j} \equiv E_i - E_j$. The small-β behaviour of Q_1 is found by inserting the series (2.2) into equation (2.3). Expanding the exponential, multiplying the two series, and making a change of variable $\beta = u^p$ where $p > 0$ is an appropriate integer, leads to

$$Q_1 \sim u^q(\gamma_0 + \gamma_1 u + \gamma_2 u^2 + \dots), \qquad u \to 0. \tag{2.5}$$

Here, q is an integer and $\gamma_0, \gamma_1, \gamma_2, \dots$ are combinations of the α_i's and E_0. We now fit a two-point Padé approximant (in the variable u) to Q_1, using just the leading term, g_0, of (2.4), and as many terms as we wish from (2.5) (see the appendix). We have thus neglected terms which are exponentially small compared with g_0.

From (2.3) and (2.1),

$$Q_1 - g_0 \sim g_1 e^{-\beta E_{1,0}} + g_2 e^{-\beta E_{2,0}} + \dots, \qquad \beta \to \infty. \tag{2.6}$$

This is of the same form as (2.1) and so, repeating the above procedure, we define

$$Q_2 = e^{\beta E_{1,0}}(Q_1 - g_0). \tag{2.7}$$

Then

$$Q_2 = g_1 + O(e^{-\beta E_{2,1}}). \tag{2.8}$$

Using (2.2) and expanding the exponential in (2.7) leads to a series of the type (2.5) for Q_2, so the Padé method can again be applied. Clearly, this process can be repeated: at the nth step we define

$$Q_n = \exp(\beta E_{n-1,n-2})(Q_{n-1} - g_{n-2}), \qquad n > 1. \tag{2.9}$$

Then

$$Q_n = g_{n-1} + O[\exp(-\beta E_{n,n-1})], \qquad \beta \to \infty, \tag{2.10}$$

and Q_n has an expansion of type (2.5) as $\beta \to 0$.

Thus at each step we include one more term from the low-T series (2.1) in the approximation. We have a choice as to how many terms we will use from the high-T series (2.2)—using more terms will increase the accuracy of the Padé approximant in the high-T region, but, as will be seen below, the best results are achieved by keeping a balance between the inputs from the high-T and low-T expressions.

2.2. Thermodynamic quantities

Once the partition function has been found, other thermodynamic quantities follow by application of the standard formulae. For example, the internal energy is

$$E = -(\partial/\partial\beta)(\ln Q)_V \tag{2.11}$$

and the heat capacity is

$$C_V/k = \beta^2(\partial^2/\partial\beta^2)(\ln Q)_V. \tag{2.12}$$

Thus successive approximations to these quantities can be found by differentiating the approximations to Q.

An alternative procedure is to calculate the low-T and high-T series for the particular thermodynamic quantity, and then to apply an approximation scheme similar to that used for Q in the previous section. For example, for the internal energy we find from (2.1), (2.2) and (2.11),

$$E \sim E_0 + (g_1/g_0)E_{1,0}\exp(-\beta E_{1,0}) + (g_2/g_0)E_{2,0}\exp(-\beta E_{2,0}) - (g_1/g_0)^2 E_{1,0}\exp(-2\beta E_{1,0}) + \ldots, \qquad \beta \to \infty, \tag{2.13}$$

$$E \sim -\nu\beta^{-1} - (\mu\alpha_1/\alpha_0)\beta^{\mu-1} + [\mu(\alpha_1^2 - 2\alpha_0\alpha_2)/\alpha_0^2]\beta^{2\mu-1} + \ldots, \qquad \beta \to 0. \tag{2.14}$$

These are of a similar form to (2.1) and (2.2), and the successive approximation method can easily be modified to handle them.

2.3. Discussion of the method

There are two essentially separate aspects to our approximation scheme. The first is contained in the sequence $Q_1, Q_2, Q_3, \ldots$. There is no problem here; provided Q exists, so does Q_n and the two are simply related by

$$Q = g_0 e^{-\beta E_0} + g_1 e^{-\beta E_1} + \ldots + g_{n-2} e^{-\beta E_{n-2}} + e^{-\beta E_{n-1}} Q_n. \tag{2.15}$$

This shows that using even the simplest approximation for Q_n, namely $Q_n = g_{n-1}$, will give a Q which becomes increasingly accurate in the low-T region as n increases.

The second aspect involves finding an approximation for Q_n which goes beyond this simple form, and this is where the Padé approximants enter. We supplement the limit

$$Q_n \to g_{n-1} \qquad \text{as } \beta \to \infty \tag{2.16}$$

by a series of the form

$$Q_n \sim u^q(\gamma_0' + \gamma_1' u + \gamma_2' u^2 + \ldots) \tag{2.17}$$

where $u \equiv \beta^{1/p} \to 0$, and fit a Padé approximant which reproduces (2.17) for small u and has the asymptotic form (2.16) as $u \to \infty$.

We now wish to say something about the convergence of the Padé scheme. In spite of much recent work on Padé approximants (Baker 1975, Baker and Graves-Morris 1981, Jones and Thron 1980, Gilewicz 1978, Wuytack 1979, de Bruin and van Rossum 1981) precise and useful statements about convergence can only be made in a limited number of cases. These include where the function being approximated is of a special type (e.g. a Stieltjes function), or where one possesses complete information about its analytic structure.

In the present case we have only a limited amount of information. From (2.15) it is clear that $Q_n(\beta)$ has the same analytic structure as $Q(\beta)$. Assuming that the original series (1.2) for $Q(\beta)$ converges for β real and positive, it follows that it is uniformly convergent for complex β with $\mathrm{Re}\,\beta > 0$, and thus defines a function analytic in this region. Also $Q(\beta)$ has an essential singularity at $\beta = \infty$. As a function of $u \equiv \beta^{1/p}$, $Q(\beta)$ is analytic in the sector $|\arg u| < \pi/2p$ and has an essential singularity at $u = \infty$.

In the general case it does not seem possible to say anything about the analytic continuation of $Q(\beta)$ outside this region. (In specific cases we may be able to say

more—for example, for the simple harmonic oscillator, considered in detail in § 3, $Q(\beta)$ is analytic in the entire β plane except for simple poles along the imaginary axis.)

Some rigorous results concerning Padé approximants also exist for the case where the function is represented by a Taylor series with a finite radius of convergence. But in our case, again with certain exceptions such as the simple harmonic oscillator, the series (2.17) will be asymptotic with a zero radius of convergence. This does not preclude the use of Padé approximants, but limits the applicability of general theorems.

In general, Padé approximants attempt to reproduce the analytic structure of a function by a suitable distribution of poles and zeros (Baker and Graves-Morris 1981, § 2.2). Poles of the function will be represented by poles of the approximant, and the positions of these will tend to stabilise as we go to higher order approximants. Essential singularities appear as a clustering of poles and zeros about a point, and branch cuts are represented by a line of roughly alternating poles and zeros. In practice, as well as these 'real' poles, Padé approximants also have 'spurious' poles. Often these occur in the form of zero–pole pairs which almost cancel each other. (Such pairs are called defects.) These spurious poles can be recognised by their unstable nature; they tend to appear and disappear, or to move about more or less at random, as we proceed along a sequence of approximants, whereas the real poles settle down at stable locations. In general it is best to reject, or at least to treat with suspicion, any Padé approximant with spurious poles in the region of interest.

Thus the information that $Q_n(\beta)$ is analytic for $\mathrm{Re}\,\beta > 0$ is actually very useful: we should select a sequence of Padé approximants with no poles in this region, or at the very least keep well clear of any such poles when calculating numerical values.

The above considerations apply equally well to one-point and two-point Padé approximants. The main effect of using two-point Padé approximants is that they change the natural region of convergence from that of a disc centred on the origin to that of a more general region including the two points (Baker 1975, § 11*H*). In practice, we find that using the two-point approximant has the very desirable feature of forcing unwanted poles out of the region of analyticity and thus dramatically increasing the reliability and accuracy of the approximant. (This feature is illustrated by the case of the rigid rotator treated in § 4 below.)

We remark that two-point Padé approximants are closely related to the type of continued fractions known as *T*-fractions (Jones and Thron 1980). There are a number of results concerning the convergence of these fractions, but they rely on establishing certain properties of the general term, and so are not useful in our case since in general we can only evaluate the first few terms.

The above considerations suggest the following practical way of proceeding. (Compare Baker and Graves-Morris 1981, § 2.2.) As many Padé approximants are calculated as is possible with the available coefficients. For each, we find the location of the poles and zeros (and it is useful also to evaluate the residues so that defects are immediately apparent). For this purpose one must have the explicit form of the numerator and denominator of the approximant, and this is a good reason for solving the defining equations directly (see the appendix), rather than employing an algorithm which gives only numerical values at specified points, or using a continued-fraction approach. We then reject those approximants with poles in the region $\mathrm{Re}\,\beta > 0$, and evaluate the rest for a range of real values of β in order to check their numerical convergence. In doing this, we pay particular attention to intermediate values of β, since by their construction the approximants must tend to the correct values for small and large β.

3. Harmonic oscillator

3.1. Partition function

We consider a single particle of mass m moving in one dimension under the harmonic oscillator potential

$$V(x)=\tfrac{1}{2}m\omega^2x^2. \tag{3.1}$$

The energy levels are

$$E_n=(n+\tfrac{1}{2})\hbar\omega, \qquad n=0,1,2,\ldots. \tag{3.2}$$

In terms of the dimensionless parameter $t=\beta\hbar\omega$ the high-T and low-T expansions are, respectively,

$$Q=1/t-t/24+7t^3/5760+\ldots, \qquad t\to 0, \tag{3.3}$$

$$Q=e^{-t/2}+e^{-3t/2}+e^{-5t/2}+\ldots, \qquad t\to\infty. \tag{3.4}$$

In (3.3), the terms are the classical partition function, and the first and second WK corrections. Series (3.4) can of course be summed explicitly to give

$$Q=\tfrac{1}{2}\operatorname{cosech}(t/2) \tag{3.5}$$

and then (3.3) is obtained from the standard expansion for cosech (Abramowitz and Stegun 1965), the complete series being

$$Q=-\sum_{n=0}^{\infty}\frac{(2^{2n-1}-1)B_{2n}}{(2n)!}\left(\frac{t}{2}\right)^{2n-1}. \tag{3.6}$$

This is convergent for $0<|t|<2\pi$, in accord with the fact that, from (3.5), Q has simple poles at $t=2k\pi i$, $k=0,\pm1,\ldots$. We note also that $t=\infty$ is an essential singularity of Q.

The most straightforward approximation procedure would be to ignore series (3.4), and simply fit a one-point Padé approximant to $Q-1/t$ using (3.3). This works well in the neighbourhood of $t=0$; in fact Montessus' theorem (Baker 1975) ensures convergence of $[L/M]$, as $L\to\infty$, in the region $|t|\leqslant\rho$ where $\rho<(M+2)\pi$. However, because convergence is based on circles centred on the origin, we need high-order approximants to get reasonable accuracy for larger values of t.

In order to obtain approximations useful for all values of t we implement the scheme of § 2.1. For the first approximation we define

$$Q_1=e^{t/2}Q. \tag{3.7}$$

Then

$$Q_1=1+O(e^{-t}), \qquad t\to\infty \tag{3.8}$$

and, using only the first term of (3.3),

$$Q_1=1/t+1/2+O(t), \qquad t\to 0. \tag{3.9}$$

Fitting a [1/1] Padé approximant to these series leads to

$$Q\simeq e^{-t/2}\left[\frac{1}{t}+\frac{1+t}{2+t}\right]. \tag{3.10}$$

(3.8) gives a maximum error of about 8% when compared with the exact expression

(3.5). This agreement is satisfactory, considering that the input to (3.10) is merely the ground-state energy and the classical limit of the partition function. Using more terms from the high-T series (3.3) has the predictable effect of increasing the accuracy at high temperatures without improving the low-temperature behaviour.

Thus we proceed to the second approximation, which uses the first two energy levels and the classical limit plus first WK correction term. This gives

$$Q \simeq e^{-t/2} + e^{-3t/2}\left[\frac{1}{t} + \frac{12+5t+t^2}{24+6t+t^2}\right]. \tag{3.11}$$

Now the accuracy is better than 0.1% over the entire temperature range. In figure 1 the high-T and low-T curves use the first two terms of (3.3) and (3.4) respectively, and thus represent the input to the approximation (3.11). The full curve is the exact partition function, which on the scale of the graph is indistinguishable from (3.11).

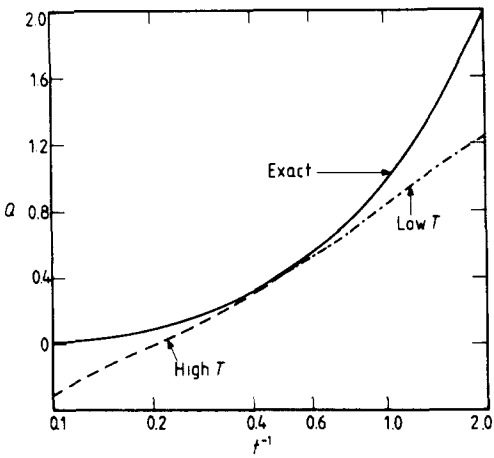

Figure 1. Partition function for the harmonic oscillator as a function of temperature. The full curve is the exact result (3.5). The high-T and low-T curves are the first two terms of (3.3) and (3.4) respectively.

The next approximation, which includes E_2 and the second WK correction, is

$$Q \simeq e^{-t/2} + e^{-3t/2} + e^{-5t/2}\left[\frac{1}{t} + \frac{180+60t+11t^2+t^3}{360+60t+12t^2+t^3}\right]. \tag{3.12}$$

This is now accurate to at least five significant figures for all temperatures. Table 1 shows numerical values of the first three approximations for selected temperatures, and illustrates the convergence of the scheme.

In all the above approximations the poles of the Padé approximants lie in the left half t plane and thus cause no problems. If we wished to locate accurately the poles of Q we would use one-point Padé approximants fitted to (3.3), as discussed above. The effect of using two-point Padé approximants is to displace the poles off the imaginary axis into the left half plane, and cause them to converge more slowly to their true positions.

Our procedure is very similar to the original application of the two-point Padé approximant by Baker *et al* (1964); they also used the value at an essential singularity

Table 1. Comparison of different approximations to the partition function for the harmonic oscillator. I, II and III are from equations (3.10), (3.11) and (3.12) respectively. EXACT is from (3.5). $(-n)$ means the corresponding entry is to be multiplied by 10^{-n}.

t^{-1}	I	II	III	EXACT
0.1	6.850 25 (−3)	6.738 25 (−3)	6.738 25 (−3)	6.738 25 (−3)
0.5	4.598 49 (−1)	4.251 35 (−1)	4.254 60 (−1)	4.254 59 (−1)
1.0	1.010 88	9.592 20 (−1)	9.595 18 (−1)	9.595 17 (−1)
2.0	2.024 88	1.979 22	1.979 32	1.979 32
5.0	5.017 73	4.991 67	4.991 68	4.991 68

at infinity to fix the asymptotic behaviour of the Padé approximant and thus improve convergence over the entire range. Similar cases have also been considered by McCabe (1975).

3.2. Thermodynamic quantities

We have calculated the internal energy by both methods outlined in § 2.2—that is, by differentiation using (2.11), and by deriving series for E and forming the successive approximations. Both methods give comparable results, with differentiation being slightly superior. Convergence is a little slower than in the partition function case, but the third approximation still gives five-figure accuracy.

A more stringent test is supplied by the heat capacity, and here it is found that the differentiation method is definitely superior. The high-T and low-T series for C_V/k, derived from (2.12), (3.3) and (3.4), are

$$C_V/k = 1 - \tfrac{1}{12}t^2 + \tfrac{1}{240}t^4 + O(t^6), \qquad t \to 0, \tag{3.13}$$

$$C_V/k = t^2 e^{-t} + 2t^2 e^{-2t} + O(e^{-3t}), \qquad t \to \infty. \tag{3.14}$$

The best approximation we can derive from these is

$$C_V/k \simeq t^2 e^{-t} + e^{-2t}\left(1 + 2t + t^2 \frac{0.916\,667 + 0.415\,240t + 0.104\,103t^2 + 0.015\,332t^3}{1 + 0.271\,171t + 0.059\,718t^2 + 0.007\,666t^3}\right). \tag{3.15}$$

This gives less than four-figure accuracy, whereas inserting (3.12) into (2.12) and performing the differentiations gives about five figures. Table 2 compares these two

Table 2. The heat capacity C_V/k for the harmonic oscillator. A is from (3.15); B is from (2.12) and (3.12); EXACT is from (3.16).

t^{-1}	A	B	EXACT
0.1	4.540 40 (−3)	4.540 42 (−3)	4.540 41 (−3)
0.5	0.723 825	0.724 043	0.724 062
1.0	0.920 624	0.920 677	0.920 674
2.0	0.979 422	0.979 425	0.979 425
5.0	0.996 673	0.996 673	0.996 673

approximations with the exact result

$$C_V/k = \tfrac{1}{4}t^2 \operatorname{cosech}^2 \tfrac{1}{2}t. \tag{3.16}$$

The reason for the superiority of the differentiation method can be seen by comparing figures 1 and 2. The full curve in figure 2 is the exact heat capacity; the high-T curve uses the first two terms of (3.13) and the low-T curve uses the first term of (3.14). Thus the input for figure 2 is the same as for figure 1, but the asymptotic curves do not approximate the true curve as well as they do in figure 1. It is thus no surprise that the approximation method works better for the partition function.

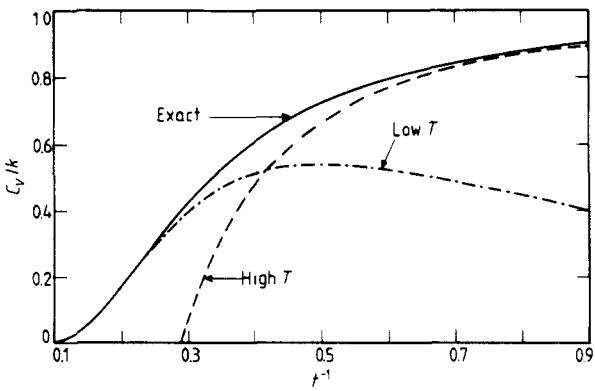

Figure 2. Heat capacity for the harmonic oscillator as a function of temperature. The full curve is the exact result (3.16). The high-T curve is the first two terms of (3.13); the low-T curve is the first term of (3.14).

4. Rigid rotator

For a rigid rotator with moment of inertia I the energy levels are

$$E_l = (\hbar^2/2I)l(l+1), \qquad l = 0, 1, 2, \ldots. \tag{4.1}$$

Since the lth level has degeneracy $2l+1$, the partition function is

$$Q = \sum_{l=0}^{\infty} (2l+1) \exp[-\sigma l(l+1)], \tag{4.2}$$

where $\sigma = \beta\hbar^2/2I$. At low temperature the behaviour of Q is determined by the first few terms of this series. The high-T behaviour can be found by application of the Euler–Maclaurin summation formula, and is (Mulholland 1928, Kilpatrick *et al* 1965)

$$Q = 1/\sigma + \tfrac{1}{3} + \tfrac{1}{15}\sigma + \tfrac{4}{315}\sigma^2 + \tfrac{1}{315}\sigma^3 + \tfrac{4}{3465}\sigma^4 + O(\sigma^5), \qquad \sigma \to 0. \tag{4.3}$$

In contrast to the simple harmonic oscillator case, this series has a zero radius of convergence and $Q - 1/\sigma$ is singular at $\sigma = 0$. (This series is discussed at length by Kilpatrick and Kayser (1975). They derive the general term and also show that the series can be converted to a convergent one by multiplying each power of σ by an infinite series of terms of the form $\sigma^{-m} \exp(-\pi^2 k^2/\sigma)$ where m and k are positive integers.)

As in the simple harmonic oscillator case, we start by fitting a one-point Padé approximant to $Q-1/\sigma$, using (4.3). This is now completely unsatisfactory; the approximants have poles which lie close to the origin on the positive real axis, and thus are virtually useless for computational purposes. This difficulty cannot be overcome by going to higher order approximants—in fact this just moves zero–pole pairs along the positive real axis closer to the origin.

We therefore implement the two-point Padé scheme of § 2.1, which in lowest order, using one term from (4.2) and two from (4.3), gives

$$Q \simeq \frac{1}{\sigma} + \frac{1+2\sigma}{3+2\sigma}. \tag{4.4}$$

The pole is now at $\sigma = -\frac{3}{2}$ and is quite harmless. The same behaviour persists if we use four terms from (4.3); the poles are still in the left half plane, at approximately $-2.213 \pm 4.936\mathrm{i}$. But if we use six terms from (4.3), still using only the leading term from (4.2), there is now a 'bad' pole at $\sigma \simeq 3.017$. As we include more terms from (4.3) more poles appear on the positive real axis. Thus the effect of going from a one-point to a two-point Padé approximant has been to force poles into the left half plane, but this effect becomes weaker as we include more terms of (4.3). Thus it is vitally important to keep a balance between the number of terms used from each of the series (4.2) and (4.3), and one way to check this balance is to find the location of the poles for each approximant evaluated.

Keeping this in mind, we give two further approximations, using two terms from (4.3) for each term from (4.2):

$$Q \simeq 1 + \mathrm{e}^{-2\sigma}\left(\frac{1}{\sigma} + \frac{12\,880 + 15\,704\sigma + 11\,073\sigma^2}{9660 + 6465\sigma + 3691\sigma^2}\right), \tag{4.5}$$

$$Q \simeq 1 + 3\,\mathrm{e}^{-2\sigma} + \mathrm{e}^{-6\sigma}\left(\frac{1}{\sigma} + \frac{2.333\,333 + 3.204\,423\sigma + 2.932\,241\sigma^2 + 1.536\,821\sigma^3}{1 + 0.487\,610\sigma + 0.647\,921\sigma^2 + 0.307\,364\sigma^3}\right). \tag{4.6}$$

The poles are all in the left half plane. The numerical values of Q calculated from (4.4), (4.5) and (4.6) have maximum errors of, respectively, 16%, 0.9% and 0.01%. Thus convergence is good, though not quite as fast as for the harmonic oscillator.

5. Particle in a box

For a particle of mass m in a box of length a the energy levels are

$$E_n = (1/2m)(\pi\hbar/a)^2 n^2, \qquad n = 1, 2, 3, \ldots, \tag{5.1}$$

and so the partition function is

$$Q = \sum_{n=1}^{\infty} \exp(-n^2\pi^2 u^2), \tag{5.2}$$

where $u = (\hbar/a)(\beta/2m)^{1/2}$. Again, the first few terms of this series describe the low-T behaviour. Application of the Poisson sum formula (Carrier *et al* 1966) yields the

high-T expansion

$$Q = -\frac{1}{2} + \frac{1}{\sqrt{\pi}u}\left(\frac{1}{2} + \sum_{n=1}^{\infty} \exp(-n^2/u^2)\right). \tag{5.3}$$

The form of this series is different to that of the previous cases, due to a finite number of inverse powers and the explicit presence of exponential terms. However, at sufficiently high temperatures, these are negligible compared with the first two terms of (5.3), and so we take the asymptotic behaviour to be

$$Q \sim \frac{1}{2\sqrt{\pi}}\frac{1}{u} - \frac{1}{2}, \qquad u \to 0. \tag{5.4}$$

The method of § 2.1 can now be applied, and the results for the first three approximations are

$$Q \simeq \exp(-\pi^2 u^2)\left(\frac{1}{2\sqrt{\pi}}\frac{1}{u} + \frac{-1+6\sqrt{\pi}u}{2+6\sqrt{\pi}u}\right), \tag{5.5}$$

$$Q \simeq \exp(-\pi^2 u^2) + \exp(-4\pi^2 u^2)\left(\frac{1}{2\sqrt{\pi}}\frac{1}{u} + \frac{-15+8\pi^{3/2}u}{10+8\pi^{3/2}u}\right), \tag{5.6}$$

$$Q \simeq \exp(-\pi^2 u^2) + \exp(-4\pi^2 u^2) + \exp(-9\pi^2 u^2)\left(\frac{1}{2\sqrt{\pi}}\frac{1}{u} + \frac{-2.5+6.250\,700u+4.509\,159u^2}{1+7.522\,710u+4.509\,159u^2}\right). \tag{5.7}$$

These have all their poles in the left half plane, and the maximum errors in Q are, respectively, 30%, 1.5% and 0.2%. Thus again convergence is satisfactory, if not as good as for the harmonic oscillator.

6. Conclusion

We have shown how to apply the method of two-point Padé approximants to the calculation of the partition function and other thermodynamic quantities of a quantum system. The input to the method is very basic—the first few energy levels, and the high-T semiclassical behaviour—and for many systems is known either precisely, or to high accuracy. The approximation takes place in the fitting, and by doing this in systematic successive stages we have a check on the convergence of the method.

It is not possible to rigorously justify the method, in the sense that we can prove that the Padé scheme will converge in all cases. (Such rigour is achieved in very few applications of Padé approximants.) But the information that $Q(\beta)$ is analytic in the half plane $\mathrm{Re}\,\beta > 0$ provides a valuable guide for the selection of appropriate sequences of approximants. In the cases we have studied this analyticity condition can be satisfied by keeping a balance between the input from the low-T and the high-T series for Q.

In this first paper we have treated only very simple systems—the method should be applicable in much more complex cases. However, it is important to show that it works well for these simple systems before attempting to apply it elsewhere. In

particular, it is reassuring to find that it works without modification for the particle in a box, since systems involving abrupt discontinuities can cause trouble with other approximation schemes (Stratt and Miller 1977, Stratt 1979, Korsch 1979).

The two-point Padé method gives results which are very accurate in the high-T and low-T regions. The maximum error occurs in the medium temperature range, but even here it is not excessive (at least for the cases we have studied). This is in contrast to many other approximation schemes (particularly semiclassical ones), which can be very accurate in one region, but become increasingly inaccurate as one moves away from that region, and eventually give even the wrong qualitative behaviour. An advantage of the present method is that the approximation is constrained to have the correct behaviour at both of its extremities. Provided the quantity we are approximating has a reasonably smooth behaviour, this would seem to give the best chance for overall accuracy.

Of course there are limitations to the method. As stated in § 2.1, a requirement is that the system have low-lying discrete energy levels which are reasonably well spaced, so that the low-T behaviour of the partition function is determined by the leading terms of (2.1). Thus the scheme will not be useful for large systems, and certainly not in the thermodynamic limit, where Q will have quite a different low-T behaviour.

In this paper, the harmonic oscillator has been treated at some length, both as an illustration of the method, and also as the prototype for the quartic and anharmonic oscillators. These will be considered in a second paper (Gibson 1984).

Appendix. Two-point Padé approximants

Two-point Padé approximants were first explicitly introduced by Baker *et al* (1964). A number of references to subsequent work can be found in Gibson (1981). A systematic fitting procedure is outlined by Isihara and Montroll (1971), but appears to be unnecessarily complicated. Thus it seems worthwhile to state the method we use.

Consider the case where $f(x)$ has expansions in x and x^{-1} about zero and infinity respectively. We first remark that it is always possible, by elementary manipulations, to relate $f(x)$ to a function $F(x)$ with the expansions

$$F(x) \sim a_0 + a_1 x + a_2 x^2 + \ldots, \qquad x \to 0, \tag{A1}$$

$$F(x) \sim b_0 + b_1 x^{-1} + b_2 x^{-2} + \ldots, \qquad x \to \infty, \tag{A2}$$

where $a_0 \neq 0$, but any number of $b_0, b_1, \ldots$ can be zero. We then fit $F(x)$ to an $[N/N]$ Padé approximant:

$$F(x) \simeq [N/N] \equiv \frac{p_0 + p_1 x + \ldots + p_N x^N}{1 + q_1 x + \ldots + q_N x^N}. \tag{A3}$$

This does not mean a restriction to diagonal approximants. We allow the possibility of any number of $p_N, p_{N-1}, \ldots$ being zero, so in effect we are fitting an $[M/N]$ approximant, where $M \leq N$.

Suppose there are $l+1$ terms in (A1) and $m+1$ in (A2), where $l+m$ is odd. We can then fit an $[N/N]$ Padé approximant, where $2N = l+m+1$. Requiring (A3) to

reproduce the small x series to $O(x^l)$ leads to the sequence of equations:

$$\left.\begin{aligned} p_0 &= a_0 \\ p_1 &= a_1 + a_0 q_1 \\ p_2 &= a_2 + a_1 q_1 + a_0 q_2 \\ &\vdots \end{aligned}\right\}. \tag{A4}$$

This pattern is continued for $l+1$ equations, with the convention that $p_r = 0$ and $q_r = 0$ if $r > N$.

Similarly, from the large-x behaviour we get the $m+1$ equations

$$\left.\begin{aligned} p_N &= b_0 q_N \\ p_{N-1} &= b_0 q_{N-1} + b_1 q_N \\ p_{N-2} &= b_0 q_{N-2} + b_1 q_{N-1} + b_2 q_N \\ &\vdots \end{aligned}\right\}, \tag{A5}$$

where again $p_r = 0$ and $q_r = 0$ if $r > N$. We now have a total of $2N+1$ equations in the $2N+1$ unknowns $p_0, \ldots, p_N, q_1, \ldots, q_N$. These can be solved analytically for small N, or numerically using a standard linear systems solver for large N.

Thus the whole procedure is purely mechanical, and one does not even have to decide on the order of the Padé approximant in advance. Simply specifying the coefficients $a_0, \ldots, a_l, b_0, \ldots, b_m$ uniquely determines the outcome.

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