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A new semiclassical expansion of the thermodynamic partition function

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Abstract. A non-perturbative semiclassical expansion of the thermodynamic partition function is derived. The expansion makes use of action–angle variables and expresses the partition function in terms of forbidden (complex-valued) classical paths. The method is contrasted with the Wigner–Kirkwood perturbation expansion and illustrated with numerical examples for the harmonic oscillator, the rotational sum and the particle in a box.

1. Introduction

The successful application of semiclassical path approximations in several areas of physics and the increasing use of mixed statistical–dynamical techniques (see e.g. Agassi *et al* 1977, Schatz *et al* 1977, Billing *et al* 1978, Miller and Skuse 1978) has led to a renewed interest in semiclassical methods in equilibrium statistical mechanics over the past decade (Feynman and Hibbs 1965, Burke and Siegel 1969, Feynman 1972, Miller 1971, 1972, 1973, 1974, Hornstein and Miller 1972, Stratt and Miller 1978, Baltin 1978). The central objects of interest here are naturally the Boltzmann density operator $\rho_\beta = \exp(-\beta\hat{H})$ $(\beta = 1/kT)$ and the thermodynamic partition function

$$Q = \mathrm{Tr}\,\hat{\rho}_\beta = \sum_n \mathrm{e}^{-\beta E_n} = \int \mathrm{d}q\, \rho_\beta(q) = \int \mathrm{d}E\, n(E)\, \mathrm{e}^{-\beta E} = \int\!\!\int \mathrm{d}p\, \mathrm{d}q\, \rho_\beta^W(p, q). \tag{1.1}$$

For simplicity we consider only the case of a single particle in a one-dimensional potential $V(q)$. An extension to higher dimensions causes no problems for integrable systems (for a recent discussion of the semiclassical dynamics for integrable and non-integrable systems see Berry (1977a, b)).

A classical path approximation for the particle density $\rho_\beta(q) = \langle q|\hat{\rho}_\beta|q\rangle$ in the coordinate representation has been derived by Miller (1971, 1972, 1973, 1974), the semiclassical limit of the density of states $n(E) = \mathrm{Tr}\,\delta(E - H)$ has been investigated by Berry and co-workers (Berry and Mount 1972, Berry and Tabor 1976, 1977), and a semiclassical expression for the equilibrium Wigner distribution $\rho_\beta^W(p, q)$ in phase space has recently been obtained by the author (Korsch 1979). An evaluation of the semiclassical partition function (1.1) by integrating the semiclassical approximations to $\rho_\beta(q)$, $n(E)$ or $\rho_\beta^W(p, q)$ over coordinate space or phase space is numerically involved in practice, because it requires the computation of complex-valued classical trajectories for each integration point (subject to certain boundary conditions). For simple systems it has been demonstrated that the semiclassical theory can account for the quantum effects almost perfectly (Miller 1971, 1972, 1973, 1974, Stratt and Miller 1978, Korsch

1978), but the simplicity of the traditional quantum correction expansion is lost. This traditional approach is the Wigner–Kirkwood perturbation expansion (Wigner 1932, Kirkwood 1933, Mayer and Band 1947, Hornstein and Miller 1972, Stratt and Miller 1978, Baltin 1978, Thakkar 1978) of the particle density $\rho_\beta(q)$ in terms of the small parameter $\lambda = (\hbar\beta)^2/2m$,

$$\rho_\beta(q) = \rho_\beta^{\mathrm{Cl}}(q)(1+\lambda A_1+\lambda^2 A_2+\ldots), \tag{1.2}$$

with the classical density

$$\rho_\beta^{\mathrm{Cl}}(q) = (1/h)(2\pi m/\beta)^{1/2}\exp(-\beta V(q)) \tag{1.3}$$

and

$$\begin{aligned} A_1 &= \tfrac{1}{12}\beta(V')^2 - \tfrac{1}{6}V'', \\ A_2 &= \tfrac{1}{288}\beta^2(V')^4 - \tfrac{11}{360}\beta(V')^2 V'' + \tfrac{1}{40}(V'')^2 + \tfrac{1}{30}V'V''' - \tfrac{1}{60}\beta^{-1}V''''. \end{aligned} \tag{1.4}$$

It should be noted that the series (1.2) is also an expansion with respect to the derivatives of the potential and therefore of little practical value for potentials containing a hard core or a discontinuity.

It is the purpose of the present article to propose an alternative approach to the semiclassical partition function and statistical averages of dynamical variables, which is intermediate between the detailed classical path description and the Wigner–Kirkwood perturbation expansion.

2. The semiclassical expansion

The statistical average of the physical observable A in thermodynamic equilibrium is given by

$$\langle A\rangle = \frac{\mathrm{Tr}\,\hat{A}\hat{\rho}_\beta}{\mathrm{Tr}\,\hat{\rho}_\beta} = \frac{1}{Q}\sum_n A_n \exp(-\beta E_n), \tag{2.1}$$

with the short notation $A_n = \langle n|\hat{A}|n\rangle$.

$$Q = \sum_n \exp(-\beta E_n) \tag{2.2}$$

is the thermodynamic partition function. In the following we derive a semiclassical expression for Q, but the formalism can easily be generalised to the statistical averages (2.1).

The decisive step of the present semiclassical approximation is similar to the well-known semiclassical evaluation of the angular momentum sum in potential scattering (see e.g. Berry and Mount 1972, Korsch and Leissing 1976). Following the work of Berry and Tabor (1976, 1977) we convert the sum over bound states in (2.1) or (2.2) into an integral over the continuous variable

$$I = \hbar(n+\alpha) \tag{2.3}$$

(the constant α is defined below) by means of the Poisson summation formula (Morse and Feshbach 1953) (see also appendix 2):

$$
\begin{aligned}
Q &= \sum_{n=0}^{\infty} \exp(-\beta E_n) \\
&= \frac{1}{\hbar} \sum_{M=-\infty}^{\infty} \exp(-2\pi \mathrm{i} M\alpha) \int_0^{\infty} \mathrm{d}I \exp\left(-\beta H(I) + \frac{2\pi \mathrm{i} MI}{\hbar}\right) \\
&= \sum_{M=-\infty}^{\infty} \exp(-2\pi \mathrm{i} M\alpha) Q_M
\end{aligned} \tag{2.4}
$$

with

$$Q_M = \frac{1}{\hbar} \int_0^{\infty} \mathrm{d}I \exp\left(-\beta H(I) + \frac{2\pi \mathrm{i} MI}{\hbar}\right). \tag{2.5}$$

It should be noted that we have $Q_{-M} = Q_M^*$, so that the sum in equation (2.4) is real valued.

The expansion (2.4) is exact, but it shows a different convergence behaviour from that of the bound state series (2.2): The series (2.2) converges quickly for large values of $\hbar$ and β, i.e. low temperatures and large level spacings, whereas the expansion (2.4) converges quickly for small values of $\hbar$ and β. The next step is to identify the continuous variable I defined in (2.3) with the classical action

$$I = \frac{1}{2\pi} \oint p(q)\, \mathrm{d}q, \tag{2.6}$$

where the integral is extended over a complete circuit. Equation (2.3) is then the well-known WKB quantisation condition. It may be worthwhile to state explicitly that (2.6) is an approximation, which is exact, however, whenever the JWKB quantisation is exact. The lowest order term $M = 0$ is recognised easily as the classical partition function

$$Q_0 = \frac{1}{\hbar} \int_0^{\infty} \mathrm{d}I\, \mathrm{e}^{-\beta H(I)} = \frac{1}{2\pi\hbar} \iint \mathrm{d}I\, \mathrm{d}\phi\, \mathrm{e}^{-\beta H(I)} = \frac{1}{h} \iint \mathrm{d}p\, \mathrm{d}q\, \mathrm{e}^{-\beta H(p,q)} \tag{2.7}$$

(here ϕ is the angle variable conjugate to the action I). The terms with $M \neq 0$ give quantum corrections to the classical result. They can be evaluated in the semiclassical limit $\hbar \to 0$ by applying the method of stationary phase (or steepest decent) to the integrals (2.5). This gives the stationary condition

$$\omega(I_M) = 2\pi \mathrm{i} M/\hbar\beta \tag{2.8}$$

(with $\omega(I) = \partial H/\partial I$), which can be rewritten in terms of the imaginary time $\tau = \mathrm{i}T = 2\pi\mathrm{i}/\omega$ (Stratt and Miller 1978) as

$$\hbar\beta = M\tau(I_M). \tag{2.9}$$

A similar condition has been found by Miller (Miller 1971, 1972, 1973, 1974, Stratt and Miller 1978). The solution of equation (2.8) or (2.9) defines the action I_M and a family of closed trajectories (Berry and Tabor 1976, 1977), which are, of course, classically forbidden and therefore complex-valued (Miller 1971, 1972, 1973, 1974, Stratt and Miller 1978; see also Korsch and Leissing 1976). The final ('primitive') semiclassical approximation to Q_M is

$$Q_M = \left(\frac{2\pi}{\beta\omega'(I_M)}\right)^{1/2} \exp\left(-\beta H(I_M) + \frac{2\pi \mathrm{i} M I_M}{\hbar}\right). \tag{2.10}$$

The sum over the different values of M in equation (2.4) is a sum over different semiclassical 'states' of the system. These states differ topologically: the trajectories belonging to the same M can be deformed continuously into one another, those with different M cannot (Berry and Mount 1972, Berry and Tabor 1976, 1977, Korsch and Leissing 1976).

The constant α in equation (2.3) is determined by the phase shifts due to reflections at the caustics in a single circuit (Maslov 1972, Berry and Mount 1972, Berry and Tabor 1976). For a smooth potential in one dimension we have $\alpha = \frac{1}{2}$, and for the particle in a box $\alpha = 1$ (there is phase jump of π for reflection at a hard wall, instead of $\pi/2$ for a smooth potential).

The primitive semiclassical formula (2.10) derived in this section shows an unexpected deficiency: it breaks down for the simple harmonic oscillator $H = \omega I$ (the stationary condition (2.8) cannot be satisfied, and ω' in the denominator of equation (2.10) is zero). This deficiency can be overcome by a uniform semiclassical approximation to the integral (2.5) (details are given in appendix 1), which gives

$$\begin{aligned} Q_M = \frac{1}{\hbar}\Bigg[\left(\frac{\pi}{2\beta\omega'(I_M)}\right)^{1/2} \operatorname{erfc}(\lambda_M) \exp\left(-\beta H(I_M) + \frac{2\pi \mathrm{i} M I_M}{\hbar}\right) \\ + \frac{1}{\beta\omega(I_M)} - \frac{1}{\lambda_M}\left(\frac{1}{2\beta\omega'(I_M)}\right)^{1/2}\Bigg], \end{aligned} \tag{2.11}$$

with $H(0) = 0$ and

$$\lambda_M = -(-\beta H(I_M) + 2\pi \mathrm{i} M I_M/\hbar)^{1/2}. \tag{2.12}$$

The error function erfc can also be computed easily for complex-valued arguments (see appendix 1). In the harmonic oscillator limit equation (2.11) reduces to the exact closed form expression

$$Q_M = (\hbar\omega\beta - 2\pi \mathrm{i} M)^{-1} \tag{2.13}$$

for the integral (2.5). Equation (2.11) is therefore expected to give a reasonable approximation also for potentials, which are approximately harmonic.

3. Examples

The following examples will give some more insight into the working of the semiclassical formalism.

3.1. *Harmonic oscillator*

For the simple harmonic oscillator the exact quantum partition function is

$$Q = (2\sinh\tfrac{1}{2}x)^{-1}, \qquad x = \hbar\beta\omega. \tag{3.1}$$

The first terms of the Wigner–Kirkwood expansion (1.2) are

$$Q = 1/x - x/24 + 7x^3/5760 + \ldots, \tag{3.2}$$

which is, of course, the beginning of the exact expansion of (3.1) in powers of x, starting with the classical result

$$Q^{\mathrm{Cl}} = 1/x. \tag{3.3}$$

The behaviour of the expansion (3.2) is shown in figure 1(*a*), where Q^{Cl}, $Q^{(1)} = 1/x - x/24$ and $Q^{(2)} = Q^{(1)} + 7x^3/5760$ are plotted along with the exact result (3.1).

The semiclassical expansion (2.4), with Q_M of equation (2.13) leads to the series

$$Q = \frac{1}{x} + 2x \sum_{M=-\infty}^{+\infty} \frac{(-1)^M}{x^2 + (2\pi M)^2}, \tag{3.4}$$

which is also an exact expansion of (3.1). It is obvious that (3.4) is *not* a perturbation expansion in powers of $\hbar$. The behaviour of the successive approximations in (3.4) is shown in figure 1(*b*). It is evident that the semiclassical expansion (3.4) is generally much better than the Wigner–Kirkwood expansion (3.2) shown in figure 1(*a*), also at surprisingly low values of $1/x = kT/\hbar\beta$.

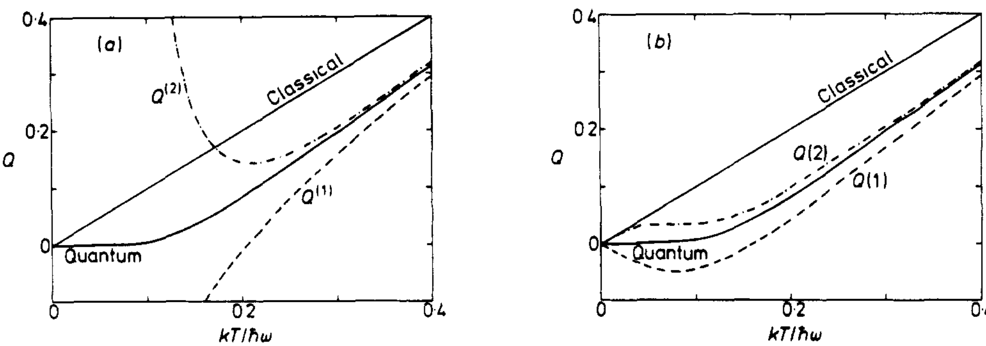

Figure 1. (*a*) Thermodynamic partition function for the harmonic oscillator as a function of the temperature. The classical and the exact quantum result are compared with the first terms of the Wigner–Kirkwood perturbation expansion. (*b*) Thermodynamic partition function for the harmonic oscillator as a function of the temperature. The classical and the exact quantum result are compared with the first terms of the non-perturbative semiclassical expansion (2.4).

3.2. The rotational sum

The partition function for the rotating diatomic molecule is in the rigid rotor approximation

$$Q = \sum_{l=0}^{\infty} (2l+1)\, \mathrm{e}^{-\beta B l(l+1)}. \tag{3.5}$$

With the usual semiclassical transformation $I = \hbar(l + \frac{1}{2})$ (for convenience we use here the letter I instead of the common L) we find for the semiclassical Q_M

$$Q_M = \frac{2}{\hbar^2} \mathrm{e}^{\beta B/4} \int_0^{\infty} \mathrm{d}I\, I \exp\left(-\frac{\beta B}{\hbar^2} I^2 + \frac{2\pi \mathrm{i} M I}{\hbar}\right), \tag{3.6}$$

where the additional factor I in the integral stems from the degeneracy $(2l+1)$ of the rotation.

The uniform semiclassical approximation (2.11) together with

$$I_M = \pi \mathrm{i} M\hbar/\beta B \tag{3.7}$$

and

$$\lambda = -\mathrm{i}\pi M/(\beta B)^{1/2} \tag{3.8}$$

gives the final result

$$Q_M = \frac{1}{\beta B}\,\mathrm{e}^{\beta B/4}(1 - 2\delta_M F(\delta_M) + \mathrm{i}\sqrt{\pi}\,\delta_M\,\mathrm{e}^{-\delta_M^2}). \tag{3.9}$$

Here $F(\delta_M)$ is Dawson's integral (see appendix 1) and $\delta_M = \pi M/(\beta B)^{1/2}$. The final semiclassical expansion is

$$Q = \frac{1}{\beta B}\,\mathrm{e}^{\beta B/4}\left\{1 + 2\sum_{M=1}^{\infty}(-1)^M[1 - 2\delta_M F(\delta_M)]\right\}. \tag{3.10}$$

The lowest-order approximations which retain only the term with $M = 0$ ($Q(0)$) and the terms $M = 0$ and $M = 1$ ($Q(1)$) are shown in figure 2 as a function of $1/\beta B = T/T_r$, where $T_r = B/k$ is the characteristic temperature of rotation. The agreement between $Q(1)$ and the exact summation of (3.5) is excellent.

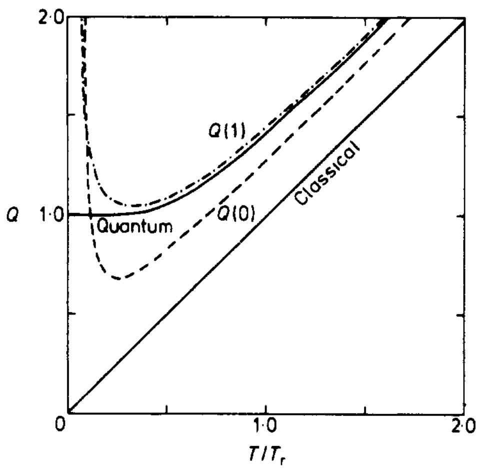

Figure 2. Classical and quantum partition function for the rigid rotor as a function of the reduced temperature. The broken and the chain curves show the first terms (up to $M = 1$ and $M = 2$) of the semiclassical expansion.

3.3. Particle in a box

Discontinuous potentials and potentials with hard walls create notorious problems in semiclassical applications (Adams and Miller 1977, Stratt and Miller 1978, Korsch 1978). It is therefore worthwhile to discuss the typical example of a particle in a box in some detail. In this case we have a phase jump of π instead of $\pi/2$ for smooth potentials caused by the reflection at the classical turning points, and therefore the proper semiclassical quantisation condition is $I = \hbar(n+1)$ ($n = 0, 1, 2, \ldots$), i.e. we have $\alpha = 1$ in equation (2.3). The semiclassical energy levels obtained in this way agree with the exact ones. For the integer value of $\alpha = 1$ the Poisson sum formula must be modified (see appendix 2) and we find for the particle (mass m) in a box (length a), instead of equation (2.4),

$$Q = -\frac{1}{2} + \sum_{M=-\infty}^{\infty} Q_M, \tag{3.11}$$

with

$$Q_M = \frac{1}{\hbar}\int_0^{\infty} \mathrm{d}I \, \exp\left[-\left(\frac{\pi I}{\hbar\theta}\right)^2 + \frac{2\pi \mathrm{i} M I}{\hbar}\right], \tag{3.12}$$

where the dimensionless parameter

$$\theta = \frac{a}{\hbar}\left(\frac{2\pi}{\beta}\right)^{1/2} \tag{3.13}$$

has been introduced (Stratt and Miller 1978).

It is easy to show that

$$Q_M + Q_{-M} = (\theta/\sqrt{\pi})\, \mathrm{e}^{-\theta^2 M^2} \tag{3.14}$$

and we finally obtain the desired semiclassical expansion

$$Q = -\frac{1}{2} + \frac{\theta}{\sqrt{\pi}}\left(\frac{1}{2} + \sum_{M=1}^{\infty} \mathrm{e}^{-M^2\theta^2}\right). \tag{3.15}$$

$\theta/2\sqrt{\pi}$ is the classical partition function.

The semiclassical expansion (3.15) is also an exact representation of the quantum mechanical series

$$Q = \sum_{n=1}^{\infty} \exp\left[-\left(\frac{\pi n}{\theta}\right)^2\right]. \tag{3.16}$$

The expansions (3.15) and (3.16) are related by the well-known theta-transformation†.

Figure 3 demonstrates the fast convergence of the semiclassical expansion (3.15). The agreement with the exact result (3.16) is very good. Also shown in figure 3 is a semiclassical approximation obtained recently by Stratt and Miller (1978) which does not reproduce the behaviour of the quantum result.

4. Concluding remarks

It has been shown that the thermodynamic partition function can be written as a series expansion in terms of a topological sum. The first term of this series is the classical partition function; the higher terms depend on complex-valued classically forbidden paths. In contrast to the Wigner–Kirkwood expansion the present semiclassical series is non-perturbative in character. Numerical examples show a rapid convergence down to surprisingly low temperatures.

† The Poisson sum formula is exact, and therefore the semiclassical expansion of the partition function is also an exact representation, provided that the semiclassical quantisation conditions are exact.

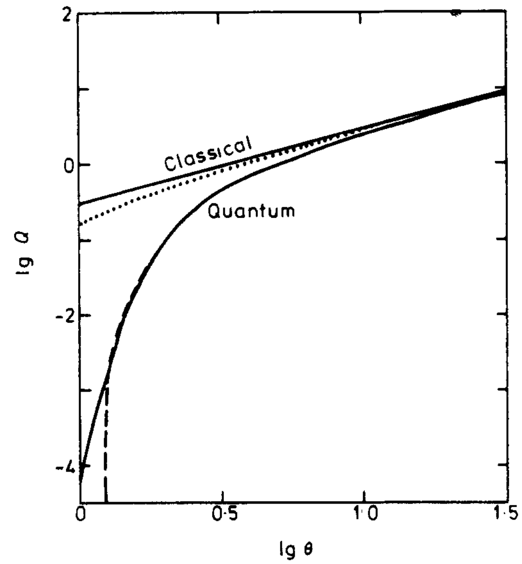

Figure 3. Classical and quantum partition function for the particle in a box ($\theta = (a/\hbar)(2\pi kT)^{1/2}$). The broken curve is the semiclassical expansion of this work (up to $M = 1$). Also shown is a semiclassical approximation by Stratt and Miller (1978) (dotted curve).

The semiclassical analysis derived in the present paper can be extended easily to the case of more than one dimension provided that the system is integrable. It would be highly desirable to extend the semiclassical theory to non-integral systems, which occur automatically if the system contains more than two particles, even if the particles interact via pair potentials.

Another interesting field for future work should be an investigation of the role of Fermi–Dirac, Bose–Einstein and Boltzmann statistics in the semiclassical limit. Studies in these directions are presently under way.

Appendix 1

A uniform approximation to the integral

$$\mathscr{I}(x_0) = \int_{x_0}^{\infty} \mathrm{d}x\, g(x)\, \mathrm{e}^{-f(x)} \tag{A1.1}$$

which takes care of the interaction between the stationary point $f'(x_s) = 0$ and the lower limit of integration x_0 can be derived by using the error function (Abramowitz and Stegun 1964)

$$\operatorname{erfc}(\lambda) = 1 - \operatorname{erf}(\lambda) = \frac{\sqrt{\pi}}{2} \int_{\lambda}^{\infty} \mathrm{d}y\, \mathrm{e}^{-y^2} \tag{A1.2}$$

as a comparison integral (see also the articles by Berry and Tabor (1976) and Kafri and Kosloff (1977)) and mapping the stationary point x_s of (A1.1) onto the stationary point

$y_s = 0$ of (A1.2) by the mapping function

$$f(x) = f(x_s) + y^2. \tag{A1.3}$$

This gives

$$\lambda = \pm(f(x_0) - f(x_s))^{1/2} \tag{A1.4}$$

($\lambda \gtreqless 0$ for $x_0 \gtreqless x_s$). Changing to variable y in (A1.1) and expanding $g(x)\,dx/dy$ up to first order in y, one finally obtains

$$\mathscr{I}(x_0 = g(x_s)\, e^{-f(x_s)}\left(\frac{\pi}{2f''(x_s)}\right)^{1/2} \operatorname{erfc}(\lambda) + \left[\frac{g(x_0)}{f'(x_0)} - \frac{g(x_s)}{\lambda}\left(\frac{1}{2f''(x_s)}\right)^{1/2}\right] e^{-f(x_0)}. \tag{A1.5}$$

For $x_0 \to -\infty$ we have $\exp(-f(x_0)) \to 0$, $\lambda \to -\infty$, and with $\operatorname{erfc}(-\infty) = 2$ we recover the usual saddle-point result. In the 'harmonic oscillator' limit (see § 2) $f(x) = a + bx + cx^2$, $c \to 0$, the last two terms of (A1.5) cancel, and the first term agrees with the exact value of the integral (A1.1) in this limit (Berry and Tabor 1976).

Finally it will be useful to give a formula for the error function in equation (A1.5) for complex values of the argument:

$$\operatorname{erfc}(u + iv) = \operatorname{erf}(u) - i(2/\sqrt{\pi})\, e^{v^2} F(v), \tag{A1.6}$$

where

$$F(v) = e^{-v^2} \int_0^v dt\, e^{t^2} \tag{A1.7}$$

is Dawson's integral, which is tabulated (Abramowitz and Stegun 1964) or can easily be calculated numerically.

Appendix 2

The Poisson sum formula is usually written as

$$\sum_{n=0}^{\infty} f(n) = \frac{1}{\hbar} \sum_{M=-\infty}^{+\infty} \exp(-2\pi i M\alpha) \int_0^{\infty} dI\, f\left(\frac{I}{\hbar} - \alpha\right) \exp(2\pi i MI/\hbar), \tag{A2.1}$$

with the continuous variable $I = \hbar(n + \alpha)$, where α is an arbitrary constant between 0 and 1 ($0 < \alpha < 1$). Equation (A2.1) can easily be proved by integrating the identity

$$\sum_{n=-\infty}^{+\infty} f(x)\delta(n - x) = \sum_{M=-\infty}^{+\infty} f(x) \exp(2\pi i Mx) \tag{A2.2}$$

over the interval $(-\alpha, +\infty)$. Equation (A2.1) is exact for well-behaved functions f. The convergence behaviour, i.e. the quality of the approximation of the lowest terms, depends on the choice of α, which is naturally determined by the semi-classical quantisation condition (see equation (2.3) and the discussion in § II). For the case of an infinitely deep square well potential we have $\alpha = 1$, and (A2.1) is no longer valid in this form. An immediate modification of (A2.1) for the integer value of $\alpha = 1$ is

$$\sum_{n=0}^{\infty} f(n) = -\frac{1}{2} f(-1) + \sum_{M=-\infty}^{+\infty} \int_0^{\infty} dI\, f\left(\frac{I}{\hbar} - 1\right) \exp(2\pi i MI/\hbar), \tag{A2.3}$$

which can be easily verified.

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