Take the gentle path
GEORGE HERBERT (1593-1633), Discipline

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Semiclassical Time Evolution Amplitude

The path integral approach renders a clear intuitive understanding of quantum-mechanical effects in terms of quantum fluctuations, exhibiting precisely how the laws of classical mechanics are modified by these fluctuations. In some limiting situations, the modifications may be small, for instance, if an electron in an atom is highly excited. Its wave packet encircles the nucleus in almost the same way as a point particle in classical mechanics. Then it is relatively easy to calculate quite accurate quantum-mechanical amplitudes by expanding them around classical expressions in powers of the fluctuation width.

4.1 Wentzel-Kramers-Brillouin (WKB) Approximation

In Schrödinger's theory, an important step towards understanding the relation between classical and quantum mechanics consists in proving that the center of a Schrödinger wave packet moves like a classical particle. The approach to the classical limit is described by the so-called *eikonal approximation*, or the *Wentzel-Kramers-Brillouin approximation* (short: *WKB approximation*), which proceeds as follows:

First, one rewrites the time-independent Schrödinger equation of a point particle

$$\left\{-\frac{\hbar^2}{2M}\boldsymbol{\nabla}^2-[E-V(\mathbf{x})]\right\}\psi(\mathbf{x})=0 \tag{4.1}$$

in the form

$$\left[-\hbar^2\boldsymbol{\nabla}^2-p^2(\mathbf{x})\right]\psi(\mathbf{x})=0, \tag{4.2}$$

where

$$p(\mathbf{x})\equiv\sqrt{2M[E-V(\mathbf{x})]} \tag{4.3}$$

is the *local classical momentum* of the particle.

In a second step, one re-expresses the wave function as an exponential

$$\psi(\mathbf{x})=e^{iS(\mathbf{x})/\hbar}. \tag{4.4}$$

For the exponent $S(\mathbf{x})$, called the *eikonal*, the Schrödinger equation amounts to the a differential equation :

$$-i\hbar\boldsymbol{\nabla}^2 S(\mathbf{x}) + [\boldsymbol{\nabla} S(\mathbf{x})]^2 - p^2(\mathbf{x}) = 0. \tag{4.5}$$

To solve this equation approximately, one assumes that the function $p(\mathbf{x})$ shows little relative change over the de Broglie wavelength

$$\lambda \equiv \frac{2\pi}{k(\mathbf{x})} \equiv \frac{2\pi\hbar}{p(\mathbf{x})}, \tag{4.6}$$

i.e.,

$$\varepsilon \equiv \frac{2\pi\hbar}{p(\mathbf{x})}\left|\frac{\boldsymbol{\nabla} p(\mathbf{x})}{p(\mathbf{x})}\right| \ll 1. \tag{4.7}$$

This condition is called the *WKB condition*. In the extreme case of $p(\mathbf{x})$ being a constant the condition is certainly fulfilled and the Riccati equation is solved by the trivial eikonal

$$S = \mathbf{p}\mathbf{x} + \text{const}\,, \tag{4.8}$$

which makes (4.4) a plain wave. For slow variations, the first term in the Riccati equation is much smaller than the others and can be treated systematically in a "smoothness expansion". Since the small ratio (4.7) carries a prefactor $\hbar$, the Planck constant may be used to count the powers of the smallness parameter ε, i.e., it may formally be considered as a small expansion parameter.

The limit $\hbar \to 0$ of the equation determines the lowest-order approximation to the eikonal, $S_0(\mathbf{x})$, by

$$[\boldsymbol{\nabla} S_0(\mathbf{x})]^2 - p^2(\mathbf{x}) = 0. \tag{4.9}$$

Being independent of $\hbar$, this is a classical equation. Indeed, it is equivalent to the Hamilton-Jacobi differential equation of classical mechanics: For time-independent systems, the action can be written as

$$A(\mathbf{x}, t) = S_0(\mathbf{x}) - tE, \tag{4.10}$$

where $S_0(\mathbf{x})$ is defined by

$$S_0(\mathbf{x}) \equiv \int dt\, \mathbf{p}(t)\dot{\mathbf{x}}(t), \tag{4.11}$$

and E is the constant energy of the orbit under consideration. The action solves the Hamilton-Jacobi equation (1.64). In three dimensions, it is a function $A(\mathbf{x}, t)$ of the orbital endpoints. According to Eq. (1.62), the derivative of $A(\mathbf{x}, t)$ is equal to the momentum $\mathbf{p}$. Since E is a constant, the same thing holds for $S_0(\mathbf{x}, t)$. Hence

$$\mathbf{p} \equiv \boldsymbol{\nabla} A(\mathbf{x}) = \boldsymbol{\nabla} S_0(\mathbf{x}). \tag{4.12}$$

In terms of the action A, the Hamilton-Jacobi equation reads

$$\frac{1}{2M}(\boldsymbol{\nabla} A)^2 + V(\mathbf{x}) = -\partial_t A. \tag{4.13}$$

By inserting Eqs. (4.10) and (4.12), we recover Eq. (4.9). This is why $S_0(\mathbf{x})$ is also called the *classical eikonal*.

The corrections to the classical eikonal are calculated most systematically by imagining $\hbar \neq 0$ to be a small quantity and expanding the eikonal around $S_0(x)$ in a power series in $\hbar$:

$$S = S_0 - i\hbar S_1 + (-i\hbar)^2 S_2 + (-i\hbar)^3 S_3 + \dots \ . \tag{4.14}$$

This is called the *semiclassical expansion* of the eikonal. Inserting it into the Riccati equation, we find the sequence of *WKB equations*

$$\begin{aligned}
(\boldsymbol{\nabla} S_0)^2 - p^2 &= 0, \\
\boldsymbol{\nabla}^2 S_0 + 2\boldsymbol{\nabla} S_0 \cdot \boldsymbol{\nabla} S_1 &= 0, \\
\boldsymbol{\nabla}^2 S_1 + (\boldsymbol{\nabla} S_1)^2 + 2\boldsymbol{\nabla} S_0 \cdot \boldsymbol{\nabla} S_2 &= 0, \\
\boldsymbol{\nabla}^2 S_2 + 2\boldsymbol{\nabla} S_1 \cdot \boldsymbol{\nabla} S_2 + 2\boldsymbol{\nabla} S_0 \cdot \boldsymbol{\nabla} S_3 &= 0, \\
&\vdots \\
\boldsymbol{\nabla}^2 S_n + \sum_{m=0}^{n+1} \boldsymbol{\nabla} S_m \cdot \boldsymbol{\nabla} S_{n+1-m} &= 0, \qquad (4.15) \\
&\vdots \qquad .
\end{aligned}$$

Note that these equations involve only the vectors

$$\mathbf{q}_n = \boldsymbol{\nabla} S_n \tag{4.16}$$

and allow for a successive determination of $S_0, S_1, S_2, \dots$, giving higher and higher corrections to the eikonal $S(\mathbf{x})$.

In one dimension we recognize in (4.5) the Riccati differential equation (2.547) fulfilled by $\partial_\tau S(x)$, if we identify x with $\tau\sqrt{2M}$, and $v(\tau)$ with $E - V(\tau)$, where (4.5) reads

$$-i\hbar\partial_\tau[\partial_\tau S(\tau)] + [\partial_\tau S(\tau)]^2 = p^2(\tau) = v(\tau). \tag{4.17}$$

If we re-express the expansion terms (2.552) in terms of $w(\tau) = \sqrt{v(\tau)}$, we may replace $w(\tau), w'(\tau), \dots$ by $p(x), p'(x), \dots$, and find directly

$$\begin{aligned}
q_0(x) &= \pm p(x), \qquad q_1(x) = -\frac{1}{2}\frac{p'(x)}{p(x)} = \frac{V'}{4(E-V)}, \\
q_2(x) &= \pm\left[\frac{1}{4}\frac{p''(x)}{p^2(x)} - \frac{3}{8}\frac{p'^2(x)}{p^3(x)}\right] = \mp\frac{4V''(E-V) + 5V'^2}{32\sqrt{2M}(E-V)^{5/2}} \equiv \mp p(x)g(x), \\
q_3(x) &= \frac{1}{2}g'(x) = \frac{15V'^3 + 18V'V''(E-V) + 4V'''(E-V)^2}{128M(E-V)^4}.
\end{aligned} \tag{4.18}$$

Note that $q_2(x)$ can also be written as

$$q_2(x) = \frac{1}{4S'(x)}\{S', x\},$$

where $\{h,x\}$ denotes the so-called *Schwartz derivative* [1]:

$$\{h,x\} \equiv \frac{h'''}{h'} - \frac{3}{2}\left(\frac{h''}{h'}\right)^2 \tag{4.19}$$

of the function $h(x)$. The equation for $q_2(x)$ defines also the quantity $g(x) \equiv q_2(x)/p(x)$ appearing in the equation for $q_3(x)$.

It is useful to introduce also the expansion

$$q(x) \equiv S'(x) = q_0(x) + \hbar q_1(x) + \hbar^2 q_2(x) + \dots\ . \tag{4.20}$$

Then the eikonal has the expansion

$$S(x) = \int dx\, q(x) = \pm \int dx\, p(x)[1+\hbar^2 g(x)] + \hbar \frac{i}{2}[\log p(x) + \hbar^2 g(x)] \pm \dots\ . \tag{4.21}$$

Keeping only terms up to the order $\hbar$, which is possible if $\hbar^2|\epsilon(x)| \ll 1$, we find the (as yet unnormalized) *WKB wave function*

$$\psi_{\rm WKB}(x) = e^{(i/\hbar)\int^x dx' q(x')} = \frac{1}{\sqrt{p(x)}} e^{\pm(i/\hbar)\int^x dx' p(x')}. \tag{4.22}$$

In the classically accessible regime $V(x) \leq E$, this is an oscillating wave function; in the inaccessible regime $V(x) \geq E$, it decreases or increases exponentially. The transition from one to the other is nontrivial since for $V(x) \approx E$, the WKB approximation breaks down. After some analytic work[1], however, it is possible to derive simple *connection rules* for the linearly independent solutions. Let $k(x) \equiv p(x)/\hbar$ in the oscillating regime and $\kappa(x) \equiv |p(x)|/\hbar$ in the exponential regime. Suppose that there is a crossover at $x=a$ connecting an inaccessible regime on the left of $x=a$ with an accessible one on the right. Then the connection rules are

$$\begin{array}{ccc} V(x) > E & & V(x) < E \\ \frac{1}{\sqrt{\kappa}} e^{-\int_x^a dx'\kappa} & \longleftrightarrow\!\!\!\!\!\!\!\rightarrow & \frac{2}{\sqrt{k}}\cos\left(\int_a^x dx' k - \frac{\pi}{4}\right), \\ \frac{1}{\sqrt{\kappa}} e^{\int_x^a dx'\kappa} & \leftarrow\!\!\!\!\!\!\!\longleftrightarrow & -\frac{1}{\sqrt{k}}\sin\left(\int_a^x dx' k - \frac{\pi}{4}\right). \end{array} \tag{4.23, 4.24}$$

In the opposite situation at the point $x=b$, they turn into

$$\begin{array}{ccc} V(x) < E & & V(x) > E \\ \frac{2}{\sqrt{k}}\cos\left(\int_x^b dx' k - \frac{\pi}{4}\right) & \leftarrow\!\!\!\!\!\!\!\longleftrightarrow & \frac{1}{\sqrt{\kappa}} e^{-\int_b^x dx'\kappa}, \\ -\frac{1}{\sqrt{k}}\sin\left(\int_x^b dx' k - \frac{\pi}{4}\right) & \longleftrightarrow\!\!\!\!\!\!\!\rightarrow & \frac{2}{\sqrt{\kappa}} e^{\int_b^x dx'\kappa}. \end{array} \tag{4.25, 4.26}$$

[1]R.E. Langer, Phys. Rev. *51*, 669 (1937). See also W.H. Furry, Phys. Rev. *71*, 360 (1947), and the textbooks S. Flügge, *Practical Quantum Mechanics*, Springer, Berlin, 1974; L.I. Schiff, *Quantum Mechanics*, McGraw-Hill, New York, 1955; N. Fröman and P.O. Fröman, *JWKB-Approximation*, North-Holland, Amsterdam, 1965.

The connection rules can be used safely only along the direction of the double arrows.

For their derivation one solves the Schrödinger equation exactly in the neighborhood of the turning points where the potential rises or falls approximately linearly. These solutions are connected with adjacent WKB wave functions. The connection formulas can also be found directly by a formal trick: When approaching the dangerous turning points, one escapes into the complex x-plane and passes around the singularities at a finite distance. This has to be sufficiently large to preserve the WKB condition (4.7), but small enough to allow for the linear approximation of the potential near the turning point. Take for example the connection rule at $x = b$. When approaching the turning point at $x = b$ from the right, the function $\kappa(x)$ is approximately proportional to $\sqrt{x-b}$. Going around this zero in the upper complex half-plane takes $\kappa(x)$ into $ik(x)$ and the wave function $\sqrt{\kappa}^{-1} e^{-\int_b^x dx'\kappa}$ becomes $e^{-i\pi/4}\sqrt{k}^{-1} e^{-i\int_b^x dx'k}$. Going around the turning point in the lower half-plane produces $e^{i\pi/4}\sqrt{k}^{-1} e^{i\int_b^x dx'k}$. The sum of the two terms is $2\sqrt{k}^{-1}\cos(\int_x^b dx'k - \pi/4)$. The argument does not show why one should use the sum rather than the average. This becomes clear only after a more detailed discussion found in quantum-mechanical textbooks[2]. The simplest derivation of the connection formulas is based on the large-distance behaviors (2.625) and (2.630) of wave the function to the right and left of a linearly rising potential and applying this to the linearly rising section of the general potential near the turning point.

In a simple potential well, the function $p(x)$ has two zeros, say one at $x = a$ and one at $x = b$. The bound-state wave functions must satisfy the boundary condition to vanish exponentially fast at $x = \pm\infty$. Imposing these, the connection formulas lead to the *semiclassical* or *Bohr-Sommerfeld quantization rule*

$$\int_a^b dx\, k(x) = (n + 1/2)\pi, \quad n = 0, \pm 1, \pm 2, \dots \,. \tag{4.27}$$

It was pointed out by Dunham[3] that due to the square-root nature of the cut between a and b, this condition implies that the anticlockwise contour integral around the cut over the eikonal expansion (4.21) up to order $\hbar$, where $q(x) \approx \pm p(x) + i(\hbar/2)\log p(x)$, is an integer multiple of $\hbar$:

$$\oint dx\, q(x) = 2\pi n\hbar. \tag{4.28}$$

The contour encloses the classical turning points and no other singularities of $q(x)$. This property ensures the single-valuedness of the wave function $\psi(x) = \exp[iS(x)/\hbar] = \exp[i\int dx\, q(x)/\hbar]$ at the semiclassical level.

Moreover, the single-valuedness is a necessary property to *all* orders in the expansion (4.21). This makes (4.28) an exact quantization rule.[4] In fact, in Sub-

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[2]See for example E. Merzbacher, *Quantum Theory*, John Wiley & Sons, New York, 1970, p. 122; M.L. Goldberger and K.M. Watson, *Collision Theory*, John Wiley & Sons, New York, 1964, p. 324. The analytic argument is given in L.D. Landau and E.M. Lifshitz, *Quantum Mechanics*, Pergamon, London, 1965, p. 158.

[3]J.L. Dunham, Phys. Rev. *41*, 21 (1932)

[4]J.R. Krieger and C. Rosenzweig, Phys. Rev. *164*, 171 (1967).

section 4.9.6 we shall arrive at the quantization condition (4.28) from a different starting point and calculate vary accurate energy levels for the quartic potential $gx^4/4$ by evaluating (4.28) to high orders in $\hbar$.

Note that the first term $-i\hbar q_1(x)$ in the semiclassical expansion (4.20) of $q(x) = S'(x)$ contributes, via Cauchy's residue theorem, a value $-\pi\hbar$ to the contour integral (4.28). This expansion term can therefore be moved from the left- to the right-hand side of (4.28) by simply changing the right-hand side from $2\pi n\hbar$ to $2\pi(n+\frac{1}{2})\hbar$. This is the origin of the difference between the Bohr-Sommerfeld quantization condition (4.27) and the old the Bohr quantization condition which has only $n\pi$ on the right-hand side of (4.27). Remarkably, the next odd expansion terms $q_3(x)$ is a pure derivative which does not contribute to the contour integral in (4.28) at all. Using all terms up to $q_4(x)$, and applying partial integrations, the quantization condition (4.28) can be re-written as

$$\oint \left\{ (E-V)^{1/2} - \tilde{\hbar}^2 \frac{V'^2}{32(E-V)^{5/2}} - \tilde{\hbar}^4 \frac{49V'^4 - 16(E-V)^2 V'V''''}{2048(E-V)^{11/2}} + \dots \right\} = 2\pi(n+\tfrac{1}{2})\tilde{\hbar},$$

where $\tilde{\hbar} \equiv \hbar/\sqrt{2M}$. In terms of $\tilde{q}^2(x) \equiv 2Mq^2(x) = E - V(x)$, this becomes

$$\oint \left\{ \tilde{q} - \frac{\tilde{\hbar}^2}{32} \frac{(\tilde{q}^2)'^2}{\tilde{q}^5} - \frac{\tilde{\hbar}^4}{2048} \left[\frac{49(\tilde{q}^2)'^4}{\tilde{q}^{11}} - \frac{16(\tilde{q}^2)'(\tilde{q}^2)'''}{\tilde{q}^7} \right] + \dots \right\} = 2\pi(n+\tfrac{1}{2})\tilde{\hbar}. \quad (4.29)$$

For the harmonic oscillator, the semiclassical quantization rule (4.27) gives the exact energy levels. Indeed, for an energy E, the classical crossover points with $V(x_E) = E$ are

$$x_c = \pm\sqrt{\frac{2E}{M\omega^2}}, \quad (4.30)$$

to be identified in (4.27) with a and b, respectively. Inserting further

$$k(x) = \frac{p(x)}{\hbar} = \sqrt{\frac{2M}{\hbar^2}\left(E - \frac{1}{2}M\omega^2 x^2\right)}, \quad (4.31)$$

we obtain the WKB approximation for the energy levels

$$\int_{-x_E}^{x_E} dx' k(x) = \frac{E}{\hbar\omega}\pi = (n + \tfrac{1}{2})\pi, \quad (4.32)$$

which indeed coincides with the exact ones. Only nonnegative values $n = 0, 1, 2, \dots$ lead to oscillatory waves.

As an example consider the quartic potential $V(x) = gx^4/2$ for which the Schrödinger equation cannot be solved exactly. Inserting this into equation (4.32), we obtain

$$\frac{1}{\hbar}\int_{-x_E}^{x_E} dx \sqrt{2M(E - gx^4/4)} \equiv \nu(E)\pi = (n + \tfrac{1}{2})\pi, \quad (4.33)$$

with the turning points $\pm x_E = \pm(4E/g)^{1/4}$. The integral is done using the formula[5]

$$\int_0^1 dt\, t^{\mu-1}(1-t^\lambda)^{\nu-1} = \frac{1}{\lambda}B(\mu/\lambda,\nu) \tag{4.34}$$

which for $\mu = 1$, $\lambda = 4$, and $\nu = 3/2$ yields $(1/4)B(1/4,3/2)$, so that the left-hand side of Eq.(4.33) can be written with $\Gamma(1/4) = 2\pi/\Gamma(3/4)\sqrt{2}$ as $\nu(E)\pi \equiv E^{3/4}2M^{1/2}\pi^{3/2}/3\hbar g^{1/4}\Gamma^2(3/4)$, and (4.33) determines the energy with principal quantum numebr n in the Bohr-Sommerfeld approximation by the consition $\nu(E) = n + \frac{1}{2}$ resulting in

$$E_{\rm BS}^{(n)} = \hbar\omega\kappa_{\rm BS}^{(n)}\left(\frac{g\hbar}{4M^2\omega^3}\right)^{1/3}, \tag{4.35}$$

with

$$\kappa_{\rm BS}^{(n)} = \frac{1}{\pi^{2/3}}\left(\frac{3}{2}\right)^{4/3}\Gamma^{8/3}(3/4)\,(n+\tfrac{1}{2})^{4/3} \approx 0.688\,253\,702 \times 2(n+\tfrac{1}{2})^{4/3}. \tag{4.36}$$

This large-n result may be compared with the precise of $\kappa^{(0)} = 0.667986\ldots$ to be derived in Section 5.19 (see Table 5.9).

If the potential contains a centrifugal term $V_{\rm cf}(r) = l(l+1)\hbar^2/2Mr^2$ in addition to the potential $V(\mathbf{x})$, the singularity at $r = 0$ is too strong to apply the WKB approximation. In addition, the factor $\hbar^2$ in front of this term ruins the systematics of the expansion terms (4.14) if one starts out with $(\boldsymbol{\nabla} S_0)^2 = p^2 = 2M[E - V - l(l+1)\hbar^2/2Mr^2]$. In this situation, the semiclassical treatment needs a modification sketched.

For a rotationally symmetric potential, the wave function in the Schrödinger equation (4.1) can be factorized into a radial part $R(r)/r$ and spherical harmonic $Y_{lm}(\theta,\phi)$ [see (1.420)]. The radial wave function satisfies the radial Schrödinger equation

$$\left\{-\frac{\hbar^2}{2M}\partial_r^2 - [E - V(r) - V_{\rm cf}(r)]\right\} R(r) = 0. \tag{4.37}$$

In this equation, one moves the singularity at $r = 0$ to $\xi = -\infty$ by a coordinate transformation $r = e^\xi$, leading to the following nonsingular equation $\xi(\xi) \equiv e^{-\xi/2}R(e^\xi)$:

$$\left[-\frac{\hbar^2}{2M}\partial_\xi^2 - q^2(\xi)\right]\chi(\xi) = 0. \tag{4.38}$$

with

$$\tilde{q}^2(\xi) \equiv e^{2\xi}\left[E - V(e^\xi) - V_{\rm cf}(e^\xi) - \frac{\hbar^2 e^{-2\xi}}{8M}\right] = e^{2\xi}\left[E - V(e^\xi) - \frac{(l+\frac{1}{2})^2\hbar^2 e^{-2\xi}}{2M}\right]. \tag{4.39}$$

Inserting this into the quantization condition (4.29), only the first semiclassical term contributes, and all the higher terms vaish, leading to the *exact* energies for the

[5] I.S. Gradshteyn and I.M. Ryzhik, op. cit., Formula 3.251.1.

Coulomb potential $V(r) = -e^2/r$ with an additional centrifugal barrier $V_{\rm cf}(x)$. They are the same as the energies obtained from the initial Bohr-Sommerfeld quantization condition (4.27) if we exchange the factor $l(l+1)$ in the centrifugal barrier by $(l+\frac{1}{2})^2$. This exchange is called the *Langer correction*. For a one-dimensional hydrogen atom, the singularity of the Coulomb potential at $r = 0$ is also so strong that one must change the variable r to ξ. Inserting $\tilde{q}^2(\xi) = e^{2\xi}\left[E + e^2 e^{-\xi} - \frac{1}{8}e^{-2\pi}\right]$ into the Bohr-Sommerfeld quantization condition (4.27), we obtain the equation, re-expressed in terms of r,

$$\int_{r_a}^{r_b} (dr/r)\sqrt{2(-1/8 + e^2 r + Er^2)} = \frac{\pi}{2} + \frac{\pi}{\sqrt{-2E}} = (n + \tfrac{1}{2})\pi,$$

where $r_{a,b}$ are the turning points $r_{a,b} = \left(e^2 \mp \sqrt{2e^2 + E}\right)/(-4E)$. For simplicity, we have gone to natural units with $\hbar = 1$, $M = 1$. Thus we find the semiclassical energies $E = -e^4/2n^2$ $(n = 1, 2, 3, \ldots)$, which are exact. Without the 1/8-term from the variable change $r = e^\xi$, the integral would have been equal to $\pi/\sqrt{-2E}$ yielding the approximate energies $E = -e^4/2(n+\frac{1}{2})^2$. These will be derived once more from another semiclassical expansion at the end of Appendix 4A.

4.2 Saddle Point Approximation

Let us now look at the semiclassical expansion within the path integral approach to quantum mechanics. Consider the time evolution amplitude

$$(x_b t_b | x_a t_a) = \int \mathcal{D}x \, e^{i\mathcal{A}[x]/\hbar}, \tag{4.40}$$

imagining Planck's constant $\hbar$ to be again a free parameter which is very small compared to the typical fluctuations of the action. With $\hbar$ appearing in the denominator of an imaginary exponent we see that in the limit $\hbar \to 0$, the path integral becomes a sum of rapidly oscillating terms which will approximately cancel each other. This phenomenon is known from ordinary integrals

$$\int \frac{dx}{\sqrt{2\pi i\hbar}} e^{ia(x)/\hbar}, \tag{4.41}$$

which converge to zero for $\hbar \to 0$ according to the Riemann-Lebesgue lemma. The precise behavior is given by the saddle point expansion of integrals which we shall first recapitulate.

4.2.1 Ordinary Integrals

The evaluation of an integral of the type (4.41) proceeds for small $\hbar$ via the so-called *saddle point approximation*. In the limit $\hbar \to 0$, the integral is dominated by the extremum of the function $a(x)$ with the smallest absolute value, call it $x_{\rm cl}$ (assuming it to be unique, for simplicity), where

$$a'(x_{\rm cl}) = 0. \tag{4.42}$$

In the path integral, the point $x_{\rm cl}$ in this example corresponds to the classical orbit for which the functional derivative vanishes. This is the reason for using the subscript cl. For x near the extremum, the oscillations of the integrand are weakest. The leading oscillatory behavior of the integral is given by

$$\int_{-\infty}^{\infty} \frac{dx}{\sqrt{2\pi i\hbar}} e^{ia(x)/\hbar} \xrightarrow{\hbar\to 0} \text{const} \times e^{ia(x_{\rm cl})/\hbar}, \tag{4.43}$$

with a constant proportionality factor independent of $\hbar$. This can be calculated by expanding $a(x)$ around its extremum as

$$a(x) = a(x_{\rm cl}) + \frac{1}{2}a''(x_{\rm cl})(\delta x)^2 + \frac{1}{3!}a^{(3)}(x_{\rm cl})(\delta x)^3 + \dots\,, \tag{4.44}$$

where $\delta x \equiv x - x_{\rm cl}$ is the deviation from $x_{\rm cl}$. It is the analog of the *quantum fluctuation* introduced in Section 2.2. Due to (4.42), the linear term in δx is absent. If $a''(x_{\rm cl}) \neq 0$ and the higher derivatives are neglected, the integral is of the Fresnel type and can be done, yielding

$$\int_{-\infty}^{\infty} \frac{dx}{\sqrt{2\pi i\hbar}} e^{ia(x)/\hbar} \to e^{ia(x_{\rm cl})/\hbar} \int_{-\infty}^{\infty} \frac{d\delta x}{\sqrt{2\pi i\hbar}} e^{ia''(x_{\rm cl})(\delta x)^2/2\hbar} = \frac{e^{ia(x_{\rm cl})/\hbar}}{\sqrt{a''(x_{\rm cl})}}. \tag{4.45}$$

The right-hand side is the *saddle point approximation* to the integral (4.41).

The saddle point approximation may be viewed as the consequence of the classical limit of the exponential function:

$$e^{ia(x)/\hbar} \xrightarrow{\hbar\to 0} \frac{\sqrt{2\pi i\hbar}}{\sqrt{a''(x_{\rm cl})}}\,\delta(x - x_{\rm cl})\,. \tag{4.46}$$

Corrections can be calculated perturbatively by expanding the integral in powers of $\hbar$, leading to what is called the *saddle point expansion*. For this we expand the remaining exponent in powers of δx:

$$\begin{aligned} \exp&\left\{\frac{i}{\hbar}\left[\frac{1}{3!}a^{(3)}(x_{\rm cl})(\delta x)^3 + \frac{1}{4!}a^{(4)}(x_{\rm cl})(\delta x)^4 + \dots\right]\right\} \\ &= 1 + \frac{i}{\hbar}\left[\frac{1}{3!}a^{(3)}(x_{\rm cl})(\delta x)^3 + \frac{1}{4!}a^{(4)}(x_{\rm cl})(\delta x)^4 + \dots\right] \\ &\quad - \frac{1}{\hbar^2}\left[\frac{1}{72}a^{(3)}(x_{\rm cl})^2(\delta x)^6 + \dots\right] + \dots \end{aligned} \tag{4.47}$$

and perform the resulting integrals of the type

$$\int_{-\infty}^{\infty} \frac{d\delta x}{\sqrt{2\pi i\hbar}} e^{ia''(x_{\rm cl})(\delta x)^2/2\hbar}(\delta x)^n = \begin{cases} \dfrac{(n-1)!!}{[a''(x_{\rm cl})]^{(1+n)/2}}(i\hbar)^{n/2}, & n = \text{even}, \\ 0, & n = \text{odd}. \end{cases} \tag{4.48}$$

Each factor δx in (4.47) introduces a power $\sqrt{\hbar/a''(x_{\rm cl})}$. This is the average relative size of the quantum fluctuations. The increasing powers of $\hbar$ ensure the decreasing importance of the higher terms for small $\hbar$. For instance, the fourth-order term $a^{(4)}(x_{\rm cl})(\delta x)^4/4!$ is accompanied by $\hbar$, and the lowest correction amounts to a factor

$$1 - ia^{(4)}(x_{\rm cl})\frac{3!!}{4!}\frac{\hbar}{[a''(x_{\rm cl})]^2}. \tag{4.49}$$

The cubic term $a^{(3)}(x_{\rm cl})(\delta x)^3/3!$ yields a factor

$$1 + i[a^{(3)}(x_{\rm cl})]^2\frac{5!!}{72}\frac{\hbar}{[a''(x_{\rm cl})]^3}. \tag{4.50}$$

Thus we obtain the saddle point expansion to the integral is

$$\int_{-\infty}^{\infty}\frac{dx}{\sqrt{2\pi i\hbar}}e^{ia(x)/\hbar} = \frac{e^{ia(x_{\rm cl})/\hbar}}{\sqrt{a''(x_{\rm cl})}}\left\{1 - i\hbar\left[\frac{1}{8}\frac{a^{(4)}(x_{\rm cl})}{[a''(x_{\rm cl})]^2} - \frac{5}{24}\frac{[a^{(3)}(x_{\rm cl})]^2}{[a''(x_{\rm cl})]^3}\right] + \mathcal{O}(\hbar^2)\right\}. \tag{4.51}$$

Expectation values in this integral can also be expanded in powers of $\hbar$, for instance $\langle x\rangle = x_{\rm cl} + \langle\delta x\rangle$ where

$$\begin{aligned}\langle\delta x\rangle = & -i\hbar\frac{1}{2}\frac{a^{(3)}(x_{\rm cl})}{[a''(x_{\rm cl})]^2}\\ & - \hbar^2\left[\frac{2}{3}\frac{a^{(3)}(x_{\rm cl})a^{(4)}(x_{\rm cl})}{[a''(x_{\rm cl})]^4} - \frac{5}{8}\frac{[a^{(3)}(x_{\rm cl})]^3}{[a''(x_{\rm cl})]^5} - \frac{1}{8}\frac{a^{(5)}(x_{\rm cl})}{[a''(x_{\rm cl})]^3}\right] + \mathcal{O}(\hbar^3).\end{aligned} \tag{4.52}$$

Since the saddle point expansion is organized in powers of $\hbar$, it corresponds precisely to the semiclassical expansion of the eikonal in the previous section.

The saddle point expansion can be used for very small $\hbar$ to calculate an integral with increasing accuracy. It is impossible, however, to achieve arbitrary accuracy since the resulting series is divergent for all physically interesting systems. It is merely an *asymptotic series* whose usefulness decreases rapidly with an increasing size of the expansion parameter. A variational expansion must be used to achieve convergence. For more details, see Sections 5.15 and 17.9.

An important property of the semiclassical approximation is that Fourier transformations become very simple. Consider the Fourier integral

$$\int_{-\infty}^{\infty} dx\, e^{-ipx/\hbar}e^{ia(x)/\hbar}. \tag{4.53}$$

For small $\hbar$, this can be done in the saddle point approximation according to the rule (4.46), and obtain

$$\int_{-\infty}^{\infty} dx\, e^{-ipx/\hbar}e^{ia(x)/\hbar} \to \sqrt{2\pi i\hbar}\frac{e^{i[a(x_{\rm cl})-px_{\rm cl}]/\hbar}}{\sqrt{a''(x_{\rm cl})}}, \tag{4.54}$$

where $x_{\rm cl}$ is now the extremum of the action with a source term p, i.e., it is determined by the equation $p = a'(x_{\rm cl})$. Note that the formula holds also if the exponential carries an x-dependent prefactor, since the x-dependence gives only corrections of the order of $\hbar$ in the exponent:

$$\int_{-\infty}^{\infty} dx\, e^{-ipx/\hbar}c(x)e^{ia(x)/\hbar} \to \sqrt{2\pi i\hbar}\, c(x_{\rm cl})\frac{e^{i[a(x_{\rm cl})-px_{\rm cl}]/\hbar}}{\sqrt{a''(x_{\rm cl})}}. \tag{4.55}$$

If the equation $p = a'(x_{\rm cl})$ is inverted to find $x_{\rm cl}$ as a function $x_{\rm cl}(p)$, the exponent $a(x_{\rm cl}) - px_{\rm cl}$ may be considered as a function of p:

$$b(p) = a(x_{\rm cl}) - px_{\rm cl}, \qquad p = a'(x_{\rm cl}). \tag{4.56}$$

This function is recognized as being the Legendre transform of the function $a(x)$ [recall (1.9)].

The original function $a(x)$ can be recovered from $b(p)$ via an inverse Legendre transformation

$$a(x) = b(p_{\rm cl}) + xp_{\rm cl}, \qquad x = -b'(p_{\rm cl}). \tag{4.57}$$

This formalism is the basis for many thermodynamic calculations. For large statistical systems, fluctuations of global properties such as the volume and the total internal energy are very small so that the saddle point approximation is very good. In this chapter, the formalism will be applied on many occasions.

4.2.2 Path Integrals

A similar saddle point expansion exists for the path integral (4.40). For small $\hbar$, the amplitudes $e^{i\mathcal{A}/\hbar}$ from the various paths will mostly cancel each other by interference. The dominant contribution comes from the functional regime where the oscillations are weakest, which is from extremum of the action

$$\delta\mathcal{A}[x] = 0. \tag{4.58}$$

This gives the classical Euler-Lagrange equation of motion. For a point particle with the action

$$\mathcal{A}[x] = \int_{t_a}^{t_b} dt \left[\frac{M}{2}\dot{x}^2 - V(x)\right], \tag{4.59}$$

it reads

$$M\ddot{x} = -V'(x). \tag{4.60}$$

Let $x_{\rm cl}(t)$ denote the classical orbit. After multiplying (4.60) by $\dot{x}$, an integration in t yields the law of energy conservation

$$E = \frac{M}{2}\dot{x}_{\rm cl}^2 + V(x_{\rm cl}) = \text{const} . \tag{4.61}$$

This implies that the classical momentum

$$p_{\rm cl}(t) \equiv M\dot{x}_{\rm cl}(t) \tag{4.62}$$

can be written as

$$p_{\rm cl}(t) = p(x_{\rm cl}(t)), \tag{4.63}$$

where $p(x)$ is the local classical momentum defined in (4.3). From (4.61), the time dependence of the classical orbit $x_{\rm cl}(t)$ is given by

$$t - t_0 = \int_0^{x_{\rm cl}} dx \frac{M}{p(x)} = \int_0^{x_{\rm cl}} dx \frac{M}{\sqrt{2M[E - V(x)]}}. \tag{4.64}$$

When solving the integral on the right-hand side we find for a given time interval $t = t_b - t_a$ the energy for which a pair of positions x_a, x_b can be connected by a classical orbit:

$$E = E(x_b, x_a; t_b - t_a). \tag{4.65}$$

The classical action is given by

$$\begin{aligned}\mathcal{A}[x_{\rm cl}] &= \int_{t_a}^{t_b} dt \left[\frac{M}{2}\dot{x_{\rm cl}}^2 - V(x_{\rm cl})\right] \\ &= \int_{t_a}^{t_b} dt \left[p_{\rm cl}(t)\dot{x}_{\rm cl} - H(p_{\rm cl}, x_{\rm cl})\right] \\ &= \int_{x_a}^{x_b} dx p(x) - (t_b - t_a)E. \end{aligned}\tag{4.66}$$

Just like E, the classical action is a function of x_b, x_a and $t_b - t_a$, to be denoted by $A(x_b, x_a; t_b - t_a)$, for which (4.66) reads more explicitly

$$A(x_b, x_a; t_b - t_a) \equiv \int_{x_a}^{x_b} dx\, p(x) - (t_b - t_a)E(x_b, x_a; t_b - t_a). \tag{4.67}$$

Recalling (4.11), the first term on the right-hand side is seen to be the classical eikonal

$$S(x_b, x_a; E) = \int_{x_a}^{x_b} dx\, p(x), \tag{4.68}$$

where E is the energy function (4.65) and $p(x)$ is given by (4.3),

The eikonal may be viewed as a functional $S_E[x]$ of paths $x(t)$ of a fixed energy, in which case it is extremal on the classical orbits. This was observed as early as 1744 by Maupertius [2]. The proof for this is quite simple: We insert the classical momentum (4.3) into $S_E[x]$ and write

$$S_E[x] \equiv \int p(x)dx = \int dt\, p(x)\dot{x} = \int dt\, L_E(x, \dot{x}) = \int dt \sqrt{2M[E - V(x)]}\dot{x}, \tag{4.69}$$

thus introducing a Lagrangian $L_E(x, \dot{x})$ for this problem. The associated Euler-Lagrange equation reads

$$\frac{d}{dt}\frac{\partial L_E}{\partial \dot{x}} = \frac{\partial L_E}{\partial x}. \tag{4.70}$$

Inserting $L_E(\mathrm{x}, \dot{x}) = p(x)\dot{x}$ we find the correct equation of motion $\dot{p} = -V'(x)$.

There is an interesting geometrical aspect to this variational procedure. In order to see this let us go to D dimensions and write the eikonal (4.69) as

$$S_E[\mathbf{x}] = \int dt\, L_E(\mathbf{x}, \dot{\mathbf{x}}) = \int dt\, \sqrt{g_{ij}(\mathbf{x})\dot{x}^i(t)\dot{x}^j(t)}, \tag{4.71}$$

with an energy-dependent metric

$$g_{ij}(\mathbf{x}) = p_E^2(\mathbf{x})\delta_{ij}. \tag{4.72}$$

Then the Euler-Lagrange equations for $\mathbf{x}(t)$ coincides with the equation (1.72) for the geodesics in a Riemannian space with a metric $g_{ij}(\mathbf{x})$. In this way, the dynamical problem has been reduced to a geometric problem. The metric $g_{ij}(\mathbf{x})$ may be called *dynamical metric* of the space with respect to the potential $V(\mathbf{x})$. This geometric view is further enhanced by the fact that the eikonal (4.69) is, in fact, independent of the parametrization of the trajectory. Instead of the time t we could have used any parameter τ to describe $\mathbf{x}(\tau)$ and write the eikonal (4.69) as

$$S_E[\mathbf{x}] = \int d\tau \sqrt{g_{ij}(\mathbf{x})\dot{x}^i(\tau)\dot{x}^j(\tau)}. \tag{4.73}$$

Einstein has certainly been inspired by this ancient description of classical trajectories when geometrizing the relativistic Kepler motion by attributing a dynamical Riemannian geometry to spacetime.

It is worth pointing out a subtlety in this variational principle, in view of a closely related situation to be encountered later in Chapter 10. The variations are supposed to be carried out at a fixed energy

$$E = \frac{M}{2}\dot{\mathbf{x}}^2 + V(\mathbf{x}). \tag{4.74}$$

This is a nonholonomic constraint which destroys the independence of the variation $\delta x(t)$ and $\delta\dot{x}$. They are related by

$$\dot{\mathbf{x}}\,\delta\dot{\mathbf{x}} = -\frac{1}{M}\boldsymbol{\nabla}V(\mathbf{x})\delta\mathbf{x}. \tag{4.75}$$

It is, however, possible to regain the independence by allowing for a simultaneous variation of the time argument in $\mathbf{x}(t)$ when varying $\mathbf{x}(\mathbf{t})$. As a consequence, we can no longer employ the standard equality $\delta\dot{x} = d\delta x/dt$ which is necessary for the derivation of the Euler-Lagrange equation (4.70). Instead, we calculate

$$\delta\dot{\mathbf{x}} = \frac{d\mathbf{x} + d\delta\mathbf{x}}{dt + d\delta t} - \dot{\mathbf{x}} = \frac{d}{dt}\delta\mathbf{x} - \dot{\mathbf{x}}\frac{d}{dt}\delta t, \tag{4.76}$$

which shows that variation and time derivatives no longer commute with each other. Combining this with the relation (4.75) we see that the variations of $\mathbf{x}$ and $\dot{\mathbf{x}}$ can be made independent if we vary t along the orbit according to the relation

$$\dot{\mathbf{x}}^2\frac{d}{dt}\delta t = \dot{\mathbf{x}}\frac{d}{dt}\delta\mathbf{x} + \frac{1}{M}\boldsymbol{\nabla}V(\mathbf{x})\delta\mathbf{x}. \tag{4.77}$$

With (4.76), the variations of the eikonal (4.71) are

$$\delta S_E[\mathbf{x}] = \int dt\left(\frac{\partial L_E}{\partial\dot{\mathbf{x}}}\frac{d}{dt}\delta\mathbf{x} + \frac{\partial L_E}{\partial\mathbf{x}}\delta\mathbf{x}\right) + \int dt\left(L_E - \frac{\partial L_E}{\partial\dot{\mathbf{x}}}\dot{\mathbf{x}}\right)\frac{d}{dt}\delta t\,, \tag{4.78}$$

where we have kept the usual commutativity of variation and time derivative of the time itself. In the second integral, we may set

$$-L_E + \frac{\partial L_E}{\partial\dot{\mathbf{x}}}\dot{\mathbf{x}} \equiv H_E. \tag{4.79}$$

The function H_E arises from L_E by the same combination of $L_E(\mathbf{x},\dot{\mathbf{x}})$ and $\partial L_E/\partial\dot{\mathbf{x}}(\mathbf{x},\dot{\mathbf{x}})$ as in a Legendre transformation which brings a Lagrangian to the associated Hamiltonian [recall (1.13)]. But in contrast to the usual procedure we do not eliminate $\dot{\mathbf{x}}$ in favor of a canonical momentum variable $\partial L_E/\partial\dot{\mathbf{x}}$ [recall (1.14)], i.e., the H_E is a function $H_E(\mathbf{x},\dot{\mathbf{x}})$. Note that it is *not* equal to the energy.

The variation (4.78) shows that the extra variation δt of the time does not change the Euler-Lagrange equations for the above Lagrangian in Eq. (4.71), $L_E = \sqrt{2M[E-V(\mathbf{x})]\dot{\mathbf{x}}^2}$. Being linear in $\dot{\mathbf{x}}$, the associated H_E vanishes identically, so that the second term disappears and we recover the ordinary equation of motion

$$\frac{d}{dt}\frac{\partial L_E}{\partial\dot{\mathbf{x}}} = \frac{\partial L_E}{\partial\mathbf{x}}. \tag{4.80}$$

In general, however, we must keep the second term. Expressing $d\delta t/dt$ via (4.77), we find

$$\begin{aligned}\delta S_E[\mathbf{x}] &= \int dt\left[\frac{\partial L_E}{\partial\dot{\mathbf{x}}} - H_E\frac{\dot{\mathbf{x}}}{\dot{\mathbf{x}}^2}\right]\frac{d}{dt}\delta\mathbf{x}\\ &+ \int dt\left[\frac{\partial L_E}{\partial\mathbf{x}} - H_E\frac{1}{\dot{\mathbf{x}}^2}\frac{1}{M}\boldsymbol{\nabla}V(\mathbf{x})\right]\delta\mathbf{x},\end{aligned} \tag{4.81}$$

and the general equation of motion becomes

$$\frac{d}{dt}\left[\frac{\partial L_E}{\partial\dot{\mathbf{x}}} - H_E\frac{\dot{\mathbf{x}}}{\dot{\mathbf{x}}^2}\right] = \frac{\partial L_E}{\partial\mathbf{x}} - H_E\frac{1}{\dot{\mathbf{x}}^2}\frac{1}{M}\boldsymbol{\nabla}V(\mathbf{x}), \tag{4.82}$$

rather than (4.80). Let us illustrate this by rewriting the eikonal as a functional

$$S_E[\mathbf{x}] = \int dt\, L'_E(\mathbf{x},\dot{\mathbf{x}}) = M\int dt\,\dot{\mathbf{x}}^2(t), \tag{4.83}$$

which is the same functional as (4.69) as long as the energy E is kept fixed. If we insert the new Lagrangian L'_E into (4.82), we obtain the correct equation of motion

$$M\ddot{\mathbf{x}} = -\boldsymbol{\nabla}V(\mathbf{x}). \tag{4.84}$$

In this case, the equation of motion can actually be found more directly. We vary the eikonal (4.83) as follows:

$$\delta S_E[\mathbf{x}] = M\int \delta dt\,\dot{\mathbf{x}}^2 + M\int dt\,\dot{\mathbf{x}}\,\delta\dot{\mathbf{x}} + M\int dt\,\dot{\mathbf{x}}\,\delta\dot{\mathbf{x}}. \tag{4.85}$$

In the last term we insert the relation (4.76) and write

$$\delta S_E[\mathbf{x}] = M\left[\int \delta dt\,\dot{\mathbf{x}}^2 + \int dt\,\dot{\mathbf{x}}\,\delta\dot{\mathbf{x}} + \int dt\,\dot{\mathbf{x}}\frac{d}{dt}\delta\mathbf{x} - \int dt\,\dot{\mathbf{x}}^2\frac{d}{dt}\delta t\right]. \tag{4.86}$$

The two terms containing δt cancel each other, so that relation (4.77) is no longer needed. Using now (4.75), we obtain directly the equation of motion (4.84).

With the help of the eikonal (4.68), we write the classical action (4.66) as

$$A(x_b, x_a; t_b - t_a) \equiv S(x_b, x_a; E) - (t_b - t_a)E, \tag{4.87}$$

where E is given by (4.65).

The action has the property that its derivatives with respect to the endpoints x_b, x_a at a fixed $t_b - t_a$ yield the initial and final classical momenta:

$$\frac{\partial}{\partial x_{b,a}} A(x_b, x_a; t_b - t_a) = \pm p(x_{b,a}). \tag{4.88}$$

Indeed, the differentiation gives

$$\frac{\partial A}{\partial x_b} = p(x_b) + \left[\int_{x_a}^{x_b} dx \frac{\partial p(x)}{\partial E} - (t_b - t_a)\right] \frac{\partial E}{\partial x_b}, \tag{4.89}$$

and using

$$\frac{\partial p(x)}{\partial E} = \frac{M}{p(x)} = \frac{1}{\dot{x}}, \tag{4.90}$$

we see that

$$\int_{x_a}^{x_b} dx \frac{\partial p(x)}{\partial E} = \int_{t_a}^{t_b} dt = t_b - t_a, \tag{4.91}$$

so that the bracket in (4.89) vanishes, and (4.88) is indeed fulfilled [compare also (4.12)]. The relation (4.91) implies that the eikonal (4.68) has the energy derivative

$$\frac{\partial}{\partial E} S(x_b, x_a; E) = t_b - t_a. \tag{4.92}$$

As a conjugate relation, the derivative of the action with respect to the time t_b at fixed x_b gives the energy with a minus sign [compare (4.10)]:

$$\frac{\partial}{\partial t_b} A(x_b, x_a; t_b - t_a) = -E(x_b, x_a; t_b - t_a). \tag{4.93}$$

This is easily verified:

$$\frac{\partial}{\partial t_b} A = \left[\int_{x_a}^{x_b} dx \frac{\partial p}{\partial E} - (t_b - t_a)\right] \frac{\partial E}{\partial t_b} - E = -E. \tag{4.94}$$

Thus, the classical action function $A(x_b, x_a; t_b - t_a)$ and the eikonal $S(x_b, x_a; E)$ are Legendre transforms of each other.

The equation

$$\frac{1}{2M} (\partial_x A)^2 + V(x) = \partial_t A \tag{4.95}$$

is, of course, the Hamilton-Jacobi equation (4.13) of classical mechanics.

We have therefore found the leading term in the semiclassical approximation to the amplitude [corresponding to the approximation (4.43)]:

$$(x_b t_b|x_a t_a) \xrightarrow{\hbar\to 0} \text{const} \times e^{iA(x_b,x_a;t_b-t_a)/\hbar}. \tag{4.96}$$

In general, this leading term will be multiplied by a fluctuation factor

$$(x_b t_b|x_a t_a) = e^{iA(x_b,x_a;t_b-t_a)/\hbar} F(x_b, x_a; t_b - t_a). \tag{4.97}$$

In contrast to the purely harmonic case in Eq. (2.153) this will depend on the initial and final coordinates x_a and x_b.

The calculation of the leading contribution to the fluctuation factor is the next step in the saddle point expansion of the path integral (4.40). For this we expand the action (4.59) in the neighborhood of the classical orbit in powers of the fluctuations

$$\delta x(t) = x(t) - x_{cl}(t). \tag{4.98}$$

This yields the fluctuation expansion

$$\begin{aligned}\mathcal{A}[x,\dot{x}] &= \mathcal{A}[x_{\rm cl}] + \int_{t_a}^{t_b} dt \frac{\delta\mathcal{A}}{\delta x(t)}\delta x(t)\\ &+\frac{1}{2}\int_{t_a}^{t_b} dt dt' \frac{\delta^2\mathcal{A}}{\delta x(t)\delta x(t')}\delta x(t)\delta x(t')\\ &+\frac{1}{3!}\int_{t_a}^{t_b} dt dt' dt'' \frac{\delta^3\mathcal{A}}{\delta x(t)\delta x(t')\delta x(t'')}\delta x(t)\delta x(t')\delta x(t'') + \dots,\end{aligned} \tag{4.99}$$

where all functional derivatives on the right-hand side are evaluated along the classical orbit $x(t) = x_{\rm cl}(t)$. The linear term in the quantum fluctuation $\delta x(t)$ is absent since $\mathcal{A}[x,\dot{x}]$ is extremal at $x_{\rm cl}(t)$. For a point particle, the quadratic term is

$$\frac{1}{2}\int_{t_a}^{t_b} dt dt' \frac{\delta^2\mathcal{A}}{\delta x(t)\delta x(t')}\delta x(t)\delta x(t') = \int_{t_a}^{t_b} dt\left[\frac{M}{2}(\delta\dot{x})^2 + \frac{1}{2}V''(x_{\rm cl}(t))(\delta x)^2\right]. \tag{4.100}$$

Thus the fluctuations behave like those of a harmonic oscillator with a time-dependent frequency

$$\Omega^2(t) = \frac{1}{M}V''(x_{\rm cl}(t)). \tag{4.101}$$

By definition, the fluctuations vanish at the endpoints:

$$\delta x(t_a) = 0, \quad \delta x(t_b) = 0. \tag{4.102}$$

If we include only the quadratic terms in the fluctuation expansion (4.99), we can integrate out the fluctuations in the path integral (4.40). Since $x(t)$ and $\delta x(t)$

differ only by a fixed additive function $x_{\rm cl}(t)$, the measure of the path integral over $x(t)$ transforms trivially into that over $\delta x(t)$. Thus we conclude that the leading semiclassical limit of the amplitude is given by the product

$$(x_bt_b|x_at_a)_{\rm sc} = e^{iA(x_b,x_a;t_b-t_a)/\hbar}F_{\rm sc}(x_b,x_a;t_b-t_a), \tag{4.103}$$

with the semiclassical fluctuation factor [compare (2.200)]

$$\begin{aligned} F_{\rm sc}(x_b,x_a;t_b-t_a) &= \int \mathcal{D}\delta x(t) \exp\left\{\frac{i}{\hbar}\int_{t_b}^{t_a} dt \frac{M}{2}[\delta\dot{x}^2 - \Omega^2(t)\delta x^2]\right\} \\ &= \frac{1}{\sqrt{2\pi i\epsilon\hbar/M}} \det\left(-\overline{\nabla}\nabla - \Omega^2(t)\right)^{-1/2} \\ &= \frac{1}{\sqrt{2\pi i\hbar(t_b-t_a)/M}} \sqrt{\frac{\det\left(-\partial_t^2\right)}{\det\left(-\partial_t^2 - \Omega^2(t)\right)}}. \end{aligned} \tag{4.104}$$

In principle, we would now have to solve the differential equation

$$[-\partial_t^2 - \Omega^2(t)]y_n(t) = [-\partial_t^2 - V''(x_{\rm cl}(t))/M]y_n(t) = \lambda_n y_n(t), \tag{4.105}$$

and find the energies of the eigenmodes $y_n(t)$ of the fluctuations. The ratio of fluctuation determinants

$$\frac{D^0}{D} = \frac{\det\left(-\partial_t^2\right)}{\det\left(-\partial_t^2 - \Omega^2(t)\right)} \tag{4.106}$$

in the second line of (4.104) would then be found from the product of ratios of eigenvalues, λ_n/λ_n^0, where λ_n^0 are the eigenvalues of the differential equation

$$-\partial_t^2 y_n(t) = \lambda_n^0 y_n(t). \tag{4.107}$$

Fortunately, we can save ourselves all this work using the Gelfand-Yaglom method of Section 2.4 which provides a much simpler and more direct way of calculating fluctuation determinants with a time-dependent frequency without the knowledge of the eigenvalues λ_n.

4.3 Van Vleck-Pauli-Morette Determinant

According to the Gelfand-Yaglom method of Section 2.4, a functional determinant of the form

$$\det\left(-\partial_t^2 - \Omega^2(t)\right)$$

is found by solving the differential equation (4.105) at zero eigenvalue

$$[-\partial_t^2 - \Omega^2(t)]D_a(t) = 0,$$

with the initial conditions

$$D_a(t_a) = 0, \qquad \dot{D}_a(t_a) = 1. \tag{4.108}$$

Then $D_a(t_b)$ is the desired fluctuation determinant. In Eq. (2.240), we have constructed the solution to these equations in terms of an arbitrary solution $\xi(t)$ of the homogenous equation

$$[-\partial_t^2 - \Omega^2(t)]\xi(t) = 0 \tag{4.109}$$

as

$$D_{\rm ren} = \xi(t)\xi(t_a)\int_{t_a}^{t_b}\frac{dt'}{\xi^2(t')}. \tag{4.110}$$

In general, it is difficult to find an analytic solution to Eq. (4.109). In the present fluctuation problem, however, the time-dependent frequency $\Omega(t)$ has a special form $\Omega^2(t) = V''(x_{\rm cl}(t))/M$ of (4.101). We shall now prove that, just as in the purely harmonic action in Section 2.5, all information on the fluctuation determinant is contained in the classical orbit $x_{\rm cl}(t)$, and ultimately in the mixed spatial derivatives $\partial_{x_b}\partial_{x_a}$ of the classical action $A(x_b, x_a; t_b - t_a)$. In fact, the solution $\xi(t)$ is simply equal to the velocity

$$\xi(t) = \dot{x}_{\rm cl}(t). \tag{4.111}$$

This is seen directly by differentiating the equation of motion (4.60) with respect to t, yielding

$$\partial_t[M\ddot{x}_{\rm cl} + V'(x_{\rm cl}(t))] = [M\partial_t^2 + V''(x_{\rm cl}(t))]\dot{x}_{\rm cl}(t) = 0, \tag{4.112}$$

which is precisely the homogenous differential equation (4.109) for $\dot{x}_{\rm cl}(t)$.

There is a simple symmetry argument to understand (4.111) as a completely general consequence of the time translation invariance of the system. The fluctuation $\delta x(t) \propto \dot{x}_{\rm cl}(t)$ describes an infinitesimal translation of the classical solution $x_{\rm cl}(t)$ in time, $x_{\rm cl}(t) \to x_{\rm cl}(t+\epsilon) = x_{\rm cl} + \epsilon\dot{x}_{\rm cl} + \ldots$. Interpreted as a *translational fluctuation* of the solution $x_{\rm cl}(t)$ along the time axis it cannot carry any energy λ_n and $y_0(t) \propto \dot{x}_{cl}(t)$ must therefore solve Eq. (4.105) with $\lambda_0 = 0$.

With the special solution (4.111), the functional determinant (4.110) becomes

$$D_{\rm ren} = \dot{x}_{\rm cl}(t_b)\dot{x}_{\rm cl}(t_a)\int_{t_a}^{t_b}\frac{dt}{\dot{x}_{\rm cl}^2(t)}. \tag{4.113}$$

Note that also the Green-function of the quadratic fluctuations associated with Eq. (4.109) can be given explicitly in terms of the classical solution $x_{\rm cl}(t)$. For Dirichlet boundary conditions, it is equal to the combination (3.61) of the solutions $D_a(t)$ and $D_b(t)$ of the homogeneous differential equation (4.109) satisfying the boundary conditions (2.228) and (2.229), whose d'Alembert construction (2.239) becomes here

$$D_a(t) = \dot{x}_{\rm cl}(t)\dot{x}_{\rm cl}(t_a)\int_{t_a}^{t}\frac{dt}{\dot{x}_{\rm cl}^2(t)}, \qquad D_b(t) = \dot{x}_{\rm cl}(t_b)\dot{x}_{\rm cl}(t)\int_{t}^{t_b}\frac{dt}{\dot{x}_{\rm cl}^2(t)}. \tag{4.114}$$

In Eqs. (2.252) and (2.269) we have found two simple expressions for the fluctuation determinant in terms of the classical action

$$D_{\rm ren} = -\left(\frac{\partial \dot{x}_b}{\partial x_a}\right)^{-1} = -M\left[\frac{\partial^2}{\partial x_b \partial x_a}\mathcal{A}_{\rm cl}\right]^{-1}. \tag{4.115}$$

These were derived for purely quadratic actions with an arbitrary time-dependent frequency $\Omega^2(t)$. But they hold for any action. First, the equality between the second and third expression is a consequence of the general relation (4.88). Second, we may consider the semiclassical approximation to the path integral as an *exact* path integral associated with the lowest quadratic approximation to the action in (4.99), (4.100):

$$\mathcal{A}_{\rm qu}[x,\dot{x}] = \mathcal{A}[x_{\rm cl}] + \int_{t_a}^{t_b} dt \left[\frac{M}{2}(\delta\dot{x})^2 + \Omega^2(t)(\delta x)^2\right], \tag{4.116}$$

with $\Omega^2(t) = V''(x_{\rm cl}(t))/M$ of (4.101). Then, since the classical orbit running from x_a to x_b satisfies the equation of motion (4.112), also a slightly different orbit $(x_{\rm cl} + \delta x_{\rm cl})(t)$ from $x'_a = x_a + \delta x_a$ to $x'_b = x_a + \delta x_b$ satisfies (4.112). Although the small change of the classical orbit gives rise to a slightly different frequency $\Omega^2(t) = V''((x_{\rm cl} + \delta x_{\rm cl})(t))/M$, this contributes only to second order in δx_a and δx_b. As a consequence, the derivative $D_a(t) = -\partial\dot{x}_b(t)/\partial x_a$ satisfies Eq. (4.112) as well. Also the boundary conditions of $D_a(t)$ are the same as those of $D_a(t)$ in Eqs. (2.228). Hence the quantity $D_a(t_b)$ is the correct fluctuation determinant also for the general action in the semiclassical approximation under study.

Another way to derive this formula makes use of the general relation (4.88), from which we find

$$\frac{\partial}{\partial x_b}\frac{\partial}{\partial x_a}A(x_b, x_a; t_b - t_a) = \frac{\partial}{\partial x_a}p(x_b) = \frac{M}{p(x_b)}\frac{\partial E}{\partial x_a}. \tag{4.117}$$

On the right-hand side we have suppressed the arguments of the function $E(x_b, x_a; t_b - t_a)$. After rewriting

$$\begin{aligned}\frac{\partial E}{\partial x_a} &= -\frac{\partial}{\partial x_a}\frac{\partial A}{\partial t_b} = -\frac{\partial}{\partial t_b}\frac{\partial A}{\partial x_a} \\ &= \frac{\partial}{\partial t_b}p(x_a) = \frac{M}{p(x_a)}\frac{\partial E}{\partial t_b},\end{aligned} \tag{4.118}$$

we see that

$$\frac{\partial}{\partial x_b}\frac{\partial}{\partial x_a}A(x_b, x_a; t_b - t_a) = \frac{1}{\dot{x}(t_b)\dot{x}(t_a)}\frac{\partial E}{\partial t_b}. \tag{4.119}$$

From (4.64) we calculate

$$\begin{aligned}\frac{\partial E}{\partial t_b} &= \left(\frac{\partial t_b}{\partial E}\right)^{-1} = \left[-\int_{x_a}^{x_b} dx \frac{M}{p^2}\frac{\partial p}{\partial E}\right]^{-1} \\ &= \left[-\int_{x_a}^{x_b} dx \frac{M^2}{p^3}\right]^{-1} = \left[-M\int_{t_a}^{t_b}\frac{dt}{p^2}\right]^{-1} = \left[-\frac{1}{M}\int_{t_a}^{t_b}\frac{dt}{\dot{x}_{\rm cl}^2(t)}\right]^{-1}.\end{aligned} \tag{4.120}$$

Inserting this into (4.119), we obtain once more formula (4.115) for the fluctuation determinant.

A relation following from (4.92):

$$\frac{\partial E}{\partial t_b} = \left(\frac{\partial^2 S}{\partial E^2}\right)^{-1}, \tag{4.121}$$

leads to an alternative expression

$$D_{\rm ren} = -M\dot{x}_{\rm cl}(t_b)\dot{x}_{\rm cl}(t_a)\frac{\partial^2 S}{\partial E^2}. \tag{4.122}$$

The fluctuation factor is therefore also here [recall the normalization from Eqs. (2.202), (2.204), and (2.212)]

$$F(x_b,t_a;t_b-t_a) = \frac{1}{\sqrt{2\pi i\hbar/M}}\left[\frac{\partial \dot{x}_b}{\partial x_a}\right]^{1/2} = \frac{1}{\sqrt{2\pi i\hbar}}[-\partial_{x_b}\partial_{x_a}A(x_b,x_a;t_b-t_a)]^{1/2}. \tag{4.123}$$

Its D-dimensional generalization of (4.123) is

$$F(\mathbf{x}_b,\mathbf{x}_a;t_b-t_a) = \frac{1}{\sqrt{2\pi i\hbar}^D}\left\{\det{}_D[-\partial_{x_b^i}\partial_{x_a^j}A(\mathbf{x}_b,\mathbf{x}_a;t_b-t_a)]\right\}^{1/2}, \tag{4.124}$$

and the semiclassical time evolution amplitude reads

$$(\mathbf{x}_b t_b|\mathbf{x}_a t_a) = \frac{1}{\sqrt{2\pi i\hbar}^D}\left\{\det{}_D[-\partial_{x_b^i}\partial_{x_a^j}A(\mathbf{x}_b,\mathbf{x}_a;t_b-t_a)]\right\}^{1/2} e^{iA(\mathbf{x}_b,\mathbf{x}_a;t_b-t_a)/\hbar}. \tag{4.125}$$

The $D\times D$ -determinant in the curly brackets is the so-called *Van Vleck-Pauli-Morette determinant*.[6] It is the analog of the determinant in the right-hand part of Eq. (2.270). As discussed there, the result is initially valid only as long as the fluctuation determinant is regular. Otherwise we must replace the determinant by its absolute value, and multiply the fluctuation factor by the phase factor $e^{-i\nu/2}$ with the Maslov-Morse index ν [see Eq. (2.271)]. Using the relation (4.88) in D dimensions

$$\partial_{x_b^i}\partial_{x_a^j}A(\mathbf{x}_b,\mathbf{x}_a;t_b-t_a) = \frac{\partial p_b^i}{\partial x_a^j}, \tag{4.126}$$

we shall often write (4.125) as

$$(\mathbf{x}_b t_b|\mathbf{x}_a t_a) = \frac{1}{\sqrt{2\pi i\hbar}^D}\left[\det{}_D\left(-\frac{\partial \mathbf{p}_b}{\partial \mathbf{x}_a}\right)\right]^{1/2} e^{iA(\mathbf{x}_b,\mathbf{x}_a;t_b-t_a)/\hbar}, \tag{4.127}$$

where the subscripts a and b can be interchanged in the determinant, if the sign is changed [recall (2.252)]. This concludes the calculation of the semiclassical approximation to the time evolution amplitude.

[6] J.H. Van Vleck, Proc. Nat. Acad. Sci. (USA) *14*, 178 (1928); W. Pauli, *Selected Topics in Field Quantization*, MIT Press, Cambridge, Mass. (1973); C. DeWitt-Morette, Phys. Rev. *81*, 848 (1951).

As a simple application, we use this formula to write down the semiclassical amplitude for a free particle and a harmonic oscillator. The first has the classical action

$$A(x_b, x_a; t_b - t_a) = \frac{M}{2} \frac{(x_b - x_a)^2}{t_b - t_a}, \tag{4.128}$$

and Eq. (4.115) gives

$$D_{\rm ren} = t_b - t_a, \tag{4.129}$$

as it should. The harmonic-oscillator action is

$$A(x_b, x_a; t_b - t_a) = \frac{M\omega}{2\sin\omega(t_b - t_a)} \left[(x_b^2 + x_a^2)\cos\omega(t_b - t_a) - 2x_b x_a\right], \tag{4.130}$$

and has the second derivative

$$-\partial_{x_b}\partial_{x_a} A = \frac{M\omega}{\sin\omega(t_b - t_a)}, \tag{4.131}$$

so that (4.123) coincides with fluctuation factor (2.216).

4.4 Fundamental Composition Law for Semiclassical Time Evolution Amplitude

The determinant ensures that the semiclassical approximation for the time evolution amplitude satisfies the fundamental composition law (2.4) in D dimensions

$$(\mathbf{x}_b t_b|\mathbf{x}_a t_a) = \prod_{n=1}^{N} \left[\int_{-\infty}^{\infty} d^D x_n\right] \prod_{n=1}^{N+1} (\mathbf{x}_n t_n|\mathbf{x}_{n-1} t_{n-1}), \tag{4.132}$$

if the intermediate $\mathbf{x}$-integrals are evaluated in the saddle point approximation. To leading order in $\hbar$, only those intermediate $\mathbf{x}$-values contribute which lie on the classical trajectory determined by the endpoints of the combined amplitude. To next order in $\hbar$, the quadratic correction to the intermediate integrals renders an inverse square root of the fluctuation determinant. If two such amplitudes are connected with each other by an intermediate integration according to the composition law (4.132), the product of the two fluctuation factors turns into the correct fluctuation factor of the combined time interval. This is seen after rewriting the matrix $\partial_{x_b^i}\partial_{x_a^j} A(\mathbf{x}_b, \mathbf{x}_a; t_b - t_a)$ with the help of (4.12) as $\partial \mathbf{p}_b/\partial \mathbf{x}_a$. The intermediate integral over $\mathbf{x}$ in the product of two amplitudes receives a contribution only from continuous paths since, at the saddle point, the adjacent momenta have to be equal:

$$\frac{\partial}{\partial \mathbf{x}} A(\mathbf{x}_b, \mathbf{x}; t_b - t) + \frac{\partial}{\partial \mathbf{x}} A(\mathbf{x}, \mathbf{x}_a; t - t_a) = -\mathbf{p}'(\mathbf{x}_b, \mathbf{x}; t_b - t) + \mathbf{p}(\mathbf{x}, \mathbf{x}_a; t - t_a) = 0. \tag{4.133}$$

To obtain the combined amplitude, we obviously need the relation

$$\det{}_D\left(-\left.\frac{\partial\mathbf{p}_b}{\partial\mathbf{x}}\right|_{\mathbf{x}_b}\right)\left\{\det{}_D\left(-\left.\frac{\partial\mathbf{p}'}{\partial\mathbf{x}}\right|_{\mathbf{x}_b}+\left.\frac{\partial\mathbf{p}}{\partial\mathbf{x}}\right|_{\mathbf{x}_a}\right)_{\mathbf{p}'=\mathbf{p}}\right\}^{-1}\det{}_D\left(-\left.\frac{\partial\mathbf{p}}{\partial\mathbf{x}_a}\right|_{\mathbf{x}}\right)$$
$$=\det{}_D\left(-\left.\frac{\partial\mathbf{p}_b}{\partial\mathbf{x}_a}\right|_{\mathbf{x}_b}\right), \tag{4.134}$$

where we have indicated explicitly the variables kept fixed in $\mathbf{p}'(\mathbf{x}_b,\mathbf{x};t_b-t)$ and $\mathbf{p}(\mathbf{x},\mathbf{x}_a;t-t_a)$ when forming the partial derivatives. To prove (4.134), we use the product rule for determinants

$$\det{}_D^{-1}\left(-\left.\frac{\partial\mathbf{p}_b}{\partial\mathbf{x}}\right|_{\mathbf{x}_b}\right)\det{}_D\left(-\left.\frac{\partial\mathbf{p}_b}{\partial\mathbf{x}_a}\right|_{\mathbf{x}_b}\right)=\det{}_D\left(\left.\frac{\partial\mathbf{x}}{\partial\mathbf{x}_a}\right|_{\mathbf{x}_b}\right) \tag{4.135}$$

to rewrite (4.134) as

$$\det{}_D\left(-\left.\frac{\partial\mathbf{p}}{\partial\mathbf{x}_a}\right|_{\mathbf{x}}\right)=\det{}_D\left(-\left.\frac{\partial\mathbf{p}'}{\partial\mathbf{x}}\right|_{\mathbf{x}_b}+\left.\frac{\partial\mathbf{p}}{\partial\mathbf{x}}\right|_{\mathbf{x}_a}\right)_{\mathbf{p}'=\mathbf{p}}\det{}_D\left(\left.\frac{\partial\mathbf{x}}{\partial\mathbf{x}_a}\right|_{\mathbf{x}_b}\right). \tag{4.136}$$

This equation is true due to the chain rule of differentiation applied to the momentum $\mathbf{p}'(\mathbf{x}_b,\mathbf{x};t_b-t)=\mathbf{p}(\mathbf{x},\mathbf{x}_a;t-t_a)$, after expressing $\mathbf{p}(\mathbf{x},\mathbf{x}_a;t-t_a)$ explicitly in terms of the variables $\mathbf{x}_b$ and $\mathbf{x}_a$ as $\mathbf{p}(\mathbf{x}(\mathbf{x}_b,\mathbf{x}_a;t_b-t_a),\mathbf{x}_a;t-t_a)$, to enable us to hold $\mathbf{x}_b$ fixed in the second partial derivative:

$$\left.\frac{\partial\mathbf{p}'}{\partial\mathbf{x}}\right|_{\mathbf{x}_b}=\left.\frac{\partial\mathbf{p}}{\partial\mathbf{x}}\right|_{\mathbf{x}_b}=\left.\frac{\partial\mathbf{p}(\mathbf{x}(\mathbf{x}_b,\mathbf{x}_a;t_b-t_a),\mathbf{x}_a;t-t_a)}{\partial\mathbf{x}}\right|_{\mathbf{x}_b}=\left.\frac{\partial\mathbf{p}}{\partial\mathbf{x}}\right|_{\mathbf{x}}\left.\frac{\partial\mathbf{x}_a}{\partial\mathbf{x}}\right|_{\mathbf{x}_b}+\left.\frac{\partial\mathbf{p}}{\partial\mathbf{x}}\right|_{\mathbf{x}_a}. \tag{4.137}$$

It may be expected, and can indeed be proved, that it is possible to proceed in the opposite direction and derive the semiclassical expressions (4.125) and (4.127) with the Van Vleck-Pauli-Morette determinant from the fundamental composition law (4.132).[7]

In the semiclassical approximation, the composition law (4.132) can also be written as a temporal integral (in D dimensions)

$$(\mathbf{x}_bt_b|\mathbf{x}_at_a)=\int dt(\mathbf{x}_bt_b|\mathbf{x}_{\rm cl}(t)t)\,\dot{\mathbf{x}}_{\rm cl}(t)\,(\mathbf{x}_{\rm cl}(t)t|\mathbf{x}_at_a) \tag{4.138}$$

over a classical orbit $\mathbf{x}_{\rm cl}(t)$, where the t-integration is done in the saddle point approximation, assuming that the fluctuation determinant does not happen to be degenerate.

Just as in the saddle point expansion of ordinary integrals, it is possible to calculate higher corrections in $\hbar$. The result is a saddle point expansion of the path

[7]H. Kleinert and B. Van den Bossche, Berlin preprint 2000 (`http://www.physik.fu-berlin.de/~kleinert/301`).

integral which is again a semiclassical expansion. The counting of the $\hbar$-powers is the same as for the integral. The lowest approximation is of the exponential form $e^{i\mathcal{A}_{\rm cl}/\hbar}$. Thus, in the exponent, the leading term is of order $1/\hbar$.[8] The fluctuation factor F contributes to this an additive term $\log F$, which is of order $\hbar^0$. To first order in $\hbar$, one finds expressions containing the third and fourth functional derivative of the action in the expansion (4.99), corresponding to the expressions (4.49) and (4.50) in the integral. Unfortunately, the functional case offers little opportunity for further analytic corrections, so we shall not dwell on this more academic possibility.

4.5 Semiclassical Fixed-Energy Amplitude

As pointed out at the end of Subsection 4.2.1, we have observed that the semiclassical approximation allows for a simple evaluation of Fourier integrals. As an application of the rules presented there, let us evaluate the Fourier transform of the time evolution amplitude, the fixed-energy amplitude introduced in (1.311). It is given by the temporal integral

$$(x_b|x_a)_E = \frac{1}{\sqrt{2\pi i\hbar}} \int_{t_a}^{\infty} dt_b [-\partial_{x_b}\partial_{x_a} A(x_b,x_a;t_b-t_a)]^{1/2} \times e^{i[A(x_b,x_a;t_b-t_a)+(t_b-t_a)E]/\hbar}, \tag{4.139}$$

which may be evaluated in the same saddle point approximation as the path integral. The extremum lies at

$$\frac{\partial}{\partial t} A(x_b,x_a;t_b-t_a) = -E. \tag{4.140}$$

Because of (4.93), the left-hand side is the function $-E(x_b,x_a;t_b-t_a)$. At the extremum, the time interval t_b-t_a is some function of the endpoints and the energy E:

$$t_b - t_a = t(x_b,x_a;E). \tag{4.141}$$

The exponent is equal to the eikonal function $S(x_b,x_a;E)$ of Eq. (4.87), whose derivative with respect to the energy gives [recalling (4.92)]

$$\frac{\partial}{\partial E} S(x_b,x_a;E) = t(x_b,x_a;E). \tag{4.142}$$

The expansion of the exponent around the extremum has the quadratic term

$$\frac{i}{\hbar}\frac{\partial^2 A(x_b,x_a;t_b-t_a)}{\partial t_b^2}[t_b-t_a-t(x_b,x_a;E)]^2. \tag{4.143}$$

The time integral over t_b yields a factor

$$\sqrt{2\pi i\hbar}\left[\frac{\partial^2 A(x_b,x_a;t_b-t_a)}{\partial t_b^2}\right]^{-1/2}. \tag{4.144}$$

[8] Since $\hbar$ has the dimension of an action, the dimensionless number $\hbar/\mathcal{A}_{\rm cl}$ should really be used as an appropriate dimensionless expansion parameter, but it has become customary to count directly the orders in $\hbar$.

With this, the fixed-energy amplitude has precisely the form (4.55):

$$(x_b|x_a)_E = \left[-\partial_{x_b}\partial_{x_a}A(x_b,x_a;t)/\partial_t^2 A(x_b,x_a;t)\right]^{1/2} e^{iS(x_b,x_a;E)/\hbar}. \tag{4.145}$$

Since the fluctuation factor has to be evaluated at a fixed energy E, it is advantageous to express it in terms of $S(x_b,x_a;E)$. For $\partial_t^2 A$, the evaluation is simple since

$$\frac{\partial^2 A}{\partial t^2} = -\frac{\partial E}{\partial t} = -\left(\frac{\partial t}{\partial E}\right)^{-1} = -\left(\frac{\partial^2 S}{\partial E^2}\right)^{-1}. \tag{4.146}$$

For $\partial_{x_b}\partial_{x_a}A$, we observe that the spatial derivatives of the action must be performed at a fixed time, so that a variation of x_b implies also a change of the energy $E(x_b,x_a;t)$. This is found from the condition

$$\frac{\partial t}{\partial x_b} = 0, \tag{4.147}$$

which after inserting (4.142), goes over into

$$\left.\frac{\partial^2 S}{\partial E\partial x_b}\right|_t = \frac{\partial^2 S}{\partial E\partial x_b} + \frac{\partial^2 S}{\partial E^2}\frac{\partial E}{\partial x_b} = 0. \tag{4.148}$$

We now use the relation

$$\left.\frac{\partial A}{\partial x_b}\right|_t = \left.\frac{\partial S}{\partial x_b}\right|_t - \left.\frac{\partial E}{\partial x_b}\right|_t t = \frac{\partial S}{\partial x_b} + \frac{\partial S}{\partial E}\left.\frac{\partial E}{\partial x_b}\right|_t - \left.\frac{\partial E}{\partial x_b}\right|_t t = \left.\frac{\partial S}{\partial x_b}\right|_E \tag{4.149}$$

and find from it

$$\begin{aligned}\left.\frac{\partial^2 A}{\partial x_b\partial x_a}\right|_t &= \frac{\partial^2 S}{\partial x_b\partial x_a} + \frac{\partial^2 S}{\partial x_b\partial E}\frac{\partial E}{\partial x_a} \\ &= \frac{\partial^2 S}{\partial x_b\partial x_a} - \frac{\partial^2 S}{\partial x_a\partial E}\,\frac{\partial^2 S}{\partial x_b\partial E}\Big/\frac{\partial^2 S}{\partial E^2}.\end{aligned} \tag{4.150}$$

Thus the fixed-energy amplitude (4.139) takes the simple form

$$(x_b|x_a)_E = D_S^{1/2} e^{iS(x_b,x_a;E)/\hbar}, \tag{4.151}$$

with the 2×2-determinant

$$D_S = \begin{vmatrix} \dfrac{\partial^2 S}{\partial x_b\partial x_a} & \dfrac{\partial^2 S}{\partial E\partial x_a} \\ \dfrac{\partial^2 S}{\partial x_b\partial E} & \dfrac{\partial^2 S}{\partial E^2}\end{vmatrix}. \tag{4.152}$$

The determinant can be simplified by the fact that a differentiation of the Hamilton-Jacobi equation

$$H\left(\frac{\partial S}{\partial x_b}, x_b\right) = E \tag{4.153}$$

with respect to x_a leads to the equation

$$\frac{\partial H}{\partial p_b}\frac{\partial^2 S}{\partial x_b \partial x_a} = \dot{x}_b \frac{\partial^2 S}{\partial x_b \partial x_a} = 0. \tag{4.154}$$

It implies the vanishing of the upper left element in (4.152), reducing D_S to

$$D_S = -\frac{\partial^2 S}{\partial x_b \partial E}\frac{\partial^2 S}{\partial x_a \partial E}. \tag{4.155}$$

Since $\partial S/\partial x_{b,a} = \pm p_{b,a}$ and $\partial p/\partial E = 1/\dot{x}$, one arrives at

$$D_S = \frac{1}{\dot{x}_b \dot{x}_a}. \tag{4.156}$$

Let us calculate the semiclassical fixed-energy amplitude for a free particle. The classical action function is

$$A(x_b, x_a; t_b - t_a) = \frac{M}{2}\frac{(x_b - x_a)^2}{t_b - t_a}, \tag{4.157}$$

so that the function $E(x_b, x_a; t_b - t_a)$ is given by

$$E(x_b, x_a; t_b - t_a) = -\frac{\partial}{\partial t_b}\frac{M}{2}\frac{(x_b - x_a)^2}{t_b - t_a} = \frac{M}{2}\frac{(x_b - x_a)^2}{(t_b - t_a)^2}. \tag{4.158}$$

By a Legendre transformation, or directly from the defining equation (4.68), we calculate

$$S(x_b, x_a; E) = \sqrt{2ME}|x_b - x_a|. \tag{4.159}$$

From this we calculate the determinant (4.156) as

$$D_s = \frac{M}{2E}, \tag{4.160}$$

and the fixed-energy amplitude (4.151) becomes

$$(x_b|x_a)_E = \sqrt{\frac{M}{2E}} e^{i\sqrt{2ME}|x_b - x_a|/\hbar}. \tag{4.161}$$

4.6 Semiclassical Amplitude in Momentum Space

The simple way of finding Fourier transforms in the semiclassical approximation can be used to derive easily amplitudes in momentum space. Consider first the time evolution amplitude $(x_b t_b|x_a t_a)_{\rm sc}$. The momentum space version is given by the two-dimensional Fourier integral [recall (2.37) and insert (4.103)]

$$(p_b t_b|p_a t_a)_{\rm sc} = \int dx_b\, dx_a\, e^{-i(p_b x_b - p_a x_a)/\hbar} e^{iA(x_b, x_a; t_b - t_a)/\hbar} F(x_b, x_a; t_b - t_a). \tag{4.162}$$

The semiclassical evaluation according to the general rule (4.55) yields

$$(p_b t_b|p_a t_a)_{\rm sc} = \frac{\sqrt{2\pi i\hbar}}{\sqrt{\det H}}[-\partial_{x_b}\partial_{x_a}A(x_b,x_a;t_b-t_a)]^{1/2}e^{i[A(x_b,x_a;t_b-t_a)-p_bx_b+p_ax_a]/\hbar}, \tag{4.163}$$

where H is the matrix

$$H = \begin{pmatrix} \partial^2_{x_b}A(x_b,x_a;t_b-t_a) & \partial_{x_b}\partial_{x_a}A(x_b,x_a;t_b-t_a) \\ \partial_{x_a}\partial_{x_b}A(x_b,x_a;t_b-t_a) & \partial^2_{x_a}A(x_b,x_a;t_b-t_a) \end{pmatrix}. \tag{4.164}$$

The exponent must be evaluated at the extremum with respect to x_b and x_a, which lies at

$$p_b = \partial_{x_b}A(x_b,x_a;t_b-t_a), \qquad p_a = -\partial_{x_b}A(x_b,x_a;t_b-t_a). \tag{4.165}$$

The exponent contains then the Legendre transform of the action $A(x_b,x_a;t_b-t_a)$ which depends naturally on p_b and p_a:

$$A(p_b,p_a;t_b-t_a) = A(x_b,x_a;t_b-t_a) - p_bx_b + p_ax_a. \tag{4.166}$$

The inverse Legendre transformation to (4.165) is

$$x_b = -\partial_{p_b}A(x_b,x_a;t_b-t_a), \qquad x_a = \partial_{x_b}A(x_b,x_a;t_b-t_a). \tag{4.167}$$

The important observation which greatly simplifies the result is that for a 2×2 matrix H_{ab} with $(a,b=1,2)$, the matrix element $-H_{12}/\det H$ is equal to H_{12}. By writing the matrix H and its inverse as

$$H = \begin{pmatrix} \dfrac{\partial p_b}{\partial x_b} & \dfrac{\partial p_b}{\partial x_a} \\ -\dfrac{\partial p_a}{\partial x_b} & -\dfrac{\partial p_a}{\partial x_a} \end{pmatrix}, \qquad H^{-1} = \begin{pmatrix} \dfrac{\partial x_b}{\partial p_b} & -\dfrac{\partial x_b}{\partial p_a} \\ \dfrac{\partial x_a}{\partial p_b} & -\dfrac{\partial x_a}{\partial p_a} \end{pmatrix}, \tag{4.168}$$

we see that, just as in the Eqs. (2.278) and (2.279):

$$H^{-1}_{12} = \frac{\partial x_a}{\partial p_b} = \frac{\partial^2 A(p_b,p_a;t_b-t_a)}{\partial p_b\partial p_a}. \tag{4.169}$$

As a result, the semiclassical time evolution amplitude in momentum space (4.163) takes the simple form

$$(p_b t_b|p_a t_a)_{\rm sc} = \frac{2\pi\hbar}{\sqrt{2\pi i\hbar}}[-\partial_{p_b}\partial_{p_a}A(p_b,p_a;t_b-t_a)]^{1/2}e^{iA(p_b,p_a;t_b-t_a)/\hbar}. \tag{4.170}$$

In D dimensions, this becomes

$$(\mathbf{p}_b t_b|\mathbf{p}_a t_a) = \frac{1}{\sqrt{2\pi i\hbar}^D}\left\{\det{}_D[-\partial_{p^i_b}\partial_{p^j_a}A(\mathbf{p}_b,\mathbf{p}_a;t_b-t_a)]\right\}^{1/2} e^{iA(\mathbf{p}_b,\mathbf{p}_a;t_b-t_a)/\hbar}, \tag{4.171}$$

or

$$(\mathbf{p}_b t_b|\mathbf{p}_p t_a) = \frac{1}{\sqrt{2\pi i\hbar}^D} \left\{ \det{}_D \left[-\frac{\partial \mathbf{p}_b}{\partial \mathbf{x}_a} \right] \right\}^{1/2} e^{iA(\mathbf{p}_b,\mathbf{p}_a;t_b-t_a)/\hbar}, \tag{4.172}$$

these results being completely analogous to the x-space expression (4.125) and (4.127), respectively. As before, the subscripts a and b can be interchanged in the determinant.

If we apply these formulas to the harmonic oscillator with a time-dependent frequency, we obtain precisely the amplitude (2.285). Thus in this case, the semiclassical time evolution amplitude $(p_b t_b|p_a t_a)_{\rm sc}$ happens to coincide with the exact one.

For a free particle with the action $A(x_b, x_a; t_b - t_a) = M(x_b - x_a)^2/2(t_b - t_a)$, the formula (4.163) cannot be applied since determinant of H vanishes, so that the saddle point approximation is inapplicable. The formal infinity one obtains when trying to apply Eq. (4.163) is a reflection of the δ-function in the exact expression (2.73), which has no semiclassical approximation. The Legendre transform of the action can, however, be calculated correctly and yields with the derivatives $p_b = \partial_{x_b} A(x_b, x_a; t_b - t_a) = p_a = -\partial_{x_a} A(x_b, x_a; t_b - t_a) = M(x_b - x_a)/(t_b - t_a) = p$ [recall (4.88)] the expression

$$A(p_b, p_a; t_b - t_a) = -\frac{p^2}{2}(t_b - t_a), \tag{4.173}$$

which agrees with the exponent of (2.73).

4.7 Semiclassical Quantum-Mechanical Partition Function

From the result (4.103) we can easily derive the quantum-mechanical partition function (1.540) in semiclassical approximation:

$$Z^{\rm sc}_{\rm QM}(t_b - t_a) = \int dx_a (x_a t_b|x_a t_a)_{\rm sc} = \int dx_a F(x_a, x_a; t_b - t_a) e^{iA(x_a,x_a;t_b-t_a)/\hbar}. \tag{4.174}$$

Within the semiclassical approximation the path integral, as the final trace integral may be performed using the saddle point approximation. At the saddle point one has [as in (4.133)]

$$\begin{aligned} \frac{\partial}{\partial x_a} A(x_a, x_a; t_b - t_a) &= \frac{\partial}{\partial x_b} A(x_b, x_a; t_b - t_a)\bigg|_{x_b = x_a} + \frac{\partial}{\partial x_a} A(x_b, x_a; t_b - t_a)\bigg|_{x_b = x_a} \\ &= p_b - p_a = 0, \end{aligned} \tag{4.175}$$

i.e., only classical orbits contribute whose momenta are equal at the coinciding endpoints. This restricts the orbits to periodic solutions of the equations of motion. The semiclassical limit selects, among all paths with $x_a = x_b$, the paths solving the equation of motion, ensuring the continuity of the internal momenta along these paths. The integration in (4.174) enforces the equality of the initial and final momenta on these paths and permits a continuation of the equations of motion beyond the final time t_b in a periodic fashion, leading to periodic orbits. Along each of these orbits, the energy $E(x_a, x_a, t_b - t_a)$ and the action $A(x_a, x_a, t_b - t_a)$ do not depend on the choice of x_a. The phase factor $e^{iA/\hbar}$ in the integral (4.174) is therefore a constant. The integral must be performed over a full period between the turning points of each orbit in the forward and backward direction. It contains a nontrivial x_a-dependence only in the fluctuation factor. Thus, (4.174) can be written as

$$Z_{\rm QM}^{\rm sc}(t_b - t_a) = \left[\int dx_a F(x_a, x_a; t_b - t_a)\right] e^{iA(x_a,x_a;t_b-t_a)/\hbar}. \tag{4.176}$$

For the integration over the fluctuation factor we use the expression (4.123) and the equation

$$\frac{\partial}{\partial x_b}\frac{\partial}{\partial x_a}A(x_b, x_a; t_b - t_a) = -\frac{1}{\dot{x}_b\dot{x}_a}\frac{\partial^2 A}{\partial t_b^2}, \tag{4.177}$$

following from (4.119) and (4.93), and have

$$F(x_b, x_a; t_b - t_a) = \frac{1}{\sqrt{2\pi i\hbar}}\left[\frac{1}{\dot{x}(t_b)\dot{x}(t_a)}\frac{\partial^2 A}{\partial t_b^2}\right]^{1/2}. \tag{4.178}$$

Inserting $x_a = x_b$ leads to

$$F(x_a, x_a; t_b - t_a) = \frac{1}{\sqrt{2\pi i\hbar}}\frac{1}{\dot{x}_a}\left[\frac{\partial^2 A}{\partial t_b^2}\right]^{1/2}. \tag{4.179}$$

The action of a periodic path does not depend on x_a,so that the x_b-integration in (4.174) requires only integrating $1/\dot{x}_a$ forward and back, which produces the total period:

$$t_b - t_a = 2\int_{x_-}^{x_+} dx_a \frac{1}{\dot{x}_a} = 2\int_{x_-}^{x_+} dx \frac{M}{\sqrt{2M[E - V(x)]}}. \tag{4.180}$$

Hence we obtain from (4.174):

$$Z_{\rm QM}^{\rm sc}(t_b - t_a) = \frac{t_b - t_a}{\sqrt{2\pi i\hbar}}\left|\frac{\partial^2 A}{\partial t_b^2}\right|^{1/2} e^{iA(t_b-t_a)/\hbar - i\pi}. \tag{4.181}$$

There is a phase factor $e^{-i\pi}$ associated with a Maslov-Morse index $\nu = 2$, first introduced in the fluctuation factor (2.271). In the present context, this phase factor arises from the fact that when doing the integral (4.176), the periodic orbit passes through the turning points x_- and x_+ where the integrand of (4.180) becomes singular, even though the integral remains finite. Near the turning points, the semiclassical approximation breaks down, as discussed in Section 4.1 in the context of the

WKB approximation to the Schrödinger equation. This breakdown required special attention in the derivation of the connection formulas relating the wave functions on one side of the turning points to those on the other side. There, the breakdown was circumvented by escaping into the complex x-plane. When going around the singularity in the clockwise sense, the prefactor $1/p(x) = 1/\sqrt{2M(E-V(x))}^{1/2}$ acquired a phase factor $e^{-i\pi/2}$. For a periodic orbit, both turning points had to be encircled producing twice this phase factor, which is precisely the phase $e^{-i\pi}$ given in (4.181).

The result (4.181) takes an especially simple form after a Fourier transform action:

$$\begin{aligned}\tilde{Z}^{\rm sc}_{\rm QM}(E) &= \int_{t_a}^{\infty} dt_b e^{iE(t_b-t_a)/\hbar} Z^{\rm sc}_{\rm QM}(t_b-t_a) \\ &= \frac{1}{\sqrt{2\pi i\hbar}} \int_{t_a}^{\infty} dt_b (t_b-t_a) \left|\frac{\partial^2 A}{\partial t_b^2}\right|^{1/2} e^{i[A(t_b-t_a)+(t_b-t_a)E]/\hbar - i\pi}. \end{aligned} \tag{4.182}$$

In the semiclassical approximation, the main contribution to the integral at a given energy E comes from the time where $t_b - t_a$ is equal to the period of the particle orbit with this energy. It is determined as in (4.139) by the extremum of

$$A(t_b-t_a) + (t_b-t_a)E. \tag{4.183}$$

Thus it satisfies

$$-\frac{\partial}{\partial t_b} A(t_b-t_a) = E. \tag{4.184}$$

As in (4.140), the extremum determines the period $t_b - t_a$ of the orbit with an energy E. It will be denoted by $t(E)$. The second derivative of the exponent is $(i/\hbar)\partial^2 A(t_b-t_a)/\partial t_b^2$. For this reason, the quadratic correction in the saddle point approximation to the integral over t_b cancels the corresponding prefactor in (4.182) and leads to the simple expression

$$\tilde{Z}^{\rm sc}_{\rm QM}(E) = t(E) e^{i[A(t)+t(E)E]/\hbar - i\pi}. \tag{4.185}$$

The exponent contains again the eikonal $S(E) = A(t) + t(E)E$, the Legendre transform of the action $A(t)$ defined by

$$S(E) = A(t) - t\frac{\partial A(t)}{\partial t}, \tag{4.186}$$

where the variable t has to be replaced by $E(t) = -\partial A(t)/\partial t$. Via the inverse Legendre transformation, the derivative $\partial S(E)/\partial E = t$ leads back to

$$A(t) = S(E) - \frac{\partial S(E)}{\partial E} E. \tag{4.187}$$

Explicitly, $S(E)$ is given by the integral (4.68):

$$S(E) = 2\int_{x_-}^{x_+} dx\, p(x) = 2\int_{x_-}^{x_+} dx\, \sqrt{2M[E-V(x)]}. \tag{4.188}$$

Finally, we have to take into account that the periodic orbit is repeatedly traversed for an arbitrary number of times. Each period yields a phase factor $e^{iS(E)/\hbar-i\pi}$. The sum is

$$\tilde{Z}_{\rm QM}^{\rm sc}(E) \;=\; \sum_{n=1}^{\infty} t(E)e^{in[S(E)/\hbar-\pi]} = -t(E)\frac{e^{iS(E)/\hbar}}{1+e^{iS(E)/\hbar}}. \qquad (4.189)$$

This expression possesses poles in the complex energy plane at points where the eikonal satisfies the condition

$$S(E_n) = 2\pi\hbar(n+1/2), \qquad n = 0, \pm 1, \pm 2, \dots\ . \qquad (4.190)$$

This condition agrees precisely with the Bohr-Sommerfeld rule (4.27) for semiclassical quantization. At the poles, one has

$$\tilde{Z}_{\rm QM}^{\rm sc}(E) \approx t(E)\frac{i\hbar}{S'(E_n)(E-E_n)}. \qquad (4.191)$$

Due to (4.92), the pole terms acquire the simple form

$$\tilde{Z}_{\rm QM}^{\rm sc}(E) \approx \frac{i\hbar}{E-E_n}. \qquad (4.192)$$

From (4.189) we derive the density of states defined in (1.583). For this we use the general formula

$$\rho(E) = \frac{1}{2\pi\hbar}{\rm disc}\,\tilde{Z}_{\rm QM}(E), \qquad (4.193)$$

where disc $Z_{\rm QM}(E)$ is the discontinuity $Z_{\rm QM}(E+i\eta) - Z_{\rm QM}(E-i\eta)$ across the singularities defined in Eq. (1.328). If we equip the energies E_n in (4.192) with the usual small imaginary part $-i\eta$, we can also write (4.193) as

$$\rho(E) = \frac{1}{\pi\hbar}{\rm Re}\tilde{Z}_{\rm QM}(E). \qquad (4.194)$$

Inserting here the Fourier representation (4.189), we obtain the semiclassical approximation

$$\bar{\rho}_{\rm sc}(E) = \frac{t(E)}{\pi\hbar}\sum_{n=1}^{\infty}\cos\{n[S(E)/\hbar-\pi]\} \qquad (4.195)$$

or

$$\Delta\rho_{\rm sc}(E) = \frac{t(E)}{2\pi\hbar}\left(-1+\sum_{n=-\infty}^{\infty} e^{in[S(E)/\hbar-\pi]}\right). \qquad (4.196)$$

We have added a Δ-symbol to this quantity since it is really the semiclasscial correction to the classical density of states $\rho(E)$, as we sall see in a moment. With the help of Poisson's summation formula (1.197), this goes over into

$$\Delta\rho_{\rm sc}(E) = -\frac{t(E)}{2\pi\hbar} + \frac{t(E)}{\hbar}\sum_{n=-\infty}^{\infty}\delta[S(E)/\hbar - 2\pi(n+1/2)]. \qquad (4.197)$$

The right-hand side contains δ-functions which are singular at the semiclassical energy values (4.190). Using once more the relation (4.92), the formula $\delta(ax) = a^{-1}\delta(x)$ leads to the simple expression

$$\Delta\rho_{\rm sc}(E) = -\frac{t(E)}{2\pi\hbar} + \sum_{n=-\infty}^{\infty} \delta(E - E_n). \tag{4.198}$$

This result has a surprising property: Consider the spacing between the energy levels

$$\Delta E_n = E_n - E_{n-1} = 2\pi\hbar\,\frac{\Delta E_n}{\Delta S_n} \tag{4.199}$$

and average the sum in (4.198) over a small energy interval ΔE containing several energy levels. Then we obtain an average density of states:

$$\rho_{\rm av}(E) = \frac{S'(E)}{2\pi\hbar} = \frac{t(E)}{2\pi\hbar}. \tag{4.200}$$

It cancels precisely the first term in (4.198). Thus, the semiclassical formula (4.189) possesses a vanishing average density of states. This cannot be correct and we conclude that in the derivation of the formula, a contribution must have been overlooked. This contribution comes from the classical partition function. Within the above analysis of periodic orbits, there are also those which return to the point of departure after an infinitesimally small time (which leaves them with no time to fluctuate). The expansion (4.189) does not contain them, since the saddle point approximation to the time integration (4.182) used for its derivation fails at short times. The reason for this failure is the singular behavior of the fluctuation factor $\propto 1/(t_b - t_a)^{1/2}$ in (4.103).

In order to recover the classical contribution, one simply uses the short-time amplitude in the form (2.349) to calculate the purely classical contribution to $Z(E)$:

$$Z_{\rm cl}(E) \equiv \int dx \int \frac{dp}{2\pi\hbar}\frac{i\hbar}{E - H(p,x)}. \tag{4.201}$$

This implies a classical contribution to the density of states

$$\rho_{\rm cl}(E) \equiv \int dx\, \rho_{\rm cl}(E;x), \tag{4.202}$$

which is a spatial integral over the *classical local density of states*

$$\rho_{\rm cl}(E;x) \equiv \int \frac{dp}{2\pi\hbar}\delta[E - H(p,x)]. \tag{4.203}$$

The δ-function in the integrand can be rewritten as

$$\delta(E - H(p,x)) = \frac{M}{p(E;x)}\left[\delta(p - p(E;x)) + \delta(p + p(E;x))\right], \tag{4.204}$$

where $p(E;x)$ is the local momentum associated with the energy E

$$p(E;x) = \sqrt{2M[E - V(x)]}, \tag{4.205}$$

which was defined in (4.3), except that we have now added the energy to the argument, to have a more explicit notation. It is then trivial to evaluate the integral (4.203) and (4.202) yielding the classical local density of states

$$\rho_{\rm cl}(E;x) = \frac{1}{\pi\hbar}\frac{M}{p(E;x)}, \tag{4.206}$$

and its integral

$$\rho_{\rm cl}(E) = \int dx\, \frac{1}{\pi\hbar}\frac{M}{p(E;x)} = \frac{1}{2\pi\hbar}t(E) = \rho_{\rm av}(E), \tag{4.207}$$

which coincides with the average classical density of states in (4.200).

Thus the full semiclassical density of states consists of the sum of (4.198) and (4.207):

$$\rho_{\rm sc}(E) = \rho_{\rm cl}(E) + \Delta\rho_{\rm sc}(E). \tag{4.208}$$

This has, on the average, the correct classical value.

Note that by Eq. (4.200), the eikonal $S(E)$ is related to the integral over the classical density of states $\rho_{\rm cl}(E)$ by a factor $2\pi\hbar$:

$$S(E) = 2\pi\hbar \int_{-\infty}^{E} dE\, \rho_{\rm cl}(E). \tag{4.209}$$

Recalling the definition (1.587) of the number of states up to the energy E we see that

$$S(E) = 2\pi\hbar N(E), \tag{4.210}$$

which shows that the Bohr-Sommerfeld quantization condition (4.190) is the semiclassical version of the completely general equation (1.588).

4.8 Multi-Dimensional Systems

The D-dimensional generalization of the classical partition function (4.201) reads

$$Z_{\rm cl}(E) \equiv \int d^Dx \int \frac{d^Dp}{2\pi\hbar}\frac{i\hbar}{E - H(\mathbf{p},\mathbf{x})}, \tag{4.211}$$

and of the density of states (4.203):

$$\rho_{\rm cl}(E;\mathbf{x}) \;\; \equiv \;\; \int \frac{d^Dp}{(2\pi\hbar)^D}\delta[E - H(\mathbf{p},\mathbf{x})]. \tag{4.212}$$

The Hamiltonian of the standard form $H(\mathbf{p},\mathbf{x}) = \mathbf{p}^2/2M + V(\mathbf{x})$ allows us to perform the momentum integration by separating it into radial and angular parts,

$$\int \frac{d^Dp}{(2\pi\hbar)^D} = \int dp\, p^{D-1} \int d\hat{\mathbf{p}}. \tag{4.213}$$

The angular integral yields the surface of a unit sphere in D dimensions:

$$\int d\hat{\mathbf{p}} = S_D = \frac{2\pi^{D/2}}{\Gamma(D/2)}. \tag{4.214}$$

The δ-function $\delta(E - H(\mathbf{p}, \mathbf{x}))$ can again be rewritten as in (4.204), which selects the momenta of magnitude

$$p(E; \mathbf{x}) = \sqrt{2M[E - V(\mathbf{x})]}. \tag{4.215}$$

Thus we find

$$\rho_{\rm cl}(E) \equiv \int d^D x \, \rho_{\rm cl}(E; \mathbf{x}), \tag{4.216}$$

where $\rho_{\rm cl}(E; \mathbf{x})$ is the *classical local density of states*.

$$\rho_{\rm cl}(E; \mathbf{x}) = S_D \frac{M}{p^2(E; \mathbf{x})} \frac{p^D(E; \mathbf{x})}{(2\pi\hbar)^D} = \frac{1}{(4\pi\hbar^2)^{D/2}} \frac{2M}{\Gamma(D/2)} \{2M[E - V(\mathbf{x})]\}^{D/2-1}, \tag{4.217}$$

generalizing expression (4.207). The number of states with energies between E and $E + dE$ in the volume element $d^D x$ is $dEd^3x\rho_{\rm cl}(E; \mathbf{x})$.

For completeness we state some features of the semiclassical results which appear when generalizing the theory to D dimensions. For a detailed derivation see the rich literature on this subject quoted at the end of the chapter.

For an arbitrary number D of dimensions. the Van Vleck-Pauli-Morette determinant (4.124) takes the form

$$F(\mathbf{x}_b, \mathbf{x}_a; t_b - t_a) = \frac{1}{\sqrt{2\pi i\hbar}^D} \left| \det{}_D[-\partial_{x_b^i} \partial_{x_a^j} A(\mathbf{x}_b, \mathbf{x}_a; t_b - t_a)] \right|^{1/2} e^{-i\pi\nu/2}, \tag{4.218}$$

where ν is the Maslov-Morse index.

The fixed-energy amplitude becomes the sum over all periodic orbits:[9]

$$(\mathbf{x}_b|\mathbf{x}_a)_E = \frac{1}{\sqrt{2\pi i\hbar}^{D-1}} \sum_p |D_S|^{1/2} e^{iS(\mathbf{x}_b, \mathbf{x}_a; E)/\hbar - i\pi\nu'/2}, \tag{4.219}$$

where $S(\mathbf{x}_b, \mathbf{x}_a; E)$ is the D-dimensional generalization of (4.68) and D_S the $(D + 1) \times (D + 1)$-determinant:

$$D_S = (-1)^{D+1} \det \begin{pmatrix} \dfrac{\partial^2 S}{\partial \mathbf{x}_b \partial \mathbf{x}_a} & \dfrac{\partial^2 S}{\partial E \partial \mathbf{x}_a} \\ \dfrac{\partial^2 S}{\partial \mathbf{x}_b \partial E} & \dfrac{\partial^2 S}{\partial E \partial E} \end{pmatrix}. \tag{4.220}$$

[9]M.C. Gutzwiller, J. Math. Phys. *8*, 1979 (1967); *11*, 1791 (1970); *12*, 343 (1971).

The factor $(-1)^{D+1}$ makes the determinant positive for short trajectories. The index ν' differs from ν by one unit if $\partial^2 S/\partial E^2 = \partial t(E)/\partial E$ is negative.

In D dimensions, the Hamilton-Jacobi equation leads to

$$\frac{\partial H}{\partial \mathbf{p}_b} \cdot \frac{\partial^2 S}{\partial \mathbf{x}_b \partial \mathbf{x}_a} = \dot{\mathbf{x}}_b \cdot \frac{\partial^2 S}{\partial \mathbf{x}_b \partial \mathbf{x}_a} = 0, \tag{4.221}$$

instead of (4.154). Only the longitudinal projection of the $D \times D$-matrix $\partial^2 S/\partial \mathbf{x}_b \partial \mathbf{x}_a$ along the direction of motion vanishes now. In this direction

$$\dot{\mathbf{x}}_b \cdot \frac{\partial^2 S}{\partial \mathbf{x}_b \partial E} = 1, \tag{4.222}$$

so that the determinant (4.220) can be reduced to

$$D_S = \frac{1}{|\dot{\mathbf{x}}_b||\dot{\mathbf{x}}_a|} \det\left(-\frac{\partial^2 S}{\partial \mathbf{x}_b^\perp \partial \mathbf{x}_a^\perp}\right), \tag{4.223}$$

instead of (4.156). Here $\mathbf{x}_{b,a}^\perp$ denotes the deviations from the orbit orthogonal to $\dot{\mathbf{x}}_{b,a}$, and we have used (2.290) to arrive at (4.223).

As an example, let us write down the D-dimensional generalization of the free-particle amplitude (4.161). The eikonal is obviously

$$S(\mathbf{x}_a, \mathbf{x}_b; E) = \sqrt{2ME}|\mathbf{x}_b - \mathbf{x}_a|, \tag{4.224}$$

and the determinant (4.223) becomes

$$D_S = \frac{M}{2E} \frac{(2ME)^{(D-1)/2}}{|\mathbf{x}_a - \mathbf{x}_b|^{D-1}}. \tag{4.225}$$

Thus we find

$$(\mathbf{x}_b|\mathbf{x}_a)_E = \sqrt{\frac{M}{2E}} \frac{1}{(2\pi i\hbar)^{(D-1)/2}} \frac{(2ME)^{(D-1)/4}}{|\mathbf{x}_a - \mathbf{x}_b|^{(D-1)/2}} e^{i\sqrt{2ME}|\mathbf{x}_b - \mathbf{x}_a|/\hbar}. \tag{4.226}$$

For $D = 1$, this reduces to (4.161).

Note that the semiclassical result coincides with the large-distance behavior (1.359) of the exact result (1.355), since the semiclassical limit implies a large momenta k in the Bessel function (1.355).

When calculating the partition function, one has to perform a D-dimensional integral over all $\mathbf{x}_b = \mathbf{x}_a$. This is best decomposed into a one-dimensional integral along the orbit and a $D-1$ -dimensional one orthogonal to it. The eikonal function $S(\mathbf{x}_a, \mathbf{x}_a; E)$ is constant along the orbit, as in the one-dimensional case. When leaving the orbit, however, this is no longer true. The quadratic deviation of S orthogonal to the orbit is

$$\frac{1}{2}(\mathbf{x} - \mathbf{x}^\perp)^T \frac{\partial^2 S(\mathbf{x}, \mathbf{x}; E)}{\partial \mathbf{x}^\perp \partial \mathbf{x}^\perp}(\mathbf{x} - \mathbf{x}^\perp), \tag{4.227}$$

where the superscript T denotes the transposed vector to be multiplied from the left with the matrix in the middle. After the exact trace integration along the orbit and a quadratic approximation in the transversal direction for each primitive orbit, which is not repeated, we obtain the contribution to the partition function

$$Z_{\rm sc} = t(E)\frac{\left|\dfrac{\partial^2 S(\mathbf{x}_b,\mathbf{x}_a;E)}{\partial \mathbf{x}_b^\perp \partial \mathbf{x}_a^\perp}\right|^{1/2}_{\mathbf{x}_b=\mathbf{x}_a=\mathbf{x}}}{\left|\dfrac{\partial^2 S(\mathbf{x},\mathbf{x};E)}{\partial \mathbf{x}^\perp \partial \mathbf{x}^\perp}\right|^{1/2}} \sum_{n=1}^{\infty} e^{in[S(E)/\hbar - i\pi\nu/2]}, \tag{4.228}$$

where ν is the Maslov-Morse index of the orbit. The ratio of the determinants is conveniently expressed in terms of the determinant of the so-called *stability matrix* M in phase space, which is introduced in classical mechanics as follows:

Consider a classical orbit in phase space and vary slightly the initial point, moving it orthogonally away from the orbit by $\delta\mathbf{x}_a^\perp, \delta\mathbf{p}_a^\perp$. This produces variations at the final point $\delta\mathbf{x}_b^\perp, \delta\mathbf{p}_b^\perp$, related to those at the initial point by the linear equation

$$\left(\begin{array}{c} \delta\mathbf{x}_b^\perp \\ \delta\mathbf{p}_b^\perp \end{array}\right) = \left(\begin{array}{cc} A & B \\ C & D \end{array}\right)\left(\begin{array}{c} \delta\mathbf{x}_a^\perp \\ \delta\mathbf{p}_a^\perp \end{array}\right) \equiv M \left(\begin{array}{c} \delta\mathbf{x}_a^\perp \\ \delta\mathbf{p}_a^\perp \end{array}\right). \tag{4.229}$$

The $2(D-1)\times 2(D-1)$-dimensional matrix is the stability matrix M. It can be expressed in terms of the second derivatives of $S(\mathbf{x}_b,\mathbf{x}_a;E)$. These appear in the relation

$$\left(\begin{array}{c} \delta\mathbf{p}_a^\perp \\ \delta\mathbf{p}_b^\perp \end{array}\right) = \left(\begin{array}{cc} -a & -b \\ b^T & c \end{array}\right)\left(\begin{array}{c} \delta\mathbf{x}_a^\perp \\ \delta\mathbf{x}_b^\perp \end{array}\right), \tag{4.230}$$

where a, b, and c are the $(D-1)\times(D-1)$-dimensional matrices

$$a = \frac{\partial^2 S}{\partial \mathbf{x}_a^\perp \partial \mathbf{x}_a^\perp}, \quad b = \frac{\partial^2 S}{\partial \mathbf{x}_a^\perp \partial \mathbf{x}_b^\perp}, \quad c = \frac{\partial^2 S}{\partial \mathbf{x}_b^\perp \partial \mathbf{x}_b^\perp}. \tag{4.231}$$

From this one calculates the matrix elements of the stability matrix (4.229):

$$A = -b^{-1}a, \quad B = -b^{-1}, \quad C = b^T - cb^{-1}a, \quad D = -cb^{-1}. \tag{4.232}$$

The stability properties of the classical orbits are classified by the eigenvalues of the stability matrix (4.229). In three dimensions, the eigenvalues are given by the zeros of the characteristic polynomial of the 4×4 -matrix M:

$$P(\lambda) = |M-\lambda| = \left|\begin{array}{cc} A-\lambda & B \\ C & D-\lambda \end{array}\right| = \left|\begin{array}{cc} -b^{-1}a-\lambda & -b^{-1} \\ b^T - cb^{-1}a & -cb^{-1}-\lambda \end{array}\right|. \tag{4.233}$$

The usual manipulations bring this to the form

$$\begin{aligned} P(\lambda) &= \left|\begin{array}{cc} -b^{-1}a-\lambda & -b^{-1} \\ b^T+\lambda & -\lambda \end{array}\right| = \frac{1}{|b|}\left|\begin{array}{cc} -a-\lambda b & -1 \\ b^T+(a+c)\lambda+\lambda^2 b & 0 \end{array}\right| \\ &= \frac{1}{|b|}\left|b^T+(a+c)\lambda+\lambda^2 b\right|. \end{aligned} \tag{4.234}$$

Precisely this expression appears, with $\mathbf{x}_b = \mathbf{x}_a$, in the prefactor of (4.228) if this is rewritten as

$$\frac{\left|\frac{\partial^2 S}{\partial \mathbf{x}_b^\perp \partial \mathbf{x}_a^\perp}\right|^{1/2}_{\mathbf{x}_b \approx \mathbf{x}_a = \mathbf{x}}}{\left|\frac{\partial^2 S}{\partial \mathbf{x}_b^\perp \partial \mathbf{x}_b^\perp} + 2\frac{\partial S}{\partial \mathbf{x}_b^\perp}\frac{\partial S}{\partial \mathbf{x}_a^\perp} + \frac{\partial^2 S}{\partial \mathbf{x}_a^\perp \partial \mathbf{x}_a^\perp}\right|^{1/2}_{\mathbf{x}_b = \mathbf{x}_a = \mathbf{x}}}. \tag{4.235}$$

Due to (4.232), this coincides with $P(1)^{-1/2}$. The semiclassical limit to the quantum-mechanical partition function takes therefore the simple form referred to as *Gutzwiller's trace formula*

$$Z_{\rm sc}(E) = t(E)\frac{1}{P(1)^{1/2}}\frac{e^{iS(E)-i\pi\nu/2}}{1-e^{iS(E)-i\pi\nu/2}}. \tag{4.236}$$

The energy eigenvalues lie at the poles and satisfy the quantization rules [compare (4.27), (4.190)]

$$S(E_n) = 2\pi\hbar(n+\nu/4). \tag{4.237}$$

The eigenvalues of the stability matrix come always in pairs $\lambda, 1/\lambda$, as is obvious from (4.234). For this reason, one has to classify only two eigenvalues. These must be either both real or mutually complex-conjugate. One distinguishes the following cases:

1. *elliptic*, if $\lambda = e^{i\chi}, e^{-i\chi}$, with a real phase $\chi \neq 0$,
2. *direct parabolic*, *inverse parabolic*, if $\lambda = 1$, $\lambda = -1$,
3. *direct hyperbolic*, *inverse hyperbolic*, if $\lambda = e^{\pm\chi}$, $\lambda = -e^{\pm\chi}$,
4. *loxodromic*, if $\lambda = e^{u\pm v}$.

In these cases,

$$P(1) = \prod_{i=1}^{2}(\lambda_i - 1)(1/\lambda_i - 1) \tag{4.238}$$

has the values

1. $4\sin^2(\chi/2)$,
2. 0 or 4,
3. $-4\sinh^2(\chi/2)$ or $4\cosh^2(\chi/2)$,
4. $4\sin[(u+v)/2]\sin[(u-v)/2]$.

Only in the parabolic case are the equations of motion integrable, this being obviously an exception rather than a rule, since it requires the fulfillment of the equation $a + c = \pm 2b$. Actually, since the transverse part of the trace integration in the partition function results in a singular determinant in the denominator of (4.236), this case requires a careful treatment to arrive at the correct result.[10] In general, a system will show a mixture of elliptic and hyperbolic behavior, and the particle orbits exhibit what is called a *smooth chaos*. In the case of a purely hyperbolic behavior one speaks of a *hard chaos*, which is simpler to understand. The semiclassical approximation is based precisely on those orbits of a system which are exceptional in a chaotic system, namely, the periodic orbits.

The expression (4.236) also serves to obtain the semiclassical density of states in D-dimensional systems via Eq. (4.193). In D dimensions the paths, with vanishing length contribute to the partition function the classical expression [compare (4.211)]. Application of semiclassical formulas has led to surprisingly simple explanations of extremely complex experimental data on highly excited atomic spectra which classically behave in a chaotic manner.

For completeness, let us also state the momentum space representation of the semiclassical fixed-energy amplitude (4.145). It is given by the momentum space analog of (4.219):

$$(\mathbf{p}_b|\mathbf{p}_a)_E = \frac{(2\pi\hbar)^D}{\sqrt{2\pi i\hbar}^{D-1}} \sum_p |\tilde{D}_S|^{1/2} e^{iS(\mathbf{p}_b,\mathbf{p}_a;E)/\hbar - i\pi\nu'/2}, \tag{4.239}$$

where $S(\mathbf{p}_b, \mathbf{p}_a; E)$ is the Legendre transform of the eikonal

$$S(\mathbf{p}_b, \mathbf{p}_a; E) = S(\mathbf{p}_b, \mathbf{p}_a; E) - \mathbf{p}_b\mathbf{x}_b + \mathbf{p}_a\mathbf{x}_a, \tag{4.240}$$

evaluated at the classical momenta $\mathbf{p}_b = \partial_{\mathbf{p}_b} S(\mathbf{p}_b, \mathbf{p}_a; E)$ and $\mathbf{p}_a = \partial_{\mathbf{p}_a} S(\mathbf{p}_b, \mathbf{p}_a; E)$. The determinant can be brought to the form:

$$D_S = \frac{1}{|\dot{\mathbf{p}}_b||\dot{\mathbf{p}}_a|} \det\left(-\frac{\partial^2 S}{\partial \mathbf{p}_b^\perp \partial \mathbf{p}_a^\perp}\right), \tag{4.241}$$

where $\mathbf{p}_a^\perp$ is the momentum orthogonal to $\dot{\mathbf{p}}_a$.

This formula cannot be applied to the free particle fixed-energy amplitude (3.219) for the same degeneracy reason as before.

Higher $\hbar$-corrections to the trace formula (4.236) have also been derived, but the resulting expressions are very complicated to handle. See the citations at the end of this chapter.

4.9 Quantum Corrections to Classical Density of States

There exists a simple way of calculating quantum corrections to the semiclassical expressions (4.207) and its D-dimensional generalization (4.216) for the density of

[10] M.V. Berry and M. Tabor, J. Phys. A *10*, 371 (1977), Proc. Roy. Soc. A *356*, 375 (1977).

states. To derive them we introduce an operator δ-function $\delta(E-\hat{H})$ via the spectral representation

$$\delta(E-\hat{H}) \equiv \sum_n \delta(E-E_n)|n\rangle\langle n|, \tag{4.242}$$

where $|n\rangle$ are the eigenstates of the Hamiltonian operator $\hat{H}$. The δ-function (4.242) has the Fourier representation [recall (1.193)]

$$\delta(E-\hat{H}) = \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} e^{-i(\hat{H}-E)t/\hbar}. \tag{4.243}$$

Its matrix elements between eigenstates $|\mathbf{x}\rangle$ of the position operator,

$$\rho(E;\mathbf{x}) \;=\; \langle\mathbf{x}|\delta(E-\hat{H})|\mathbf{x}\rangle = \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} e^{iEt/\hbar}\langle\mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}\rangle, \tag{4.244}$$

define the *quantum-mechanical local density of states*. The amplitude on the right-hand side is the time evolution amplitude

$$\langle\mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}\rangle = (\mathbf{x}\,t|\mathbf{x}\,0), \tag{4.245}$$

which can be represented by a path integral as described in Chapter 2. In the semiclassical limit, only the short-time behavior of $(\mathbf{x}\,t|\mathbf{x}\,0)$ is relevant.

4.9.1 One-Dimensional Case

For a one-dimensional harmonic oscillator, the short-time expansion of (4.245) can easily be derived. We shall to do this for a slightly generalized harmonic potential which contains also a linear term to

$$V(x) = \frac{\omega^2}{2}(x^2-2ax) = \frac{\omega^2}{2}(x-a)^2 - \frac{\omega^2}{2}a^2. \tag{4.246}$$

Then the diagonal amplitude (4.245) becomes [see also (2.333)]

$$(x\,t_b|x\,t_a) = \frac{1}{\sqrt{2\pi i\hbar/M}}\sqrt{\frac{\omega}{\sin\omega t}}\exp\left[i\frac{M\omega}{\hbar}\left(\tan\frac{\omega t}{2}\,(x-a)^2 - \frac{\omega t a^2}{2}\right)\right]. \tag{4.247}$$

For $t \equiv t_b - t_a < 1/\omega$, we expand this in a power series of t as follows:

$$(x\,t_b|x\,t_a) = \frac{e^{-i\frac{M}{2}\omega^2(x^2-2ax)t/\hbar}}{\sqrt{2\pi i\hbar t/M}}\left\{1+\frac{t^2\omega^2}{12} - \frac{iM}{\hbar}\frac{t^3}{24}\omega^4(x-a)^2 \right.$$
$$\left. + \frac{t^4\omega^4}{160} - \frac{iM}{\hbar}\frac{11\,t^5\omega^2}{1440}\omega^4(x-a)^2 + \dots\right\}. \tag{4.248}$$

This expansion can be generalized to an arbitrary smooth potential $V(x)$ if the exponential prefactor containing the harmonic potential is replaced by

$$e^{-iV(x)t/\hbar}, \tag{4.249}$$

whereas ω^2 and $\omega^4 x^2$ are substituted as follows:

$$\omega^2 \rightarrow \frac{1}{M}V''(x), \tag{4.250}$$

$$\omega^4(x-a)^2 \rightarrow \frac{1}{M^2}[V'(x)]^2. \tag{4.251}$$

The presence of a is important for this identification. Without it we could not tell whether the harmonic term $\omega^4 x^2$ represents $[V'(x)]^2/M^2$ or $2V(x)V''(x)/M^2$. Thus we find

$$(x\,t_b|x\,t_a) = \frac{e^{-iV(x)t/\hbar}}{\sqrt{2\pi i\hbar t/M}}\left\{1+\frac{t^2}{12M}V''(x)-\frac{i}{\hbar}\frac{t^3}{24M}[V'(x)]^2 + \frac{t^4}{160}[V''(x)]^2 - \frac{i}{\hbar}\frac{11\,t^5}{1440M}[V'(x)]^2V''(x)+\dots\right\}. \tag{4.252}$$

For positive $E-V(x)$, the integration along the real axis can be deformed into the upper complex plane to enclose the square-root cut along the positive imaginary t-axis in the anti-clockwise sense. Setting $t = i\tau$ and using the fact that the discontinuity across a square root cut produces a factor two, the lowest three terms become

$$\rho(E;x) = 2\int_0^\infty \frac{d\tau}{2\pi\hbar}\frac{e^{-[E-V(x)]\tau/\hbar}}{\sqrt{2\pi\hbar\tau/M}}\left\{1-\frac{\tau^2}{12M}V''(x)-\frac{1}{\hbar}\frac{\tau^3}{24M}[V'(x)]^2+\dots\right\}. \tag{4.253}$$

The first term can easily be integrated for $E > V(x)$, and yields the classical local density of states (4.207):

$$\rho_{\rm cl}(E;x) = \frac{1}{\pi\hbar}\frac{M}{\sqrt{2M[E-V(x)]}} = \frac{M}{\pi\hbar}\frac{1}{p(E;x)}. \tag{4.254}$$

In order to calculate the effect of the correction terms in the expansion (4.253), we observe that a factor τ in the integrand is the same as a derivative $\hbar d/dV$ applied to the exponential. Thus we find directly the semiclassical expansion for the density of states (4.253), valid for $E > V(x)$:

$$\rho(E;x) = \left\{1-\frac{\hbar^2}{12M}V''(x)\frac{d^2}{dV^2}-\frac{\hbar^2}{24M}[V'(x)]^2\frac{d^3}{dV^3}+\dots\right\}\rho_{\rm cl}(E;x). \tag{4.255}$$

Inserting (4.254) and performing the differentiations with respect to V we obtain

$$\rho(E;x) = \frac{1}{\pi\hbar}\sqrt{\frac{M}{2}}\left\{\frac{1}{[E-V(x)]^{1/2}}-\frac{\hbar^2}{12M}V''(x)\frac{3}{4}\frac{1}{[E-V(x)]^{5/2}} - \frac{\hbar^2}{24M}[V'(x)]^2\,\frac{15}{8}\frac{1}{[E-V(x)]^{7/2}}+\dots\right\}. \tag{4.256}$$

Note that the higher expansion terms contain powers of higher and higher gradients of the potential. It is a so-called *gradient expansion* of the density of states.

The integral over (4.256) yields a gradient expansion for $\rho(E)$ [3] . The second term can be integrated by parts which, under the assumption that $V(x)$ vanishes at the boundaries, simply changes the sign of the third term, so that we find

$$\rho(E)=\frac{1}{\pi\hbar}\sqrt{\frac{M}{2}}\int dx\left\{\frac{1}{[E-V(x)]^{1/2}}+\frac{\hbar^2}{24M}[V'(x)]^2\frac{15}{8}\frac{1}{[E-V(x)]^{7/2}}+\dots\right\}. \tag{4.257}$$

4.9.2 Arbitrary Dimensions

In D dimensions, the short-time expansion of the time evolution amplitude (4.252) takes the form

$$(\mathbf{x}\, t_b|\mathbf{x}\, t_a) = \frac{e^{-iV(\mathbf{x})t/\hbar}}{\sqrt{2\pi i\hbar t/M}^D}\left\{1+\frac{t^2}{12M}\boldsymbol{\nabla}^2V(\mathbf{x})-\frac{i}{\hbar}\frac{t^3}{24M}[\boldsymbol{\nabla}V(\mathbf{x})]^2+\dots\right\}. \tag{4.258}$$

Recalling the $i\eta$-prescription on page 115, according to which the singularity at $t=0$ has to be shifted slightly into the upper half plane by replacing $t\to t-i\eta$, we use the formula[11]

$$\int_{-\infty}^{\infty}\frac{dt}{2\pi}\frac{1}{(it+\eta)^\nu}e^{ita}=\Theta(a)\frac{a^{\nu-1}}{\Gamma(\nu)}e^{-a\eta}, \tag{4.259}$$

and obtain the obvious generalization of (4.255):

$$\rho(E;\mathbf{x})=\left\{1-\frac{\hbar^2}{12M}\boldsymbol{\nabla}^2V(\mathbf{x})\frac{d^2}{dV^2}-\frac{\hbar^2}{24M}[\boldsymbol{\nabla}V(\mathbf{x})]^2\frac{d^3}{dV^3}+\dots\right\}\rho_{\rm cl}(E;\mathbf{x}), \tag{4.260}$$

where $\rho_{\rm cl}(E;\mathbf{x})$ is the classical D-dimensional local density of states (4.217). The way this appears here is quite different from that in the earlier classical calculation (4.212), which may be expressed with the help of the local momentum (4.215) as an integral

$$\rho_{\rm cl}(E;\mathbf{x})=\int\frac{d^Dp}{(2\pi\hbar)^D}\delta[E-H(\mathbf{p},\mathbf{x})]=\int\frac{d^Dp}{(2\pi\hbar)^D}\frac{M}{p(E;\mathbf{x})}\delta[p-p(E;\mathbf{x})]. \tag{4.261}$$

In order to see the relation to the appearance in (4.260) we insert the Fourier decomposition of the leading term of the short-time expansion of the time evolution amplitude

$$(\mathbf{x}\, t|\mathbf{x}\, 0)_{\rm cl} \;=\; \int\frac{d^Dp}{(2\pi\hbar)^D}e^{-i[\mathbf{p}^2/2M+V(\mathbf{x})]t/\hbar} \tag{4.262}$$

[11] I.S. Gradshteyn and I.M. Ryzhik, *op. cit.*, Formula 3.382.6. The formula is easily derived by expressing $(it+\eta)^{-\nu}=\Gamma^{-1}(\nu)\int_0^\infty d\tau\tau^{\nu-1}e^{-\tau(it+\eta)}$.

into the integral representation (4.244) which takes the form

$$\rho(E;\mathbf{x}) = \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} \int \frac{d^Dp}{(2\pi\hbar)^D} e^{-i[p^2-p^2(E;\mathbf{x})]t/2M\hbar}. \tag{4.263}$$

By doing the integral over the time first, the size of the momentum is fixed to the local momentum $p^2(E;\mathbf{x})$ resulting in the original representation (4.261). The expression (4.217) for the density of states, on the other hand, corresponds to first integrating over *all* momenta. The time integration selects from the result of this the correct local momenta $p^2(E;\mathbf{x})$.

This generalizes (4.256) to

$$\begin{aligned}\rho(E;\mathbf{x}) &= \left(\frac{M}{2\pi\hbar^2}\right)^{D/2} \left\{ \frac{1}{\Gamma(D/2)}[E-V(\mathbf{x})]^{D/2-1} \right.\\ &- \frac{\hbar^2}{12M}\left[\boldsymbol{\nabla}^2 V(\mathbf{x})\right]\frac{1}{\Gamma(D/2-2)}[E-V(\mathbf{x})]^{D/2-3}\\ &+ \left.\frac{\hbar^2}{24M}\left[\boldsymbol{\nabla} V(\mathbf{x})\right]^2\frac{1}{\Gamma(D/2-3)}[E-V(\mathbf{x})]^{D/2-4}+\dots\right\}.\end{aligned} \tag{4.264}$$

When integrating the density (4.264) over all $\mathbf{x}$, the second term in the curly brackets can again be converted into the third term changing its sign, as in (4.257). The right-hand side can easily be integrated for all pure power potentials. This will be done in Appendix 4A.

4.9.3 Bilocal Density of States

It is useful to generalize the local density of states (4.244) and introduce a *bilocal density of states*:

$$\begin{aligned}\rho(E;\mathbf{x}_b,\mathbf{x}_a) &= \langle\mathbf{x}_b|\delta(E-\hat{H})|\mathbf{x}_a\rangle = \int_{-\infty}^{\infty}\frac{dt}{2\pi\hbar}e^{iEt/\hbar}\,\langle\mathbf{x}_b|e^{-i\hat{H}t/\hbar}|\mathbf{x}_a\rangle\\ &= \int_{-\infty}^{\infty}\frac{dt}{2\pi\hbar}e^{iEt/\hbar}\,(\mathbf{x}_b\,t|\mathbf{x}_a\,0).\end{aligned} \tag{4.265}$$

The semiclassical expansion requires now the nondiagonal version of the short-time expansions (4.258). For a D-dimensional harmonic oscillator, the expansion (4.248) with $a=0$ is generalized to

$$\begin{aligned}(\mathbf{x}_bt_b|\mathbf{x}_at_a) &= \frac{e^{iM\Delta\mathbf{x}^2/2t\hbar}}{\sqrt{2\pi i\hbar t/M}^D}e^{-iM\omega^2\bar{\mathbf{x}}^2t/2\hbar}\left\{1+\frac{t^2D}{12}\omega^2-\frac{iM}{\hbar}\frac{t^3}{24}\omega^4\bar{\mathbf{x}}^2-\frac{iM}{\hbar}\frac{t}{24}\Delta\mathbf{x}^2\omega^2\right.\\ &\left.-\frac{iM}{\hbar}\frac{t^3}{1440}\Delta\mathbf{x}^2\omega^4-\frac{iM}{\hbar}\frac{t^3D}{288}\Delta\mathbf{x}^2\omega^4+\frac{t^4(D+\frac{5}{4}D^2)}{360}\omega^4-\frac{1}{\hbar^2}\Delta\mathbf{x}^4\frac{t^2}{1152}\omega^4\bar{\mathbf{x}}^2+\dots\right\},\end{aligned} \tag{4.266}$$

where $\bar{\mathbf{x}} = (\mathbf{x}_b+\mathbf{x}_a)/2$ is the mean position of the two endpoints. In this expansion we have included all terms whose size is of the order t^4, keeping in mind that $\Delta\mathbf{x}^2$

is of the order $\hbar$ in a finite amplitude. Performing the substitutions (4.250) and (4.251), for $a = 0$, this expansion is generalized to

$$(\mathbf{x}_b t_b|\mathbf{x}_a t_a) = \frac{e^{iM\Delta\mathbf{x}^2/2t\hbar}}{\sqrt{2\pi i\hbar t/M}^D} e^{-iV(\bar{\mathbf{x}})t/\hbar} \left\{ 1 + \frac{t^2}{12M}\boldsymbol{\nabla}^2 V - \frac{i}{\hbar}\frac{t^3}{24M}[\boldsymbol{\nabla}V]^2 - \frac{i}{\hbar}\frac{t}{24}(\Delta\mathbf{x}\boldsymbol{\nabla})^2 V \right.$$
$$-\frac{i}{\hbar}\frac{t^3}{1440M}[(\Delta\mathbf{x}\boldsymbol{\nabla})\Delta x_i \nabla_j V]\nabla_i\nabla_j V] - \frac{iM}{\hbar}\frac{t^3}{288}(\Delta\mathbf{x})^2[\boldsymbol{\nabla}^2 V]^2 + \frac{t^4}{360M^2}\left([\nabla_i\nabla_j V]^2 + \frac{5}{4}[\boldsymbol{\nabla}V]^2\right)$$
$$\left. - \frac{t^2}{1152\hbar^2}[\Delta x_i \Delta x_j \nabla_k \nabla_l V][\Delta x_k \Delta x_l \nabla_i \nabla_j V] + \ldots \right\}. \tag{4.267}$$

where we have omitted the arguments $\bar{\mathbf{x}}$ in all potentials. The substitution of the term $\Delta\mathbf{x}^2 M\omega^2$ in (4.266) by

$$\Delta\mathbf{x}^2 M\omega^2 \to (\Delta\mathbf{x}\boldsymbol{\nabla})^2 V(\bar{\mathbf{x}}), \tag{4.268}$$

rather than $\Delta\mathbf{x}^2\boldsymbol{\nabla}^2 V(\bar{\mathbf{x}})$, follows from the fact that there is no factor D. The other substitutions follow similary.

For a derivation without the substitution tricks (4.250), (4.251), (4.268), see Appendix 4B.

A recursive calculation is possible by writing the amplitude as

$$(\mathbf{x}\, t|\mathbf{x}'0) = \frac{e^{iM\Delta\mathbf{x}^2/2t\hbar}}{\sqrt{2\pi i\hbar t/M}^D} A(\mathbf{x}, \Delta\mathbf{x}, t), \tag{4.269}$$

with the the amplitude $A(\mathbf{x}, \Delta\mathbf{x}'; t)$, satisfying the differential equation

$$\hbar i\partial_t A(\mathbf{x}, \Delta\mathbf{x}'; t) = \left[-\frac{\hbar^2}{2M}\boldsymbol{\nabla}^2 - V(\mathbf{x})\right] A - \frac{i\hbar}{t}\Delta\mathbf{x}\boldsymbol{\nabla} A(\mathbf{x}, \Delta\mathbf{x}; t). \tag{4.270}$$

After expanding

$$A(\mathbf{x}, \Delta\mathbf{x}; t) = 1 + \sum_{n=1}^{\infty} t^n \sum_{p=0}^{\infty} \Delta x_{i_1} \cdots \Delta x_{i_p}\, a^{(n)}_{i_1,\ldots,i_p}(\mathbf{x}), \tag{4.271}$$

we can calculate the coefficients order by order in n and p.

Inserting the amplitude (4.267) into the integral in Eq. (4.265), we obtain from the lowest expansion terms the bilocal density of states

$$\rho(E; \mathbf{x}_b, \mathbf{x}_a) = \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} \frac{e^{iM\Delta\mathbf{x}^2/2t\hbar}}{\sqrt{2\pi i\hbar t/M}^D} e^{-i[V(\bar{\mathbf{x}})-E]t/\hbar}$$
$$\times \left\{ 1 + \frac{t^2}{12M}\boldsymbol{\nabla}^2 V(\bar{\mathbf{x}}) - \frac{i}{\hbar}\frac{t^3}{24M}[\boldsymbol{\nabla}V(\bar{\mathbf{x}})]^2 - \frac{i}{\hbar}\frac{t}{24}(\Delta\mathbf{x}\boldsymbol{\nabla})^2 V(\bar{\mathbf{x}}) + \ldots \right\}. \tag{4.272}$$

The leading term is simply the time evolution amplitude of the free-particle in a constant potential $V(\bar{\mathbf{x}})$ which has the Fourier decomposition [recall (1.335)]:

$$(\mathbf{x}_b t_b|\mathbf{x}_a t_a)_{\rm cl} \;\; = \;\; \int \frac{d^D p}{(2\pi\hbar)^D} e^{i\mathbf{p}(\mathbf{x}_b-\mathbf{x}_a)/\hbar} e^{-iH(\mathbf{p},\bar{\mathbf{x}})t/\hbar}. \tag{4.273}$$

Indeed, inserting this into (4.265), and performing the integration over time, we find

$$\rho_{\rm cl}(E;\mathbf{x}_b,\mathbf{x}_a) = \int \frac{d^D p}{(2\pi\hbar)^D} \delta(E-H(\mathbf{p},\bar{\mathbf{x}})) e^{i\mathbf{p}(\mathbf{x}_b-\mathbf{x}_a)/\hbar}. \tag{4.274}$$

Decomposing the momentum integral into radial and angular parts as in (4.213), we can integrate out the radial part as in (4.203), whereas the angular integral yields the following function of $R = |\mathbf{x}_b - \mathbf{x}_a|$:

$$\int d\hat{\mathbf{p}}\, e^{i\mathbf{p}(\mathbf{x}_b-\mathbf{x}_a)/\hbar} = S_D(pR/\hbar), \tag{4.275}$$

which is a direct generalization of the surface of a sphere in D dimensions (4.214). It reduces to it for $p = 0$. This integral will be calculated in Section 9.1. The result is

$$S_D(z) = (2\pi)^{D/2} J_{D/2-1}(z)/z^{D/2-1}, \tag{4.276}$$

where $J_\nu(z)$ are Bessel functions. For small z, these behave like[12]

$$J_\nu(z) \approx \frac{(z/2)^\nu}{\Gamma(\nu+1)}, \tag{4.277}$$

thus ensuring that $S_D(kR)$ is indeed equal to S_D at $R = 0$.

Altogether, the classical limit of the bilocal density of states is

$$\rho_{\rm cl}(E;\mathbf{x}_b,\mathbf{x}_a) = \left(\frac{1}{2\pi\hbar^2}\right)^{D/2} M \frac{J_{D/2-1}(p(E;\bar{\mathbf{x}})R/\hbar)}{(R/\hbar)^{D/2-1}}. \tag{4.278}$$

At $\mathbf{x}_b = \mathbf{x}_a$, this reduces to the density (4.212).

In three dimensions, the Bessel function becomes

$$J_{1/2}(z) = \sqrt{\frac{2}{\pi z}} \sin z, \tag{4.279}$$

and (4.278) yields

$$\rho_{\rm cl}(E;\mathbf{x}_b,\mathbf{x}_a) = \left(\frac{1}{2\pi\hbar^2}\right)^{3/2} \frac{1}{\Gamma(3/2)} \frac{M}{\sqrt{2}} \frac{\sin[p(E;\bar{\mathbf{x}})R/\hbar]}{R/\hbar}. \tag{4.280}$$

From the D-dimensional version of the short-time expansion (4.272) we obtain, after using once more the equivalence of t and $i\hbar d/dV$,

$$\rho(E;\mathbf{x}_b,\mathbf{x}_a) = \left\{1 - \frac{\hbar^2}{12M}\left[\boldsymbol{\nabla}^2 V(\bar{\mathbf{x}})\right]\frac{d^2}{dV^2} - \frac{\hbar^2}{24M}[\boldsymbol{\nabla} V(\bar{\mathbf{x}})]^2 \frac{d^3}{dV^3} \right.$$
$$\left. + \frac{1}{24}[(\mathbf{x}_b-\mathbf{x}_a)\boldsymbol{\nabla}]^2 V(\bar{\mathbf{x}}) \frac{d}{dV} + \dots \right\} \rho_{\rm cl}(E;\mathbf{x}_b,\mathbf{x}_a). \tag{4.281}$$

[12] M. Abramowitz and I. Stegun, *op. cit.*, Formula 9.1.7.

4.9.4 Gradient Expansions of Tracelog of Hamiltonian Operator

Starting point is formula (1.590) for the tracelog of the Hamiltonian operator. By performing the trace in the local basis $|\mathbf{x}\rangle$, we arrive at the useful formula involving the density of states (4.244)

$$\mathrm{Tr}\log\hat{H} = \int d^Dx \int_{-\infty}^{\infty} dE\,\rho(E;\mathbf{x})\log E. \tag{4.282}$$

Inserting here the classical density of states (4.217), the integral over the classical spectrum $E \in (E_0, \infty)$ can be performed, where E_0 is the bottom of the potential $V(\mathbf{x})$, and yields the classical limit of the tracelog:

$$[\mathrm{Tr}\log\hat{H}]_{\mathrm{cl}} = \int d^Dx \int_{E_0}^{\infty} dE\,\rho_{\mathrm{cl}}(E;\mathbf{x})\log E = \left(\frac{M}{2\pi\hbar^2}\right)^{D/2} \int d^Dx\, I_{D/2}(V(\mathbf{x})), \tag{4.283}$$

where

$$I_\alpha(V) \equiv \frac{1}{\Gamma(\alpha)} \int_V^\infty dE\,(E-V)^{\alpha-1}\,\log E. \tag{4.284}$$

The integrals $I_{D/2}(V(\mathbf{x}))$ diverge, but can be calculated with the techniques explained in Section 2.15 from the analytically regularized integrals[13]

$$I^\eta_\alpha(V) \equiv \frac{1}{\Gamma(\alpha)} \int_V^\infty dE\,(E-V)^{\alpha-1}\,E^{-\eta} = V^{\alpha-\eta}\frac{\Gamma(-\alpha+\eta)}{\Gamma(\eta)}. \tag{4.285}$$

Since $E^{-\eta} = 1 - \eta\log E + \mathcal{O}(\eta^2)$, the coefficient of $-\eta$ in the Taylor series of $I^\eta_\alpha(V)$ will yield the desired integral. Since $1/\Gamma(\eta) \approx \eta$, we obtain directly

$$I_\alpha(V) = -\Gamma(-\alpha)V^\alpha, \tag{4.286}$$

so that (4.283) becomes

$$[\mathrm{Tr}\log\hat{H}]_{\mathrm{cl}} = -\left(\frac{M}{2\pi\hbar^2}\right)^{D/2} \Gamma(-D/2) \int d^Dx\,[V(\mathbf{x})]^{D/2}. \tag{4.287}$$

The same result can be obtained with the help of formulas (4.244), (4.258), and (2.506) as

$$[\mathrm{Tr}\log\hat{H}]_{\mathrm{cl}} = -\int d^Dx \int_{-\infty}^{\infty} dE \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar}\frac{e^{it[E-V(\mathbf{x})]/\hbar}}{(2\pi i\hbar t/M)^{D/2}} \int_0^\infty \frac{dt'}{t'} e^{-iEt'/\hbar}. \tag{4.288}$$

Integrating over the energy yields

$$[\mathrm{Tr}\log\hat{H}]_{\mathrm{cl}} = -\int d^Dx \int_0^\infty \frac{dt}{t}\frac{1}{(2\pi i\hbar t/M)^{D/2}} e^{-itV(\mathbf{x})/\hbar}. \tag{4.289}$$

Deforming the contour of integration by the substitution $t = -i\tau$, we arrive at the integral representation of the Gamma function (2.498) which reproduces immediately the result (4.287).

The full quantum mechanical expression for the trace log contains the diagonal time evolution amplitude

$$\mathrm{Tr}\log\hat{H} = -\int d^Dx \int_0^\infty \frac{dt}{t}\langle\mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}\rangle. \tag{4.290}$$

Inserting here the short-time expansion (4.258), we obtain the semiclassical expansion for the trace of the logarithm. If the factors t^n in the integrand are repaced by derivatives with respect to the

[13] I.S. Gradshteyn and I.M. Ryzhik, *op. cit.*, Formula 3.196.2.

potential $V(\mathbf{x})$, we obtain the semiclassical expansion containing the prefactor in curly brackets in the expansion (4.260):

$$\begin{aligned}\mathrm{Tr}\log\hat{H} &= -\left(\frac{M}{2\pi\hbar^2}\right)^{D/2}\Gamma(-D/2)\\ &\times\int d^Dx\left\{1-\frac{\hbar^2}{12M}\boldsymbol{\nabla}^2V(\mathbf{x})\frac{d^2}{dV^2}-\frac{\hbar^2}{24M}[\boldsymbol{\nabla}V(\mathbf{x})]^2\frac{d^3}{dV^3}+\ldots\right\}[V(\mathbf{x})]^{D/2}. \qquad (4.291)\end{aligned}$$

The second term can be integrated by parts, which replaces $\boldsymbol{\nabla}^2V(\mathbf{x})\rightarrow-[\boldsymbol{\nabla}V(\mathbf{x})]^2d/dV$, so that we obtain the gradient expansion

$$\mathrm{Tr}\log\hat{H}=-\left(\frac{M}{2\pi\hbar^2}\right)^{D/2}\Gamma(-D/2)\int d^Dx\left\{1+\frac{\hbar^2}{24M}[\boldsymbol{\nabla}V(\mathbf{x})]^2\frac{d^3}{dV^3}+\ldots\right\}[V(\mathbf{x})]^{D/2}. \qquad (4.292)$$

The expression in curly brackets can obviously be replaced by

$$\left\{1-\frac{\hbar^2}{24M}\,\frac{\Gamma(3-D/2)}{\Gamma(-D/2)}\frac{[\boldsymbol{\nabla}V(\mathbf{x})]^2}{[V(\mathbf{x})]^3}+\ldots\right\}. \qquad (4.293)$$

In one dimension and with $M=1/2$, this amounts to the formula

$$\mathrm{Tr}\log[-\hbar^2\partial_x^2+V(x)]=\frac{1}{\hbar}\int dx\sqrt{V(x)}\left\{1+\frac{\hbar^2}{32}\frac{[V'(x)]^2}{V^3(x)}+\ldots\right\}. \qquad (4.294)$$

It is a useful exercise to rederive this with the help of the Gelfand-Yaglom method in Section 2.4.

There exists another method for deriving the gradient expansion (4.291). We split $V(\mathbf{x})$ into a constant term V and a small $\mathbf{x}$-dependent term $\delta V(\mathbf{x})$, and rewrite

$$\begin{aligned}\mathrm{Tr}\log\left[-\frac{\hbar^2}{2M}\boldsymbol{\nabla}^2+V(\mathbf{x})\right] &= \mathrm{Tr}\log\left[-\frac{\hbar^2}{2M}\boldsymbol{\nabla}^2+V+\delta V(\mathbf{x})\right]\\ &= \mathrm{Tr}\log\left(-\frac{\hbar^2}{2M}\boldsymbol{\nabla}^2+V\right)+\mathrm{Tr}\log\left(1+\Delta_V\,\delta V\right), \qquad (4.295)\end{aligned}$$

where Δ_V denotes the functional matrix

$$\Delta_V(\mathbf{x},\mathbf{x}')=\left(-\frac{\hbar^2}{2M}\boldsymbol{\nabla}^2+V\right)^{-1}=\int\frac{d^Dp}{(2\pi\hbar)^D}\frac{e^{i\mathbf{p}(\mathbf{x}-\mathbf{x}')/\hbar}}{\mathbf{p}^2/2M+V}\equiv\Delta_V(\mathbf{x}-\mathbf{x}'). \qquad (4.296)$$

This coincides with the fixed-energy amplitude $(i/\hbar)(\mathbf{x}|\mathbf{x}')_E$ at $E=-V$ [recall Eq. (1.348)].

The first term in (4.295) is equal to (4.287) if we replace $V(\mathbf{x})$ in that expression by the constant V, so that we may write

$$\mathrm{Tr}\log\hat{H}=[\mathrm{Tr}\log\hat{H}]_{\rm cl}\Big|_{V(\mathbf{x})\rightarrow V}+\mathrm{Tr}\log\left(1+\Delta_V\,\delta V\right). \qquad (4.297)$$

We now expand the remainder

$$\mathrm{Tr}\log\left(1+\Delta_V\,\delta V\right)=\mathrm{Tr}\,\Delta_V\,\delta V-\frac{1}{2}\mathrm{Tr}\left(\Delta_V\,\delta V\right)^2+\ldots\;, \qquad (4.298)$$

and evaluate the expansion terms. The first term is simply

$$\mathrm{Tr}\,\Delta_V\,\delta V=\int d^Dx\,\Delta_V(\mathbf{x},\mathbf{x})\delta V(\mathbf{x})=\Delta_V(\mathbf{0})\int d^Dx\,\delta V(\mathbf{x}). \qquad (4.299)$$

where

$$\Delta_V(\mathbf{0})=\int\frac{d^Dp}{(2\pi\hbar)^D}\frac{1}{\mathbf{p}^2/2M+V}=\partial_V[\mathrm{Tr}\log\hat{H}]_{\rm cl}\big|_{V(\mathbf{x})\rightarrow V}. \qquad (4.300)$$

The result of the integration was given in Eq. (1.352).

The second term in the remainder (4.298) reads explicitly

$$-\frac{1}{2}\mathrm{Tr}\ (\Delta_V\,\delta V)^2 = -\frac{1}{2}\int d^Dx \int d^Dx'\,\Delta_V(\mathbf{x},\mathbf{x}')\delta V(\mathbf{x}')\Delta_V(\mathbf{x}',\mathbf{x})\delta V(\mathbf{x}). \tag{4.301}$$

We now make use of the operator relation

$$[f(\hat{A}),\hat{B}] = f'(\hat{A})[\hat{A},\hat{B}] - \frac{1}{2}f''(\hat{A})[\hat{A},[\hat{A},\hat{B}]] + \dots\ , \tag{4.302}$$

to expand

$$\delta V\,\Delta_V = \Delta_V\,\delta V + \Delta_V^2\left[\hat{T},\delta V\right] + \Delta_V^3\left[\hat{T},[\hat{T},\delta V]\right] + \dots\ , \tag{4.303}$$

where $\hat{T}$ is the operator of the kinetic energy $\hat{\mathbf{p}}^2/2M$. It commutes with any function $f(\mathbf{x})$ as follows:

$$[\hat{T},f] \;=\; -\frac{\hbar^2}{2M}\left[\left(\boldsymbol{\nabla}^2 f\right) + 2\left(\boldsymbol{\nabla} f\right)\cdot\boldsymbol{\nabla}\right], \tag{4.304}$$

$$[\hat{T},[\hat{T},f]] \;=\; \frac{\hbar^4}{4M^2}\left\{\left[(\boldsymbol{\nabla}^2)^2 f\right] + 4[\boldsymbol{\nabla}\boldsymbol{\nabla}^2 f]\cdot\boldsymbol{\nabla} + 4[\nabla_i\nabla_i f]\nabla_i\nabla_j\right\}, \tag{4.305}$$

$$\vdots \qquad .$$

Inserting this into (4.301), we obtain a first contribution

$$-\frac{1}{2}\int d^Dx \int d^Dx'\,\Delta_V(\mathbf{x},\mathbf{x}')\Delta_V(\mathbf{x}',\mathbf{x})[\delta V(\mathbf{x})]^2. \tag{4.306}$$

The spatial integrals are performed by going to momentum space, where we derive the general formula

$$\int d^Dx \int d^Dx_1\cdots\int d^Dx_n\,\Delta_V(\mathbf{x},\mathbf{x}_1)\Delta_V(\mathbf{x}_1,\mathbf{x}_2)\cdots\Delta_V(\mathbf{x}_{n-1},\mathbf{x}_n)\Delta_V(\mathbf{x}_n,\mathbf{x})$$
$$= \int\frac{d^Dp}{(2\pi\hbar)^D}\frac{1}{\left(\mathbf{p}^2/2M+V\right)^{n+1}} = \frac{(-1)^n}{n!}\partial_V^n\,\Delta_V(\mathbf{0}). \tag{4.307}$$

This simplifies (4.306) to

$$\frac{1}{2}\,\partial_V\Delta_V(\mathbf{0})\int d^Dx\,[\delta V(\mathbf{x})]^2. \tag{4.308}$$

We may now combine the non-gradient terms of $\delta V(\mathbf{x})$ consisting of the first term in (4.297), of (4.299), and of (4.308), and replace in the latter $\Delta_V(\mathbf{0})$ according to (4.300), to obtain the first three expansion terms of $[\mathrm{Tr}\log\hat{H}]_{\rm cl}$ with the full $\mathbf{x}$-dependent $V(\mathbf{x})$ in Eq. (4.287).

The next contribution to (4.301) coming from (4.304) is

$$\frac{\hbar^2}{4M}\int d^Dx\int d^Dx_1\int d^Dx_2\,\Delta_V(\mathbf{x},\mathbf{x}_1)\Delta_V(\mathbf{x}_1,\mathbf{x}_2)\Delta_V(\mathbf{x}_2,\mathbf{x})$$
$$\times\left\{\left[\boldsymbol{\nabla}^2\delta V(\mathbf{x})\right]\delta V(\mathbf{x}) + 2\left[\boldsymbol{\nabla}\delta V(\mathbf{x})\right]^2 + 2[\boldsymbol{\nabla}\delta V(\mathbf{x})]\delta V(\mathbf{x})\boldsymbol{\nabla}\right\}, \tag{4.309}$$

where the last $\boldsymbol{\nabla}$ acts on the first $\mathbf{x}$ in $\Delta_V(\mathbf{x},\mathbf{x}_1)$, due to the trace. It does not contribute to the integral since it is odd in $\mathbf{x}-\mathbf{x}_1$.

We now perform the integrals over $\mathbf{x}_1$ and $\mathbf{x}_2$ using formula (4.307) and find

$$\frac{\hbar^2}{8M}\int d^Dx\,\left\{\left[\boldsymbol{\nabla}^2\delta V(\mathbf{x})\right][\delta V(\mathbf{x})]+2\left[\boldsymbol{\nabla}\delta V(\mathbf{x})\right]^2\right\}\partial_V^2\Delta_V(\mathbf{0}). \tag{4.310}$$

The first term can be integrated by parts, after which it removes half of the second term.

A third contribution to (4.301) which contains only the lowest gradients of $\delta V(\mathbf{x})$ comes from the third term in (4.305):

$$-\frac{\hbar^4}{8M^2}\int d^Dx\int d^Dx_1\int d^Dx_2\int d^Dx_3\Delta_V(\mathbf{x},\mathbf{x}_1)\Delta_V(\mathbf{x}_1,\mathbf{x}_2)\Delta_V(\mathbf{x}_2,\mathbf{x}_3)\Delta_V(\mathbf{x}_3,\mathbf{x}) \times 4\left[\nabla_i\nabla_j\delta V(\mathbf{x})\right]\delta V(\mathbf{x})\nabla_i\nabla_j, \tag{4.311}$$

where the last $\nabla_i\nabla_j$ acts again on we men the first $\mathbf{x}$ in $\Delta_V(\mathbf{x},\mathbf{x}_1)$, as a consequence of the trace. In momentum space, we encounter the integral

$$\begin{aligned}\int\frac{d^Dp}{(2\pi\hbar)^D}\frac{-4p_ip_j/\hbar^2}{(\mathbf{p}^2/2M+V)^4} &= -\frac{8M}{\hbar^2}\frac{\delta_{ij}}{D}\int\frac{d^Dp}{(2\pi\hbar)^D}\left[\frac{1}{(\mathbf{p}^2/2M+V)^3}-\frac{V}{(\mathbf{p}^2/2M+V)^4}\right]\\ &= -\frac{8M}{\hbar^2}\frac{\delta_{ij}}{D}\left(\frac{1}{2}\partial_V^2+\frac{1}{6}V\partial_V^3\right)\Delta_V(\mathbf{0}).\end{aligned} \tag{4.312}$$

so that the third contribution to (4.301) reads, after an integration by parts,

$$-\frac{\hbar^2}{M}\int d^Dx\left[\boldsymbol{\nabla}\delta V(\mathbf{x})\right]^2\frac{\delta_{ij}}{D}\left(\frac{1}{2}\partial_V^2+\frac{1}{6}V\partial_V^3\right)\Delta_V(\mathbf{0}). \tag{4.313}$$

Combining all gradient terms in $[\boldsymbol{\nabla}V(\mathbf{x})]^2$ and replacing $\Delta_V(\mathbf{0})$ according to (4.300), we recover the previous result (4.292) with the curly brackets (4.293).

For the one-dimensional tracelog, this leads to the formula

$$\mathrm{Tr}\log[-\hbar^2\partial_x^2+V(x)]=\frac{1}{\hbar}\int dx\,\sqrt{V(x)}\left\{1+\frac{\hbar^2}{32}\frac{[V'(x)]^2}{V^3(x)}+\dots\right\}. \tag{4.314}$$

It is a useful exercise to rederive this with the help of the Gelfand-Yaglom method in Section 2.4.

This one-dimensional result can easily be carried to much higher order, with the help of the gradient expansion of the trace of the logarithm of the operator $-\hbar^2\partial_\tau^2+w^2(\tau)$ derived in Subsection 2.15.4. If we replace τ by $x/\hbar$ and $v(\tau)$ by $V(x)$, we obtain from (2.550)–(2.552):

$$\begin{aligned}\frac{1}{\hbar}\int dx\,\sqrt{V(x)}\Bigg\{1-\hbar\frac{V'}{4V^{3/2}}-\hbar^2\left(\frac{5V'^2}{32V^3}-\frac{V''}{8V^2}\right)-\hbar^3\left(\frac{15V'^3}{64V^{9/2}}-\frac{9V'V''}{32V^{7/2}}+\frac{V^{(3)}}{16V^{5/2}}\right)\\ -\ \hbar^4\left(\frac{1105V'^4}{2048V^6}-\frac{221V'^2V''}{256V^5}+\frac{19V''^2}{128V^4}+\frac{7V'V^{(3)}}{32V^4}-\frac{V^{(4)}}{32V^3}\right)\Bigg\}.\end{aligned} \tag{4.315}$$

The terms accompanying the odd powers of $\hbar$ in the curly brackets can be combined to a total derivative and can be ignored if $V(x)$ is the same at the upper and lower boundaries. The $\hbar^2$ term goes over into the $\hbar^2$-term in (4.314). The $\hbar^4$-terms in the curly brackets can be integrated by parts, which brings $V'^4/V^6\to\frac{2}{3}V'^2V''/V^5$, $V'V^{(3)}/V^4\to\frac{7}{2}V'^2V''/V^5-V''^2/V^4$, $V^{(4)}/V^3\to\frac{35}{4}V'^2V''/V^5-\frac{5}{2}V''^2/V^4$, so that the total $\hbar^4$-term is equivalent to $-\hbar^4(-\frac{35}{3072}V'^2V''/V^5+\frac{1}{128}V''^2/V^4)$.

A third procedure to find the gradient expansion is based on an operator calculation [4]. We write the amplitude in (4.265) as

$$\langle\mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}'\rangle=e^{-it[\hat{\mathbf{p}}^2/2M+V(\mathbf{x})]/\hbar}\langle\mathbf{x}|\mathbf{x}'\rangle=\int\frac{d^Dk}{(2\pi)^D}e^{-it[-\hbar^2\boldsymbol{\nabla}^2/2M+V(\mathbf{x})]/\hbar}e^{i\mathbf{k}(\mathbf{x}-\mathbf{x}')}, \tag{4.316}$$

and take the plane wave exponential to the left of the time evolution operator with the help of Lie's expansion formula (1.297)

$$e^{-i\mathbf{kx}}\boldsymbol{\nabla}e^{i\mathbf{kx}}=\boldsymbol{\nabla}+i\mathbf{k}. \tag{4.317}$$

In this way we obtain the formula

$$\langle \mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}'\rangle = \int \frac{d^Dk}{(2\pi)^D} e^{i\mathbf{k}(\mathbf{x}-\mathbf{x}')} e^{-it[-\hbar^2(\boldsymbol{\nabla}+i\mathbf{k})^2/2M+V(\mathbf{x})]/\hbar}, \tag{4.318}$$

We rewrite this as

$$\langle \mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}'\rangle = \int \frac{d^Dk}{(2\pi)^D} e^{i\mathbf{k}(\mathbf{x}-\mathbf{x}')-it\hbar\mathbf{k}^2/2M} e^{-itV(\mathbf{x})/\hbar} C(\mathbf{x};\mathbf{k},t) \tag{4.319}$$

where

$$C(\mathbf{x};\mathbf{k},t) \equiv e^{it[\hbar^2k^2+V(\mathbf{x})]/\hbar} e^{-it[-\hbar^2(\boldsymbol{\nabla}+i\mathbf{k})^2/2M+V(\mathbf{x})]/\hbar} = e^{itV(\mathbf{x})/\hbar} e^{-it[\hat{H}-i\hbar^2\mathbf{k}\boldsymbol{\nabla}/M]/\hbar}. \tag{4.320}$$

We now expand $C(\mathbf{x};\mathbf{k},t)$ in powers of t:

$$C(\mathbf{x};\mathbf{k},t) = \sum_{n=0}^{\infty} t^n C^{(n)}(\mathbf{x};\mathbf{k}). \tag{4.321}$$

The expansion coefficients are most easily obtained by expanding only the second exponential in powers of t and dropping the pure $b$the power o the potential $V(\mathbf{x})$. After this we evaluate the integrals over powers of $\mathbf{k}$ with the help of the Gaussian formula

$$\int \frac{d^Dk}{(2\pi)^D} e^{i\mathbf{k}(\mathbf{x}-\mathbf{x}')-it\hbar\mathbf{k}^2/2M} = \frac{1}{(2\pi i\hbar/M)^{D/2}} e^{iM(\mathbf{x}-\mathbf{x}')^2/2\hbar t}. \tag{4.322}$$

If we define the momentum average with respect to this integral as

$$\langle f(\mathbf{k})\rangle_k \equiv \int \frac{d^Dk}{(2\pi)^D} e^{i\mathbf{k}(\mathbf{x}-\mathbf{x}')-it\hbar\mathbf{k}^2/2M} f(\mathbf{k}) \Big/ \int \frac{d^Dk}{(2\pi)^D} e^{i\mathbf{k}(\mathbf{x}-\mathbf{x}')-it\hbar\mathbf{k}^2/2M}, \tag{4.323}$$

we see that

$$\langle f(\mathbf{k})\rangle_k = f(-i\boldsymbol{\nabla}_{\mathbf{x}}) e^{iM(\mathbf{x}-\mathbf{x}')^2/2\hbar t}, \tag{4.324}$$

so that the expectation values of products of momenta are

$$\begin{aligned}
\langle k_i\rangle_k &= -i\nabla_i\, e^{iM(\mathbf{x}-\mathbf{x}')^2/2\hbar t} = \kappa_i e^{iM(\Delta\mathbf{x})^2/2\hbar t}, \qquad \kappa_i \equiv \frac{M}{\hbar}\frac{(x-x')_i}{t},\\
\langle k_ik_j\rangle_k &= i\nabla_i\nabla_j e^{iM(\mathbf{x}-\mathbf{x}')^2/2\hbar t} = \left(\kappa_i\kappa_j + \frac{M}{i\hbar t}\delta_{ij}\right) e^{iM(\Delta\mathbf{x})^2/2\hbar t},\\
\langle k_ik_jk_k\rangle_k &= -\nabla_i\nabla_j\nabla_k e^{iM\Delta\mathbf{x}^2/2\hbar t} = \left[\kappa_i\kappa_j\kappa_k + \frac{M}{i\hbar t}(\delta_{ij}\kappa_k + \delta_{jk}\kappa_i + \delta_{ki}\kappa_j)\right] e^{iM(\Delta\mathbf{x})^2/2\hbar t}.
\end{aligned} \tag{4.325}$$

The list can easily be continued using Leibnitz' chain rule of differentiation and the derivative $-i\nabla_i\kappa_j = \delta_{ij}M/i\hbar t$. A compact formula for the result is

$$\begin{aligned}
\langle \mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}'\rangle &= \frac{1}{(2\pi i\hbar/M)^{D/2}} \langle C(\mathbf{x},\mathbf{k},t)\rangle_q\\
&= \frac{1}{(2\pi i\hbar/M)^{D/2}} C(\mathbf{x};-i\boldsymbol{\nabla}_{\mathbf{x}},t) e^{iM(\mathbf{x}-\mathbf{x}')^2/2\hbar t}.
\end{aligned} \tag{4.326}$$

Our goal is to obtain the amplitude $\langle \mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}'\rangle$ as a short-time expansion

$$\langle \mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}'\rangle = \frac{e^{iM(\Delta\mathbf{x})^2/2\hbar t}}{(2\pi i\hbar/M)^{D/2}} \sum_{n=0}^{\infty} t^n a_n(\mathbf{x},\Delta\mathbf{x}). \tag{4.327}$$

The above **k**-averages show, however, that the expectations of the coefficients of the expansion (4.321) contain powers of t up to t^n. These must be rearranged to find the power series (4.327). An explicit expression for the expansion coefficients $a_n(\mathbf{x}, \Delta\mathbf{x})$ is found by by rescaling **k** and introducing $\mathbf{q} \equiv \mathbf{k}\sqrt{t\hbar/Mi}$ and rewriting $C(\mathbf{x}; \mathbf{q}\sqrt{iM/t\hbar}, t)$ as

$$C(\mathbf{x}; \mathbf{q}\sqrt{M/t\hbar}, t) = \left[e^{-it[-\hbar^2\boldsymbol{\nabla}^2/2M+V(\mathbf{x})-i\mathbf{q}\sqrt{i\hbar/Mt}\,\hbar\boldsymbol{\nabla}]/\hbar}\right]_{\not{V}^n}, \tag{4.328}$$

where the symbol $[\ldots]_{\not{V}^n}$ indicates that we have to drop all pure powers $V^n(x)$ in the $n$the expansion coefficients of the exponential. With this we can rewrite (4.319) as

$$\langle\mathbf{x}|e^{-i\hat{H}t/\hbar}|\mathbf{x}'\rangle = \frac{e^{iM(\Delta\mathbf{x})^2/2\hbar t}}{(2\pi i\hbar/M)^{D/2}}\left[e^{-\Delta\mathbf{x}^2/2}\left\langle C(\mathbf{x}, \mathbf{q}\sqrt{M/t\hbar}, t)\right\rangle_q\right]_{\not{V}^n}, \tag{4.329}$$

where the **q**-averages are obtained from formulas (4.325) in which and M is set equal to $i\hbar t$. They are defined by the Gaussian integrals

$$\langle\, f(\mathbf{q})\,\rangle_q \equiv \int \frac{d^Dq}{(2\pi)^D} f(\mathbf{q}) e^{i\mathbf{q}\Delta\mathbf{x}-q^2/2} \Bigg/ \int \frac{d^Dq}{(2\pi)^D} e^{i\mathbf{q}\Delta\mathbf{x}-q^2/2}. \tag{4.330}$$

whose power series can be evaluated with the help of the integrals

$$\int \frac{d^Dq}{(2\pi)^D} e^{-q^2/2}\left\{1, q_iq_j, q_{i_1}q_{i_2}q_{i_3}q_4, \ldots\ldots, q_{i_1}q_{i_2}\cdots q_{i_{2n-1}}q_{i_{2n}}, \ldots\right\}$$
$$= \frac{1}{(2\pi)^{D/2}}\left\{1, \delta_{ij}, \delta_{i_1i_2i_3i_4}, \ldots, \delta_{i_1i_2\ldots i_{2n-1}i_{2n}}, \ldots\right\}. \tag{4.331}$$

The results are the analogs of the equations in (4.325):

$$\begin{aligned}
\langle q_i\rangle_q &= -i\nabla_i\, e^{-(\Delta\mathbf{x})^2/2} = \Delta x_i e^{-(\Delta\mathbf{x})^2/2},\\
\langle q_iq_j\rangle_q &= i\nabla_i\nabla_j e^{-(\mathbf{x}-\mathbf{x}')^2/2} = (\Delta x_i\Delta x_j + \delta_{ij})\, e^{-(\Delta\mathbf{x})^2/2},\\
\langle q_iq_jq_q\rangle_q &= -\nabla_i\nabla_j\nabla_k e^{iM\Delta\mathbf{x}^2/2} = \left[\Delta x_i\Delta x_j\Delta x_k + (\delta_{ij}\Delta x_k + \delta_{jk}\Delta x_i + \delta_{ki}\Delta x_j)\right] e^{-(\Delta\mathbf{x})^2/2}.
\end{aligned} \tag{4.332}$$

Here $\delta_{i_1i_2\ldots i_{2n-1}i_{2n}}$ are the so-called *contraction tensors* defined for $n > 2$ recursively by the relation

$$\delta_{i_1\ldots i_{2n}} = \delta_{i_1i_2}\delta_{i_3i_4\ldots i_{2n}} + \delta_{i_1i_3}\delta_{i_2i_4\ldots i_{2n}} + \ldots + \delta_{i_1i_{2n}}\delta_{i_2i_3\ldots i_{2n-1}}. \tag{4.333}$$

With these formulas, the calculation of the diagonal expansion coefficients which have $\Delta\mathbf{x} = 0$ is quite simple. For the sake of generality we also allow for the presence of a vector potential via the minimal substitution law (2.644). In the operator language, where **p** is represented by the differential operator $\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}$ [recall (1.89), the derivatives $\boldsymbol{\nabla}$ in (4.328) must be replaced by the covariant derivatives $\mathbf{D} \equiv \boldsymbol{\nabla} - i(e/c\hbar)\mathbf{A}$. The commutator of these derivatives is no longer zero but proportional to the magnetic field:

$$[D_i, D_j] = -i\epsilon_{ijk}(e/c\hbar)B_k \tag{4.334}$$

Expanding (4.328) up to second order in t we find

$$\begin{aligned}
a_0 &= 1, \quad a_1 = 0,\\
a_2 &= \left\langle \frac{1}{2}(-\hat{H}^2 - V^2) - \frac{\hbar^2}{3!M}\left[\hat{H}(\mathbf{qD})^2 + (\mathbf{qD})\hat{H}(\mathbf{qD}) + (\mathbf{qD})^2\hat{H}\right] - \frac{\hbar^4}{4!M^2}(\mathbf{qD})^4\right\rangle_q.
\end{aligned} \tag{4.335}$$

Performing the momentum averages with the help of (4.332), a_2 becomes

$$a_2 = -\frac{1}{2}(\hat{H}^2 - V^2) - \frac{\hbar^2}{3!M}\left[\hat{H}\mathbf{D}^2 + \mathbf{D}\hat{H}\mathbf{D} + \mathbf{D}^2\hat{H}\right] - \frac{\hbar^4}{8M^2}(\mathbf{D}^4 + D_iD_jD_iD_j + D_i\mathbf{D}^2D_i). \tag{4.336}$$

Inserting here $\hat{H} = -\hbar^2\mathbf{D}^2/2M + V$, this takes the form

$$a_2 = -\frac{1}{2}\left[\left(\frac{\hbar^2\mathbf{D}^2}{2M}\right)^2 - \frac{\hbar^2}{2M}(\mathbf{D}^2V + V\mathbf{D}^2)\right] - \frac{\hbar^2}{3!M}\left[\hat{H}\mathbf{D}^2 + \mathbf{D}\hat{H}\mathbf{D} + \mathbf{D}^2\hat{H}\right]$$
$$-\frac{\hbar^4}{8M^2}(\mathbf{D}^4 + D_iD_jD_iD_j + D_i\mathbf{D}^2D_i). \tag{4.337}$$

After some algebra this becomes

$$a_2 = \frac{\hbar^2}{12M}[\mathbf{D}^2V(x) + V(x)\mathbf{D}^2] - \frac{\hbar^2}{6M}D_iV(x)D_i - \frac{\hbar^4}{48M^2}[D_i, D_j]^2, \tag{4.338}$$

where the derivative terms which have no functions of $\mathbf{x}$ behind it vanish. In the absence of a magnetic field, a_2 reduces to

$$a_2 = \frac{\hbar^2}{12M}\boldsymbol{\nabla}^2V(x), \tag{4.339}$$

in agreement with the second expansion term in Eq. (4.258). A magnetic field $\mathbf{B}$ orthogonal to the 12-plane adds to this a term

$$\Delta a_2^B = -\frac{\hbar^4}{48M^2}([D_1, D_2]^2 + [D_2, D_1]^2) = \frac{\hbar^2}{24M^2}\left(\frac{e}{c}\right)^2 B^2. \tag{4.340}$$

This can be compared to the exact result in Eq. (2.668) where the diagonal amplitude has a unit exponential factor, and the small-t expansion is coming only from the Taylor series of the fluctuation factor $(\omega_L t/2)/\sin(\omega_L t/2)$. This starts out like $1+\omega_L^2t^2/24 = 1+t^2(\hbar^2/24M^2)(e/c)^2B^2$, in agreement with the above magnetic term.

4.9.5 Local Density of States on a Circle

For future use, let us also calculate this determinant for x on a circle $x = (0, b)$, so that, as a side result, we obtain also the gradient expansion of the tracelog of the operator $(-\partial_\tau^2 + \omega^2(\tau))$ at a finite temperature. For this we recall that for a τ-independent frequency, the starting point is Eq. (2.558), according to which the tracelog of the operator $(-\partial_\tau^2 + \omega^2)$ with periodic boundary conditions in $\tau \in (0, \hbar\beta)$ is given by

$$F_\omega = -\frac{\hbar}{\sqrt{\pi}}\int_0^\infty \frac{d\tau}{\tau}\tau^{-1/2}\left[1 + 2\sum_{n=1}^\infty e^{-(n\hbar\beta)^2/4\tau}\right]e^{-\tau\omega^2}. \tag{4.341}$$

The first term is the zero-temperature expression, the second comes from the Poisson summation formula and gives the finite-temperature effects. In the first (classical) term of the density (4.253), the factor $1/\sqrt{2\pi\hbar\tau/M}$ came from the integral over the Boltzmann factor involving the kinetic energy $\int_{-\infty}^\infty (dk/2\pi)e^{-\tau\hbar k^2/2M}$. For periodic boundary conditions in $x \in (0, b)$, this is changed to $(1/b)\sum_m e^{-\tau\hbar k_m^2/2M}$, where $k_m = 2\pi m/b$. By Poisson's formula (1.205), this can be replaced by the integral and an auxiliary sum

$$\frac{1}{b}\sum_m e^{-\tau\hbar k_m^2/2M} = \sum_{n=-\infty}^\infty \int_{-\infty}^\infty \frac{dk}{2\pi}e^{-\tau\hbar k^2/2M + ibkn} = \frac{1}{\sqrt{2\pi\hbar\tau/M}}\sum_{n=-\infty}^\infty e^{-n^2Mb^2/2\hbar\tau}. \tag{4.342}$$

If the sum is inserted into the integral (4.253), we obtain the density $\rho(E; x)$ on a circle of circumference b, with the classical contribution

$$\rho_{\rm cl}(b, E; x) = 2\int_0^\infty \frac{d\tau}{2\pi\hbar}\sum_{n=-\infty}^\infty \frac{e^{-n^2Mb^2/2\hbar\tau - \tau[E-V(x)]/\hbar}}{(2\pi\hbar\tau/M)^{1/2}}. \tag{4.343}$$

The $n = 0$ -term in the sum leads back to the original expression (4.253) on an infinite x-axis. The τ-integrals are now done with the help of formula (2.559) which yields, due to $K_\nu(z) = K_{-\nu}(z)$,

$$\int_0^\infty \frac{d\tau}{\tau} \tau^\nu e^{-n^2Mb^2/2\hbar\tau-[E-V(x)]\tau/\hbar} = 2\left[\frac{nMb}{p(E;x)}\right]^\nu K_\nu(np(E;x)b/\hbar), \tag{4.344}$$

and we obtain, instead of (4.254),

$$\rho_{\rm cl}(b,E;x) = \frac{1}{\pi\hbar}\frac{1}{\sqrt{2\pi\hbar/M}} 2\sum_{n=0}^\infty \left[\frac{nMb}{p(E;x)}\right]^{1/2} K_{1/2}(np(E;x)b/\hbar). \tag{4.345}$$

Inserting $K_{1/2}(z) = \sqrt{\pi/2z}\, e^{-z}$ [recall (2.561)], this becomes

$$\rho_{\rm cl}(b,E;x) = \frac{M}{\pi\hbar}\frac{1}{p(E;x)}\left(1+2\sum_{n=1}^\infty e^{-np(E;x)b/\hbar}\right). \tag{4.346}$$

The sum $\sum_{n=1}^\infty \alpha^n$ is equal to $\alpha/(1-\alpha)$, so that we obtain

$$\rho_{\rm cl}(b,E;x) = \frac{M}{\pi\hbar}\frac{\coth[p(E;x)b/2\hbar]}{p(E;x)} = \frac{M}{\pi\hbar}\frac{\coth\sqrt{2M[E-V(x)]}\,b/2\hbar}{\sqrt{2M[E-V(x)]}}. \tag{4.347}$$

For $b \to \infty$, this reduces to the previous density (4.254).

If we include the higher powers of τ in (4.253), we obtain the generalization of expression (4.255):

$$\rho(b,E;x) = \left\{1 - \frac{\hbar^2}{12M}V''(x)\frac{d^2}{dV^2} - \frac{\hbar^2}{24M}[V'(x)]^2\frac{d^3}{dV^3} + \dots\right\}\rho_{\rm cl}(b,E;x). \tag{4.348}$$

The tracelog is obtained by integrating this over $dE\log E$ from $V(x)$ to infinity. The integral diverges, and we must employ analytic regularization. We proceed as in (4.288), by using the real-time version of (4.343) and rewriting $\log E$ as an integral $-\int_0^\infty (dt'/t')e^{-iEt'/\hbar}$, so that the leading term in (4.348) is given by

$$[{\rm Tr}\log\hat H]_{\rm cl} = -\int_0^b dx\int_{-\infty}^\infty dE\int_{-\infty}^\infty \frac{dt}{2\pi\hbar}\sum_{n=-\infty}^\infty \frac{e^{-in^2Mb^2/2\hbar t+it[E-V(x)]/\hbar}}{(2\pi i\hbar t/M)^{1/2}}\int_0^\infty \frac{dt'}{t'}e^{-iEt'/\hbar}. \tag{4.349}$$

The integral over E leads now to

$$[{\rm Tr}\log\hat H]_{\rm cl} = -\sum_{n=-\infty}^\infty \int_0^b dx\int_0^\infty \frac{dt}{t}\frac{1}{(2\pi i\hbar t/M)^{1/2}}e^{-in^2Mb^2/2\hbar t-itV(x)/\hbar}. \tag{4.350}$$

Deforming again the contour of integration by the substitution $t = -i\tau$, creating the τ^{-1} in the denominator by an integration over $V(x)/\hbar$, we see that

$$\begin{aligned}[{\rm Tr}\log\hat H]_{\rm cl} &= -\pi\int_0^b dx\int_{V(x)}^\infty dV\,\rho_{\rm cl}(b,E;x)\Big|_{E-V(x)\to V}\\ &= \pi\int_0^b dx\int_{V(x)}^\infty \frac{dV}{E_b}\frac{1}{4\pi b}\frac{\coth\frac12\sqrt{V/E_b}}{\frac12\sqrt{V/E_b}},\end{aligned} \tag{4.351}$$

where $E_b \equiv \hbar/2Mb^2$ is the energy associated with the length b. The integration over V produces a factor $\hbar/\tau$ in the integrand.

Thus we obtain

$$\mathrm{Tr}\log\hat{H}=\int_0^b dx\left\{1+\frac{\hbar^2}{24M}[V'(x)]^2\frac{d^3}{dV^3}+\dots\right\}\frac{2}{b}\log\left\{2\sinh\left[\frac{1}{2}\sqrt{\frac{V(x)}{E_b}}\right]\right\}. \tag{4.352}$$

For $M=\hbar^2/2$, this give us the finite-b correction to formula (4.314). Replacing x by the Euclidean time τ, b by $\hbar\beta$, and $V(x)$ by the time-dependent square frequency $\omega^2(\tau)$, we obtain the gradient expansion

$$\mathrm{Tr}\log[-\partial_\tau^2+\omega^2(\tau)]=\int_0^{\hbar\beta}d\tau\left\{1+\frac{[\partial_\tau\omega^2(\tau)]^2}{12}\partial_{\omega^2}^3+\dots\right\}\frac{2}{\hbar\beta}\log\left[2\sinh\frac{\hbar\beta\omega(\tau)}{2}\right]. \tag{4.353}$$

4.9.6 Quantum Corrections to Bohr-Sommerfeld Approximation

The expansion (4.315) can be used to obtain a higher-order expansion of the density of states $\rho(E)$, thereby extending Eq. (4.257). For this we recall Eq. (1.595) according to which we can calculate the exact density of states from the formula

$$\rho(E)=-\frac{1}{\pi}\partial_E\,\mathrm{Im}\,\mathrm{Tr}\log\left\{-\partial_x^2+[V(x)-E]\right\}. \tag{4.354}$$

Integrating this over the energy yields, according to Eq. (1.596), the number of states times π, and thus the simple *exact* quantization condition for a nondegenerate one-dimensional system:

$$-\mathrm{Im}\,\mathrm{Tr}\log\left\{-\partial_x^2+[V(x)-E]\right\}=\pi(n+1/2). \tag{4.355}$$

By comparison with Eq. (4.209) we may define a fullly quantum corrected version of the classical eikonal:

$$S_{\rm qc}(E)=-2\hbar\,\mathrm{Im}\;\mathrm{Tr}\log\left\{-\partial_x^2+[V(x)-E]\right\}. \tag{4.356}$$

The semiclassical expansion of this can be obtained from our earlier result (4.315) by replacing $V(x)\to V(x)-E$, so that $\sqrt{V(x)}\to -i\sqrt{E-V(x)}$, yielding

$$S_{\rm qc}(E)=2\int dx\,\sqrt{E-V(x)}\left\{1+\hbar^2\left[\frac{5V'^2}{32(E-V)^3}+\frac{V''}{8(E-V)^2}\right]\right.$$
$$\left.-\hbar^4\left[\frac{1105V'^4}{2048(E-V)^6}+\frac{221V'^2V''}{256(E-V)^5}+\frac{19V''^2}{128(E-V)^4}+\frac{7V'V^{(3)}}{32(E-V)^4}+\frac{V^{(4)}}{32(E-V)^3}+\dots\right]\right\}. \tag{4.357}$$

The first term in the expansion corresponds to the Bohr-Sommerfeld approximation (4.27), the remaining ones yield the quantum corrections. The integrand agrees, of course, with the WKB expansion of the eikonal (4.14) after inserting the expansion terms $S_0,S_1,\dots$, obtained by integrating the relations (4.20) over the functions $q_0(x),q_1(x),\dots$ of Eq. (4.18).

Using Eq. (4.354) we obtain from $S_{\rm qc}(E)$ the density of states

$$\rho(E)=\frac{1}{2\pi\hbar}S_{\rm qc}(E)=\frac{1}{2\pi\hbar}\int dx\frac{1}{\sqrt{E-V}}\left\{1-\hbar^2\left[\frac{25\,V'^2}{32\,(E-V)^3}+\frac{3\,V''}{8\,(E-V)^2}\right]\right.$$
$$\left.+\hbar^3\left[\frac{12155\,V'^4}{2048\,(E-V)^6}+\frac{1989\,V'^2\,V''}{256\,(E-V)^5}+\frac{133\,V''^2}{128\,(E-V)^4}+\frac{49\,V'\,V^{(3)}}{32\,(E-V)^4}+\frac{5\,V^{(4)}}{32\,(E-V)^3}\right]\right\}. \tag{4.358}$$

Let us calculate the quantum corrections to the semiclassical energies for a purely quartic potential $V(x) = gx^4/4$, where the integral over the first term in (4.357) between the turning points $\pm x_E = \pm(4E/g)^{1/4}$ gave the Bohr-Sommerfeld approximation (4.33). The integrals of the higher terms in (4.357) are divergent, but can be calculated in analytically regularized form using once more the integral formula (4.34). This extends the Bohr-Sommerfeld equation $\nu(E) = n+1/2$ to the exact equation $N(E) \equiv S_{\rm qc}/2\pi\hbar = n + 1/2$ [recall (1.596)]. If we express $N(E)$ in terms of $\nu(E)$ defined in Eq. (4.33) rather than E, we obtain the expansion

$$N(\nu) = \nu - \frac{1}{12\pi\nu} + \frac{11\pi^2}{10368\Gamma^8(\frac{3}{4})\nu^3} + \frac{4697\pi}{1866240\Gamma^8(\frac{3}{4})\nu^5} - \frac{390065\pi^4}{501645312\Gamma^{16}(\frac{3}{4})\nu^7} - \frac{53352893\pi^3}{7739670528\Gamma^{16}(\frac{3}{4})\nu^9} + \dots \;\; = n + 1/2. \tag{4.359}$$

The function is plotted in Fig. 4.359 for increasing orders in y. Given a solution $\nu^{(n)}$ of this equation, we obtain the energy $E^{(n)}$ from Eq. (4.35) with

$$\kappa^{(n)} = [\nu^{(n)} 3\Gamma(3/2)^2/2\sqrt{\pi}]^{4/3}. \tag{4.360}$$

For large n, where $\nu^{(n)} \to n$, we recover the Bohr-Sommerfeld result (4.36). We can invert the

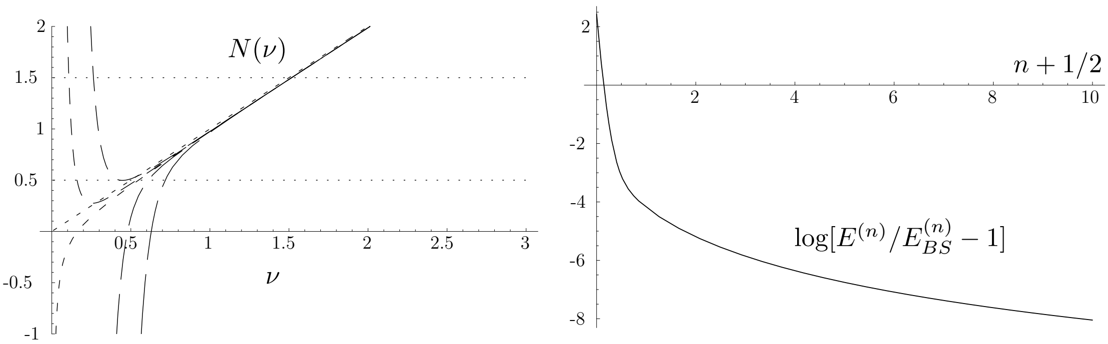

Figure 4.1 Determination of energy eigenvalues $E^{(n)}$ for purely quartic potential $gx^4/4$ in semiclassical expansion. The intersections of $N(\nu)$ with the horizontal lines yield $\nu^{(n)}$, from which $E^{(n)}$ is obtained via Eqs. (4.360) and (4.35). The increasing dash lengths show the expansions of $N(\nu)$ to increasing orders in ν. For the ground state with $n = 0$, the expansion is too divergent to give improvements to the lowest approximation without resumming the series; Right: Comparison between exact and semiclassical energies. The plot is for $\log[E^{(n)}/E^{(n)}_{BS} - 1]$.

series (4.359) and obtain

$$\nu^{(n)} = (n+\tfrac{1}{2})\left[1 + \frac{0.026525823}{(n+\frac{1}{2})^2} - \frac{0.002762954}{(n+\frac{1}{2})^4} - \frac{0.001299177}{(n+\frac{1}{2})^6} + \frac{0.003140091}{(n+\frac{1}{2})^8} + \frac{0.007594497}{(n+\frac{1}{2})^{10}} + \dots \right]. \tag{4.361}$$

The results are compared with the exact ones in Table 4.1, which approach rapidly the Bohr-Sommerfeld limit 0.688 253 702... The approach is illustrated in the right-hand part of Fig. 4.1 where $\log[\nu^{(n)}/(n+\frac{1}{2})^{4/3} - 1] = \log[E^{(n)}/E^{(n)}_{BS} - 1]$ is plotted once for the exact values and once for the semiclassical expansion in Fig. 4.1. The second excited states is very well represented by the series. Although the series is only asymptotic, the results for higher n are excellent. For a detailed study of the convergence properties of the semiclassical expansion see Ref. [5].

Table 4.1 Particle energies in purely anharmonic potential $gx^4/4$ for $n = 0, 2, 4, 6, 8, 10$.

n	$E^{(n)}/(g\hbar/4M^2)^{1/3}$	$\kappa^{(n)}/2(n+1/2)^{4/3}$
0	0.667 986 259 155 777 108 3	0.841 609 948 950 895 526
2	4.696 795 386 863 646 196 2	0.692 125 685 914 981 314
4	10.244 308 455 438 771 076 0	0.689 449 772 359 340 765
6	16.711 890 073 897 950 947 1	0.688 828 486 600 234 466
8	23.889 993 634 572 505 935 5	0.688 590 146 947 993 676
10	31.659 456 477 221 552 442 8	0.688 474 290 179 981 433

Having obtained the quantum-corrected eikonal $S_{\rm qc}(E)$ we can write down a quantum-corrected partition function replacing the classical eikonal $S(E)$ in Eq. (4.236):

$$Z_{\rm qc}(E) = t_{\rm qc}(E)\frac{1}{P_{\rm qc}(1)^{1/2}}\frac{e^{iS_{\rm qc}(E)-i\pi\nu/2}}{1-e^{iS_{\rm qc}(E)-i\pi\nu/2}}. \tag{4.362}$$

where $t_{\rm qc}(E) \equiv S'_{\rm qc}(E)$ [compare (4.198)], and $P_{\rm qc}(1)^{1/2}$ is the quantum-corrected determinant (4.234) whose calculation will require extra work.

4.10 Thomas-Fermi Model of Neutral Atoms

The density of states calculated in the last section forms the basis for the *Thomas-Fermi model* of neutral atoms. If an atom has a large nuclear charge Z, most of the electrons move in orbits with large quantum numbers. For $Z \to \infty$, we expect them to be described by semiclassical limiting formulas, which for decreasing values of Z require quantum corrections. The largest quantum correction is expected for electrons near the nucleus which must be calculated separately.

4.10.1 Semiclassical Limit

Filling up all negative energy states with electrons of both spin directions produces some local particle density $n(\mathbf{x})$, which is easily calculated from the classical local density (4.217) over all negative energies, yielding the *Thomas-Fermi density of states*

$$\rho_{\rm cl}^{(-)}(\mathbf{x}) = \int_{V(\mathbf{x})}^{0} dE\,\rho_{\rm cl}(E;\mathbf{x}) = \left(\frac{M}{2\pi\hbar^2}\right)^{D/2}\frac{1}{\Gamma(D/2+1)}[-V(\mathbf{x})]^{D/2}. \tag{4.363}$$

This expression can also be obtained directly from the phase space integral over the accessible free-particle energies. At each point $\mathbf{x}$, the electrons occupy all levels up to a *Fermi energy*

$$E_F = \frac{p_F(\mathbf{x})^2}{2M} + V(\mathbf{x}). \tag{4.364}$$

The associated local *Fermi momentum* is equal to the local momentum function (4.215) at $E = E_F$:

$$p_F(\mathbf{x}) = p(E_F;\mathbf{x}) = \sqrt{2M[E_F - V(\mathbf{x})]}. \tag{4.365}$$

The electrons fill up the entire Fermi sphere $|\mathbf{p}| \leq p_F(\mathbf{x})$:

$$\rho_{\rm cl}^{(-)}(\mathbf{x}) = \int_{|\mathbf{p}|\leq p_F(\mathbf{x})} \frac{d^D p}{(2\pi\hbar)^D} = \frac{1}{(2\pi\hbar)^D} S_D \int_0^{p_F(\mathbf{x})} dp\, p^{D-1} = \frac{1}{(2\pi\hbar)^D} \frac{2\pi^{D/2}}{\Gamma(D/2)} \frac{p_F^D(\mathbf{x})}{D}. \tag{4.366}$$

For neutral atoms, the Fermi energy is zero and we recover the density (4.363).

By occupying each state of negative energy twice, we find the classical electron density

$$n(\mathbf{x}) = 2\rho_{\rm cl}^{(-)}(\mathbf{x}). \tag{4.367}$$

The potential energy density associated with the levels of negative energy is obviously

$$E_{\rm pot\,TF}^{(-)}(\mathbf{x}) = V(\mathbf{x})\rho_{\rm cl}^{(-)}(\mathbf{x}) = -\left(\frac{M}{2\pi\hbar^2}\right)^{D/2} \frac{1}{\Gamma(D/2+1)}[-V(\mathbf{x})]^{D/2+1}. \tag{4.368}$$

To find the kinetic energy density we integrate

$$\begin{aligned} E_{\rm kin\,TF}^{(-)}(\mathbf{x}) &= \int_{V(\mathbf{x})}^0 dE\,[E - V(\mathbf{x})]\rho_{\rm cl}(E;\mathbf{x}) \\ &= \frac{D/2}{D/2+1} \left(\frac{M}{2\pi\hbar^2}\right)^{D/2} \frac{1}{\Gamma(D/2+1)}[-V(\mathbf{x})]^{D/2+1}. \end{aligned} \tag{4.369}$$

As in the case of the density of states (4.366), this expression can be obtained directly from the phase space integral over the free-particle energies

$$E_{\rm kin\,TF}^{(-)}(\mathbf{x}) = \int_{|\mathbf{p}|\leq p_F(\mathbf{x})} \frac{d^D p}{(2\pi\hbar)^D} \frac{p^2}{2M}. \tag{4.370}$$

Performing the momentum integral on the right-hand side yields the energy density

$$E_{\rm kin\,TF}^{(-)}(\mathbf{x}) = \frac{1}{(2\pi\hbar)^D} S_D \frac{1}{2M} \int_0^{p_F(\mathbf{x})} dp\, p^{D+1} = \frac{1}{(2\pi\hbar)^D} \frac{S_D}{D+2} \frac{p_F^{D+2}(\mathbf{x})}{2M}, \tag{4.371}$$

in agreement with (4.369). The sum of the two is the Thomas-Fermi energy density

$$\begin{aligned} E_{\rm TF}^{(-)}(\mathbf{x}) &= \int_{V(\mathbf{x})}^0 dE\, E\, \rho_{\rm cl}(E;\mathbf{x}) \\ &= -\frac{1}{D/2+1} \left(\frac{M}{2\pi\hbar^2}\right)^{D/2} \frac{1}{\Gamma(D/2+1)}[-V(\mathbf{x})]^{D/2+1}. \end{aligned} \tag{4.372}$$

The three energies are related by

$$E_{\rm TF}^{(-)}(\mathbf{x}) = -\frac{1}{D/2} E_{\rm kin\,TF}^{(-)}(\mathbf{x}) = \frac{1}{D/2+1} E_{\rm pot\,TF}^{(-)}(\mathbf{x}). \tag{4.373}$$

Note that the Thomas-Fermi model can also be applied to ions.[14] Then the energy levels are filled up to a nonzero Fermi energy E_F, so that the density of

[14] H.J. Brudner and S. Borowitz, Phys. Rev. *120*, 2054 (1960).

states (4.363) and the kinetic energy (4.369) have $-V$ replaced by $E_F - V$. This follows immediately from the representations (4.366) and (4.370) where the right-hand sides depend only on $p_F(\mathbf{x}) = \sqrt{2M[E_F - V(\mathbf{x})]}$. In the potential energy (4.368), the expression $(-V)^{D/2+1}$ is replaced by $(-V)(E_F - V)^{D/2}$, whereas in the Thomas-Fermi energy density (4.372) it becomes $(1 - E_F\partial/E_F)(E_F - V)^{D/2+1}$.

4.10.2 Self-Consistent Field Equation

The total electrostatic potential energy $V(\mathbf{x})$ caused by the combined charges of the nucleus and the electron cloud is found by solving the Poisson equation

$$\boldsymbol{\nabla}^2 V(\mathbf{x}) = 4\pi e^2[Z\delta^{(3)}(\mathbf{x}) - n(\mathbf{x})] \equiv 4\pi e^2[n_{\rm C}(\mathbf{x}) - n(\mathbf{x})]. \tag{4.374}$$

The nucleus is treated as a point charge which by itself gives rise to the Coulomb potential

$$V_{\rm C}(\mathbf{x}) = -\frac{Ze^2}{r}. \tag{4.375}$$

Recall that in these units $e^2 = \alpha\hbar c$, where α is the dimensionless fine-structure constant (1.505). A single electron near the ground state of this potential has orbits with diameters of the order na_H/Z, where n is the principal quantum number and a_H the *Bohr radius* of the hydrogen atom, which will be discussed in detail in Chapter 13. The latter is expressed in terms of the electron charge e and mass M as

$$a_H = \frac{\hbar^2}{Me^2} = \frac{1}{\alpha}\lambda_M^{\rm C}. \tag{4.376}$$

This equation implies that a_H is about 137 times larger than the *Compton wavelength* of the electron

$$\lambda_M^{\rm C} \equiv \hbar/Mc \approx 3.861\,593\,23 \times 10^{-13}\,\text{cm}. \tag{4.377}$$

It is convenient to describe the screening effect of the electron cloud upon the Coulomb potential (4.375) by a multiplicative dimensionless function $f(\mathbf{x})$. Restricting our attention to the ground state, which is rotationally symmetric, we shall write the solution of the Poisson equation (4.374) as

$$V(\mathbf{x}) = -\frac{Ze^2}{r}f(r). \tag{4.378}$$

At the origin the function $f(r)$ is normalized to unity,

$$f(0) = 1, \tag{4.379}$$

to ensure that the nuclear charge is not changed by the electrons.

It is useful to introduce a length scale of the electron cloud

$$a_{\rm TF} = \frac{1}{e^2 Z^{1/3}}\frac{2\pi\hbar^2}{M}\left[\frac{\Gamma(5/2)}{2\cdot 4\pi}\right]^{2/3} = \frac{1}{2}\left(\frac{3\pi}{4}\right)^{2/3}\frac{a_H}{Z^{1/3}} \approx 0.8853\frac{a_H}{Z^{1/3}}, \tag{4.380}$$

which is larger than the smallest orbit a_H/Z by roughly a factor $Z^{2/3}$. All length scales will now be specified in units of $a_{\rm TF}$, i.e., we set

$$r = a_{\rm TF}\,\xi. \tag{4.381}$$

In these units, the electron density (4.367) becomes simply

$$n(\mathbf{x}) = -\frac{(2Ze^2M)^{3/2}}{3\pi^2\hbar^3}\left[\frac{f(\xi)}{a_{\rm TF}\,\xi}\right]^{3/2} = \frac{Z}{4\pi a_{\rm TF}^3}\left[\frac{f(\xi)}{\xi}\right]^{3/2}. \tag{4.382}$$

The left-hand side of the Poisson equation (4.374) reads

$$\boldsymbol{\nabla}^2 V(\mathbf{x}) = \frac{1}{r}\frac{d}{dr^2}rV(\mathbf{x}) = -\frac{Ze^2}{a_{\rm TF}^3}\frac{1}{\xi}f''(\xi), \tag{4.383}$$

so that we obtain the self-consistent *Thomas-Fermi equation*

$$f''(\xi) = \frac{1}{\sqrt{\xi}}f^{3/2}(\xi), \qquad \xi > 0. \tag{4.384}$$

This equation ensures that the volume integral over the above electron density is equal to Z. The condition $\xi > 0$ excludes the nuclear charge from the equation, whose correct magnitude is incorporated by the initial condition (4.379).

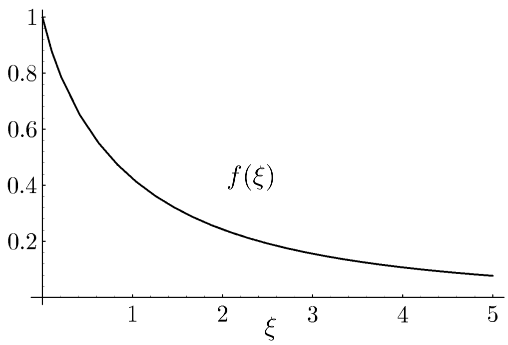

Figure 4.2 Solution for screening function $f(\xi)$ in Thomas-Fermi model.

The differential equation (4.384) is solved numerically by the function shown in Fig. 4.2. Near the origin, it starts out like

$$f(\xi) = 1 - s\xi + \dots\ , \tag{4.385}$$

with a slope

$$s \approx 1.58807. \tag{4.386}$$

The higher powers of the expansion can be calculated recursively as shown in Appendix 4C. The are, however, useless for an evaluation of the function since the expansion is divergent. A technique for evaluating such expansions will be developed in Chapter 5.

For large ξ, the function goes to zero like

$$f(\xi) \approx \frac{144}{\xi^3}. \tag{4.387}$$

This power falloff is a weakness of the model since the true screened potential should fall off exponentially fast. The right-hand side by itself happens to be an exact solution of (4.384), but does not satisfy the desired boundary condition $f(0) = 1$.

4.10.3 Energy Functional of Thomas-Fermi Atom

Let us derive an energy functional whose functional extremization yields the Thomas-Fermi equation (4.384). First, there is the kinetic energy of the spin-up and spin-down electrons in a potential $V(\mathbf{x})$. It is given by the volume integral over twice the Thomas-Fermi expression (4.369):

$$E_{\rm kin}^{(-)} = 2\,\frac{3}{5}\left(\frac{M}{2\pi\hbar^2}\right)^{3/2}\frac{1}{\Gamma(5/2)}\int d^3x\,[-V(\mathbf{x})]^{5/2}. \tag{4.388}$$

This can be expressed in terms of the electron density (4.367) as

$$E_{\rm kin}^{(-)} = \frac{3}{5}\kappa\int d^3x\, n^{5/3}(\mathbf{x}), \tag{4.389}$$

where

$$\kappa \equiv \frac{\hbar}{2M}\left(3\pi^2\right)^{2/3}. \tag{4.390}$$

The potential energy

$$E_{\rm pot}^{(-)} = \int d^3x\, V(\mathbf{x})n(\mathbf{x}) \tag{4.391}$$

is related to $E_{\rm kin}^{(-)}$ via relation (4.373) as

$$E_{\rm pot}^{(-)} = -\frac{5}{3}E_{\rm kin}^{(-)}, \tag{4.392}$$

and the total electron energy in the potential $V(\mathbf{x})$ is

$$E_{\rm e}^{(-)} = E_{\rm kin}^{(-)} + E_{\rm pot}^{(-)} = \frac{2}{5}\,E_{\rm pot}^{(-)}. \tag{4.393}$$

We now observe that if we consider the energy as a functional of an *arbitrary* density $n(\mathbf{x})$,

$$E_{\rm e}^{(-)} = \mathcal{E}_{\rm e}[n] \equiv \frac{3}{5}\kappa\int d^3x\, n^{5/3}(\mathbf{x}) + \int d^3x\, V(\mathbf{x})n(\mathbf{x}), \tag{4.394}$$

the physical particle density (4.367) constitutes a minimum of the functional, which satisfies $\kappa n^{2/3}(\mathbf{x}) = -V(\mathbf{x})$. In the Thomas-Fermi atom, $V(\mathbf{x})$ on the right-hand side of (4.394) is, of course, the nuclear Coulomb potential, i.e.,

$$E_{\rm pot}^{(-)} = E_{\rm C}^{(-)} \equiv \int d^3x\, V_{\rm C}(\mathbf{x})\, n(\mathbf{x}). \tag{4.395}$$

The energy $E_{\rm e}^{(-)}$ has to be supplemented by the energy due to the Coulomb repulsion between the electrons

$$E_{\rm ee}^{(-)} = \mathcal{E}_{\rm ee}[n] = \frac{e^2}{2}\int d^3x d^3x'\, n(\mathbf{x})\frac{1}{|\mathbf{x}-\mathbf{x}'|}n(\mathbf{x}'). \tag{4.396}$$

The physical energy density should now be obtained from the minimum of the combined energy functional

$$\mathcal{E}_{\rm tot}[n] = \frac{3}{5}\kappa\int d^3x\, n^{5/3}(\mathbf{x}) + \int d^3x\, V_{\rm C}(\mathbf{x})\, n(\mathbf{x}) + \frac{e^2}{2}\int d^3x d^3x'\, n(\mathbf{x})\frac{1}{|\mathbf{x}-\mathbf{x}'|}n(\mathbf{x}'). \tag{4.397}$$

Since we are not very familiar with extremizing nonlocal functionals, it will be convenient to turn this into a local functional. This is done as follows. We introduce an auxiliary local field $\varphi(\mathbf{x})$ and rewrite the interaction term as

$$\mathcal{E}_{\rm ee}[n,\varphi] = \mathcal{E}_{\varphi}[n,\varphi] - \mathcal{E}_{\varphi\varphi}[\varphi] \equiv \int d^3x\, \varphi(\mathbf{x})n(\mathbf{x}) - \frac{1}{8\pi e^2}\int d^3x\, \boldsymbol{\nabla}\varphi(\mathbf{x})\boldsymbol{\nabla}\varphi(\mathbf{x}). \tag{4.398}$$

Extremizing this in $\varphi(\mathbf{x})$, under the assumption of a vanishing $\varphi(\mathbf{x})$ at spatial infinity, yields the electric potential of the electron cloud

$$\boldsymbol{\nabla}^2\varphi(\mathbf{x}) = -4\pi e^2 n(\mathbf{x}), \tag{4.399}$$

which is the same as (4.374), but without the nuclear point charge at the origin. Inserting this into (4.398) we reobtain precisely to the repulsive electron-electron interaction energy (4.396).

Replacing the last term in (4.397) by the functional (4.398), we obtain a total energy functional $\mathcal{E}_{\rm tot}[n,\varphi]$, for which it is easy to find the extremum with respect to $n(\mathbf{x})$. This lies at

$$\kappa\, n^{2/3}(\mathbf{x}) = -V(\mathbf{x}), \tag{4.400}$$

where

$$V(\mathbf{x}) = V_{\rm C}(\mathbf{x}) + \varphi(\mathbf{x}) \tag{4.401}$$

is the combined Thomas-Fermi potential of the nucleus and the electron cloud solving the Poisson equation (4.374).

If the extremal density (4.400) is inserted into the total energy functional $\mathcal{E}_{\rm tot}[n,\varphi]$, we may use the relation (4.392) to derive the following functional of $\varphi(\mathbf{x})$:

$$\mathcal{E}_{\rm tot}[\varphi] = -\frac{2}{5}\int d^3x\, V(\mathbf{x})n(\mathbf{x}) + \frac{1}{8\pi e^2}\int d^3x\, \varphi(\mathbf{x})\boldsymbol{\nabla}^2\varphi(\mathbf{x}). \tag{4.402}$$

When extremizing this expression with respect to $\varphi(\mathbf{x})$ we must remember that $V(\mathbf{x}) = V_{\rm C}(\mathbf{x}) + \varphi(\mathbf{x})$ is also present in $n(\mathbf{x})$ with a power $3/2$. The extremum lies therefore again at a field satisfying the Poisson equation (4.399).

4.10.4 Calculation of Energies

We now proceed to calculate explicitly the energies occuring in Eq. (4.402). They turn out to depend only on the slope of the screening function $f(\xi)$ at the origin. Consider first $E_{\rm pot}^{(-)}$. The common prefactor appearing in all energy expressions can be expressed in terms of the Thomas-Fermi length scale $a_{\rm TF}$ of Eq. (4.380) as

$$2\,\frac{M^{3/2}}{(2\pi\hbar)^{3/2}}\frac{4\pi}{\Gamma(5/2)}e^3=\frac{Z^{-1/2}}{a_{\rm TF}^{3/2}}. \tag{4.403}$$

We therefore obtain the simple energy integral involving the screening function $f(\xi)$:

$$E_{\rm pot}^{(-)}=-\frac{Z^2e^2}{a}\int_0^\infty d\xi\frac{1}{\sqrt{\xi}}f^{5/2}(\xi). \tag{4.404}$$

The interaction energy between the electrons at the extremal $\varphi(\mathbf{x})$ satisfying (4.399) becomes simply

$$E_{\rm ee}^{(-)}=\frac{1}{2}\int d^3x\,n(\mathbf{x})\varphi(\mathbf{x}), \tag{4.405}$$

which can be rewritten as

$$E_{\rm ee}^{(-)}=\frac{1}{2}\int d^3x\,n(\mathbf{x})[V(\mathbf{x})-V_{\rm C}(\mathbf{x})]=\frac{1}{2}E_{\rm pot}^{(-)}-\frac{1}{2}E_{\rm C}^{(-)}. \tag{4.406}$$

Inserting this into (4.402) we find the alternative expression for the total energy

$$E_{\rm tot}^{(-)}=\frac{2}{5}E_{\rm pot}^{(-)}-E_{\rm ee}^{(-)}=-\frac{1}{10}E_{\rm pot}^{(-)}+\frac{1}{2}E_{\rm C}^{(-)}. \tag{4.407}$$

The energy $E_{\rm C}^{(-)}$ of the electrons in the Coulomb potential is evaluated as follows. Replacing $n(\mathbf{x})$ by $-\boldsymbol{\nabla}^2\varphi(\mathbf{x})/4\pi e^2$, we have, after two partial integrations with vanishing boundary terms and recalling (4.374),

$$E_{\rm C}^{(-)}=-\frac{1}{4\pi e^2}\int d^3x\,\varphi(\mathbf{x})\boldsymbol{\nabla}^2V_{\rm C}(\mathbf{x})=-\int d^3x\,\varphi(\mathbf{x})n_{\rm C}(\mathbf{x}). \tag{4.408}$$

Now, since

$$\varphi(\mathbf{x})=V(\mathbf{x})-V_{\rm C}(\mathbf{x})=-\frac{Ze^2}{r}[f(\xi)-1],\qquad n_{\rm C}=Z\delta^{(3)}(\mathbf{x}), \tag{4.409}$$

we see that the Coulomb energy $E_{\rm C}^{(-)}$ depends only on $\varphi(\mathbf{0})$, which can be expressed in terms of the negative slope (4.386) of the function $f(\xi)$ as:

$$\varphi(\mathbf{0})=\frac{Ze^2}{a}s. \tag{4.410}$$

Thus we obtain

$$E_{\rm C}^{(-)}=-\frac{Z^2e^2}{a}s. \tag{4.411}$$

We now turn to the integral associated with the potential energy in Eq. (4.404):

$$I[f] = \int_0^\infty d\xi \frac{1}{\sqrt{\xi}} f^{5/2}(\xi). \tag{4.412}$$

By a trick it can again be expressed in terms of the slope parameter s. We express the energy functional (4.402) in terms of the screening function $f(\xi)$ as

$$\mathcal{E}_{\rm tot}[\varphi] = -\frac{Z^2 e^2}{a_{\rm TF}} \varepsilon[f], \tag{4.413}$$

with the dimensionless functional

$$\varepsilon[f] \equiv \frac{2}{5} I[f] + \frac{1}{2} J[f] = \int_0^\infty d\xi \left\{ \frac{2}{5} \frac{1}{\sqrt{\xi}} f^{5/2}(\xi) - \frac{1}{2} [f(\xi) - 1] f''(\xi) \right\}. \tag{4.414}$$

The second integral can also be rewritten as

$$J[f] = \int_0^\infty d\xi \, [f'(\xi)]^2. \tag{4.415}$$

This follows from a partial integration

$$J[f] = -\int_0^\infty d\xi \, [f(\xi) - 1] f''(\xi) = \int_0^\infty d\xi \, [f'(\xi)]^2 - [f(\xi) - 1] f'(\xi)|_0^\infty, \tag{4.416}$$

inserting the boundary condition $f(\xi) - 1 = 0$ at $\xi = 0$ and $f'(\xi) = 0$ at $\xi = \infty$.

We easily verify that the Euler-Lagrange equation following from $\varepsilon[f]$ is the Thomas-Fermi differential equation (4.384).

As a next step in calculating the integrals I and J, we make use of the fact that under a scaling transformation

$$f(\xi) \to \bar{f}(\xi) = f(\lambda \xi), \tag{4.417}$$

the functional $\varepsilon[f]$ goes over into

$$\varepsilon_\lambda[f] = \frac{2}{5} \lambda^{-1/2} I[f] + \frac{1}{2} \lambda J[f]. \tag{4.418}$$

This must be extremal at $\lambda = 1$, from which we deduce that for $f(\xi)$ satisfying the differential equation (4.384):

$$I[f] = \frac{5}{2} J[f]. \tag{4.419}$$

This relation permits us to express the integral J in terms of the slope of $f(\xi)$ at the origin. For this we separate the two terms in (4.416), and replace $f''(\xi)$ via the Thomas-Fermi differential equation (4.384) to obtain

$$J = -\int_0^\infty d\xi \, f(\xi) f''(\xi) + \int_0^\infty d\xi \, f''(\xi) = -\int_0^\infty d\xi \, \frac{1}{\sqrt{\xi}} f^{5/2}(\xi) - f'(0) = -I + s. \tag{4.420}$$

Together with (4.419), this implies

$$I = \frac{5}{7}\,s, \qquad J = \frac{2}{7}\,s. \tag{4.421}$$

Thus we obtain for the various energies:

$$\begin{aligned} E_{\rm kin}^{(-)} &= \frac{3}{5}\frac{Z^2e^2}{a_{\rm TF}}\frac{5}{7}\,s, & E_{\rm pot}^{(-)} &= -\frac{Z^2e^2}{a_{\rm TF}}\frac{5}{7}\,s, & E_{\rm e}^{(-)} &= -\frac{2}{5}\frac{Z^2e^2}{a_{\rm TF}}\frac{5}{7}\,s,\\ E_{\rm C}^{(-)} &= -\frac{Z^2e^2}{a_{\rm TF}}\,s, & E_{\rm ee}^{(-)} &= \frac{Z^2e^2}{a_{\rm TF}}\frac{1}{7}\,s, \end{aligned} \tag{4.422}$$

and the total energy is

$$E_{\rm tot}^{(-)} = \frac{2}{5}\,E_{\rm pot}^{(-)} - E_{\rm ee}^{(-)} = -\frac{1}{10}E_{\rm pot}^{(-)} + \frac{1}{2}E_{\rm C}^{(-)} = -\frac{3}{7}\frac{Z^2e^2}{a_{\rm TF}}\,s \approx -0.7687\,Z^{7/3}\frac{e^2}{a_H}. \tag{4.423}$$

The energy increases with the nuclear charge Z like $Z^2/a_{\rm TF} \propto Z^{7/3}$.

At the extremum, we may express the energy functional $\varepsilon[f]$ with the help of (4.420) as

$$\bar\varepsilon[f] = -\frac{1}{10}\int_0^\infty d\xi \frac{1}{\sqrt{\xi}} f^{5/2}(\xi) - \frac{1}{2}f(0)f'(0), \tag{4.424}$$

or in a form corresponding to (4.407):

$$\bar{\bar\varepsilon}[f] \equiv -\frac{1}{10}I[f] + \frac{1}{2}J_{\rm C}[f] = -\frac{1}{10}\int_0^\infty d\xi\frac{1}{\sqrt{\xi}}f^{5/2}(\xi) + \frac{1}{2}\int_0^\infty d\xi\frac{1}{\sqrt{\xi}}f^{3/2}(\xi). \tag{4.425}$$

Using the Thomas-Fermi equation (4.384), the second integral corresponding to the Coulomb energy can be reduced to a surface term yielding $J_{\rm C}[f] = s$, so that (4.425) gives the same total energy as (4.414).

4.10.5 Virial Theorem

Note that the total energy is equal in magnitude and opposite in sign to the kinetic energy. This is a general consequence of the so-called *viral theorem* for Coulomb systems. The kinetic energy of the many-electron Schrödinger equation contains the Laplace differential operator proportional to $\boldsymbol{\nabla}^2$, whereas the Coulomb potentials are proportional to $1/r$. For this reason, a rescaling $x \to \lambda x$ changes the sum of kinetic and total potential energies

$$E_{\rm tot} = E_{\rm kin} + E_{\rm pot} \tag{4.426}$$

into

$$\lambda^2 E_{\rm kin} + \lambda E_{\rm pot}. \tag{4.427}$$

Since this must be extremal at $\lambda = 1$, one has the relation

$$2E_{\rm kin} + E_{\rm pot} = 0, \tag{4.428}$$

which proves the virial theorem

$$E_{\rm tot} = -E_{\rm kin}. \tag{4.429}$$

In the Thomas-Fermi model, the role of total potential energy is played by the combination $E_{\rm pot}^{(-)} - E_{\rm ee}^{(-)}$, and Eq. (4.422) shows that the theorem is satisfied.

4.10.6 Exchange Energy

In many-body theory it is shown that due to the Fermi statistics of the electronic wave functions, there exists an additional electron-electron *exchange interaction* which we shall now take into account. For this purpose we introduce the bilocal density of all states of negative energy by analogy with (4.363):

$$\rho_{\rm cl}^{(-)}(\mathbf{x}_b, \mathbf{x}_a) = \int_{V(\bar{\mathbf{x}})}^{0} dE \rho_{\rm cl}^{(-)}(E; \mathbf{x}_b, \mathbf{x}_a). \tag{4.430}$$

In three dimensions we insert (4.280) and rewrite the energy integral as

$$\int_{V(\bar{\mathbf{x}})}^{0} dE = \frac{1}{M} \int_{0}^{p_F(\bar{\mathbf{x}})} dp\, p\,, \tag{4.431}$$

with the Fermi momentum $p_F(\bar{\mathbf{x}})$ of the neutral atom at the point $\bar{\mathbf{x}}$ [see (4.365)]. In this way we find

$$\rho_{\rm cl}^{(-)}(\mathbf{x}_b, \mathbf{x}_a) = \frac{p_F^3(\bar{\mathbf{x}})}{2\pi^2\hbar^3} \frac{1}{z^3} (\sin z - z \cos z), \tag{4.432}$$

where

$$z \equiv p_F(\bar{\mathbf{x}}) R/\hbar. \tag{4.433}$$

This expression can, incidentally, be obtained alternatively by analogy with the local expression (4.366) from a momentum integral over free wavefunctions

$$\rho_{\rm cl}^{(-)}(\mathbf{x}_b, \mathbf{x}_a) = \int_{|\mathbf{p}| \leq p_F(\bar{\mathbf{x}})} \frac{d^3p}{(2\pi\hbar)^D} e^{i\mathbf{p}(\mathbf{x}_b - \mathbf{x}_a)/\hbar}. \tag{4.434}$$

The simplest way to derive the exchange energy is to re-express the density of states $\rho^{(-)}(E; \mathbf{x})$ as the diagonal elements of the bilocal density

$$\rho^{(-)}(\mathbf{x}) = \rho^{(-)}(\mathbf{x}_b, \mathbf{x}_a) \tag{4.435}$$

and rewrite the electron-electron energy (4.396) as

$$E_{\rm ee}^{(-)} = 4 \times \frac{e^2}{2} \int d^3x d^3x' \rho^{(-)}(\mathbf{x}, \mathbf{x}) \frac{1}{4\pi|\mathbf{x} - \mathbf{x}'|} \rho^{(-)}(\mathbf{x}', \mathbf{x}'). \tag{4.436}$$

The factor 4 accounts for the four different spin pairs in the first and the second bilocal density.

$$\uparrow\ \uparrow;\uparrow\ \uparrow;\quad \uparrow\ \uparrow;\downarrow\ \downarrow;\quad \downarrow\ \downarrow;\uparrow\ \uparrow;\quad \downarrow\ \downarrow;\downarrow\ \downarrow.$$

In the first and last case, there exists an exchange interaction which is obtained by interchanging the second arguments of the bilocal densities and changing the sign. This yields

$$E_{\rm exch}^{(-)} = -2 \times \frac{e^2}{2} \int d^3x d^3x' \rho^{(-)}(\mathbf{x}, \mathbf{x}') \frac{1}{4\pi|\mathbf{x} - \mathbf{x}'|} \rho^{(-)}(\mathbf{x}', \mathbf{x}). \tag{4.437}$$

The integral over $\mathbf{x}-\mathbf{x}'$ may be performed using the formula

$$\int_0^\infty dz z^2 \frac{1}{z}\left[\frac{1}{z^3}(\sin z - z\cos z)\right]^2 = \frac{1}{4}, \tag{4.438}$$

and we obtain the exchange energy

$$E_{\rm exch}^{(-)} = -\frac{e^2}{4\pi^3}\int d^3\bar{\mathbf{x}}\left[\frac{p_F(\bar{\mathbf{x}})}{\hbar}\right]^4. \tag{4.439}$$

Inserting

$$p_F(\mathbf{x}) = \sqrt{\frac{2Z}{a_H a_{\rm TF}}\frac{f(\xi)}{\xi}}, \tag{4.440}$$

the exchange energy becomes

$$E_{\rm exch}^{(-)} = -\frac{4}{\pi^2}\frac{a_{\rm TF}}{a_H} I_2 \frac{Z^2}{a_H} \approx -0.3588\, Z^{5/3}\frac{e^2}{a_H} I_2, \tag{4.441}$$

where I_2 is the integral

$$I_2 \equiv \int_0^\infty d\xi\, f^2(\xi) \approx 0.6154. \tag{4.442}$$

Hence we obtain

$$E_{\rm exch}^{(-)} \approx -0.2208 Z^{5/3}\frac{e^2}{a_H}, \tag{4.443}$$

giving rise to a correction factor

$$C_{\rm exch}(Z) = 1 + 0.2872\, Z^{-2/3} \tag{4.444}$$

to the Thomas-Fermi energy (4.423).

4.10.7 Quantum Correction Near Origin

The Thomas-Fermi energy with exchange corrections calculated so far would be reliable for large-Z only if the potential was smooth so that the semiclassical approximation is applicable. Near the origin, however, the Coulomb potential is singular and this condition is no longer satisfied. Some more calculational effort is necessary to account for the quantum effects near the singularity, based on the following observation [6]. For levels with an energy smaller than some value $\varepsilon < 0$, which is large compared to the ground state energy Z^2e^2/a_H, but much smaller than the average Thomas Fermi energy per particle $Z^2e^2/aZ \sim Z^2e^2/a_H Z^{2/3}$, i.e., for

$$\frac{Z^2e^2}{a_H}\frac{1}{Z^{2/3}} \ll -\varepsilon \ll \frac{Z^2e^2}{a_H}, \tag{4.445}$$

we have to recalculate the energy. Let us define a parameter ν by

$$-\varepsilon \equiv \frac{Z^2}{2a_H\nu^2}, \tag{4.446}$$

which satisfies

$$1 \ll \nu^2 \ll Z^{2/3}. \tag{4.447}$$

The contribution of the levels with energy

$$\frac{p^2}{2M} - \frac{Ze^2}{r} < -\varepsilon \tag{4.448}$$

to $E^{(-)}_{\rm kin,TF}$ is given by an integral like (4.371), where the momentum runs from 0 to $p_{-\varepsilon}(\mathbf{x}) = \sqrt{2M[-\varepsilon - V(\mathbf{x})]}$. In the kinetic energy (4.372), the potential $V(\mathbf{x})$ is simply replaced by $-\varepsilon - V(\mathbf{x})$, and the spatial integral covers the small sphere of radius $r_{\rm max}$, where $-\varepsilon - V(\mathbf{x}) > 0$. For the screening function $f(\xi) = V(r)r/Ze^2$ this implies the replacement

$$f(\xi) \to [-\varepsilon - V(r)]\frac{r}{Ze^2} = f(\xi) - \xi/\xi_{\rm m}, \tag{4.449}$$

where

$$\xi_{\rm m} = \frac{2\nu^2}{Z}\frac{a_H}{a} \tag{4.450}$$

is small of the order $Z^{-2/3}$. Using relation (4.429) between total and kinetic energies we find the additional total energy

$$\Delta E^{(-)}_{\rm tot} = -\frac{3}{5}\frac{Z^2e^2}{a}\int_0^{\xi_{\rm max}} d\xi \frac{1}{\sqrt{\xi}}\left[f(\xi) - \xi/\xi_{\rm m}\right]^{5/2}, \tag{4.451}$$

where $\xi_{\rm max} \equiv r_{\rm max}/a$ is the place at which the integrand vanishes, i.e., where

$$\xi_{\rm max} = Ze^2\varepsilon f(\xi_{\rm max})/a, \tag{4.452}$$

this being the dimensionless version of

$$-\varepsilon - V(r_{\rm max}) = 0. \tag{4.453}$$

Under the condition (4.447), the slope of $f(\xi)$ may be ignored and we can use the approximation

$$\xi_{\rm max} \approx \xi_{\rm m} \tag{4.454}$$

corresponding to $r_{\rm max} = Ze^2/\varepsilon$, with an error of relative order $Z^{-2/3}$. After this, the integral

$$\int_0^{1/c} d\lambda \frac{1}{\sqrt{\lambda}}(1 - c\lambda)^{5/2} \;=\; \frac{1}{\sqrt{c}}B\left(1/2, 7/2\right) = \frac{1}{\sqrt{c}}\frac{5}{8}\pi, \tag{4.455}$$

yielding a Beta function $B(x, y) \equiv \Gamma(x)\Gamma(y)/\Gamma(x + y)$, leads to an energy

$$\Delta E^{(-)}_{\rm tot} = -\frac{3}{5}\frac{Z^2e^2}{a}\frac{5}{8}\frac{\pi}{M}\sqrt{\frac{a_H}{2a}}\frac{\nu}{Z^{1/3}}, \tag{4.456}$$

showing that the correction to the energy will be of relative order $1/Z^{1/3}$. Expressing a in terms of a_H via (4.380), we find

$$\Delta E_{\rm tot}^{(-)} = -\frac{Z^2 e^2}{a_H}\nu. \tag{4.457}$$

The point is now that this energy can easily be calculated more precisely. Since the slope of the screening function can be ignored in the small selected radius, the potential is Coulomb-like and we may simply sum all occupied exact quantum-mechanical energies E_n in a Coulomb potential $-Ze^2/r$ which lie below the total energy $-\varepsilon$. They depend on the principal quantum number n in the well-known way:

$$E_n = -\frac{Z^2 e^2}{a_H}\frac{1}{2n^2}. \tag{4.458}$$

Each level occurs with angular momentum $l = 0, \dots, n-1$, and with two spin directions so that the total degeneracy is $2n^2$. By Eq. (4.446), the maximal energy $-\varepsilon$ corresponds to a maximal quantum number $n_{\rm max} = \nu$. The sum of all energies E_n up to the energy ε is therefore given by

$$\begin{aligned} \Delta_{\rm QM} E_{\rm tot}^{(-)} &= -2\frac{Z^2 e^2}{a_H}\frac{1}{2}\sum_{n=0}^{\nu} 1 \\ &= -\frac{Z^2 e^2}{a_H}\left[\nu\right], \end{aligned} \tag{4.459}$$

where $[\nu]$ is the largest integer number smaller than ν. The difference between the semiclassical energy (4.456) and the true quantum-mechanical one (4.459) yields the desired quantum correction

$$\Delta E_{\rm corr}^{(-)} = -\frac{Z^2 e^2}{a_H}([\nu] - \nu). \tag{4.460}$$

For large ν, we must average over the step function $[\nu]$, and find

$$\langle [\nu] \rangle = \nu - \frac{1}{2}, \tag{4.461}$$

and therefore

$$\Delta E_{\rm corr}^{(-)} = \frac{Z^2 e^2}{a_H}\frac{1}{2}. \tag{4.462}$$

This is the correction to the energy of the atom due to the failure of the quasi-classical expansion near the singularity of the Coulomb potential. With respect to the Thomas-Fermi energy (4.423) which grows with increasing nuclear charge Z like $-0.7687\, Z^{7/3} e^2/a_H$, this produces a correction factor

$$C_{\rm sing}(Z) = 1 - \frac{7a_{\rm TF}}{6a_H s} \approx 1 - 0.6504\, Z^{-1/3} \tag{4.463}$$

to the Thomas-Fermi energy (4.423).

4.10.8 Systematic Quantum Corrections to Thomas-Fermi Energies

Just as for the density of states in Section 4.9, we can derive the quantum corrections to the energies in the Thomas-Fermi atom. The electrons fill up all negative-energy levels in the combined potential $V(\mathbf{x})$. The density of states in these levels can be selected by a Heaviside function of the negative Hamiltonian operator as follows:

$$\rho^{(-)}(\mathbf{x}) = \langle \mathbf{x}|\Theta(-\hat{H})|\mathbf{x}\rangle. \tag{4.464}$$

Using the Fourier representation (1.312) for the Heaviside function we write

$$\Theta(-\hat{H}) = \int_{-\infty}^{\infty} \frac{dt}{2\pi i(t-i\eta)} e^{-i\hat{H}t/\hbar}, \tag{4.465}$$

and obtain the integral representation

$$\rho^{(-)}(\mathbf{x}) = \int_{-\infty}^{\infty} \frac{dt}{2\pi i(t-i\eta)} (\mathbf{x}\,t|\mathbf{x}\,0). \tag{4.466}$$

Inserting the short-time expansion (4.258), and the correspondence $t \to i\hbar d/dV$ in the time integral, we find

$$\rho(\mathbf{x}) = \left\{1 - \frac{\hbar^2}{12M}\boldsymbol{\nabla}^2 V(\mathbf{x})\frac{d^2}{dV^2} - \frac{\hbar^2}{24M}[\boldsymbol{\nabla}V(\mathbf{x})]^2\frac{d^3}{dV^3} + \ldots\right\}\rho_{\rm TF}(\mathbf{x}). \tag{4.467}$$

The potential energy is simply given by

$$E^{(-)}_{\rm pot}(\mathbf{x}) = \langle \mathbf{x}|V(\mathbf{x})\Theta(-\hat{H})|\mathbf{x}\rangle = \int d^3x V(\mathbf{x})\rho^{(-)}(\mathbf{x}). \tag{4.468}$$

With (4.467), this becomes

$$E^{(-)}_{\rm pot}(\mathbf{x}) = V(\mathbf{x})\left\{1 - \frac{\hbar^2}{12M}\boldsymbol{\nabla}^2 V(\mathbf{x})\frac{d^2}{dV^2} - \frac{\hbar^2}{24M}[\boldsymbol{\nabla}V(\mathbf{x})]^2\frac{d^3}{dV^3} + \ldots\right\}\rho_{\rm TF}(\mathbf{x}). \tag{4.469}$$

For the energy of all negative-energy states we may introduce a density function

$$E^{(-)}(\mathbf{x}) = \langle \mathbf{x}|\hat{H}\Theta(-\hat{H})|\mathbf{x}\rangle. \tag{4.470}$$

The derivative of this with respect to $V(\mathbf{x})$ is equal to the density of states (4.464):

$$\frac{\partial}{\partial V(\mathbf{x})} E^{(-)}(\mathbf{x}) = \rho^{(-)}(\mathbf{x}). \tag{4.471}$$

This follows right-away from $\partial \hat{H}/\partial V(\mathbf{x}) = 1$ and $\partial[x\Theta(x)]/\delta x = \Theta(x)$.

Inserting the representation (4.465), the factor $\hat{H}$ can be obtained by applying the differential operator $i\hbar\partial_t$ to the exponential function. After a partial integration, we arrive at the integral representation

$$E^{(-)}(\mathbf{x}) = i\hbar\int_{-\infty}^{\infty} \frac{dt}{2\pi i(t-i\eta)^2} (\mathbf{x}\,t|\mathbf{x}\,0). \tag{4.472}$$

Inserting on the right-hand side the expansion (4.258), the leading term produces the local *Thomas-Fermi energy* density (4.372):

$$E^{(-)}_{\rm TF}(\mathbf{x}) = -\left(\frac{M}{2\pi\hbar}\right)^{D/2} \frac{1}{\Gamma(D/2+2)}[-V(\mathbf{x})]^{D/2+1}. \tag{4.473}$$

The short-time expansion terms yield, with the correspondence $t \to i\hbar d/dV$, the energy including the quantum corrections

$$E^{(-)}(\mathbf{x}) = \left\{ 1 - \frac{\hbar^2}{12M} \boldsymbol{\nabla}^2 V(\mathbf{x}) \frac{d^2}{dV^2} - \frac{\hbar^2}{24M} [\boldsymbol{\nabla} V(\mathbf{x})]^2 \frac{d^3}{dV^3} + \ldots \right\} E^{(-)}_{\rm TF}(\mathbf{x}). \tag{4.474}$$

One may also calculate selectively the kinetic energy density from the expression

$$E^{(-)}(\mathbf{x}) = \frac{1}{2M} \langle \mathbf{x} | \hat{\mathbf{p}}^2 \Theta(-\hat{H}) | \mathbf{x} \rangle. \tag{4.475}$$

This can obviously be extracted from (4.472) by a differentiation with respect to the mass:

$$\begin{aligned} E^{(-)}_{\rm kin}(\mathbf{x}) &= -M \frac{\partial}{\partial M} i\hbar \int_{-\infty}^{\infty} \frac{dt}{2\pi i (t - i\eta)^2} \langle \mathbf{x} | e^{-i\hat{H}t/\hbar} | \mathbf{x} \rangle \\ &= -M \frac{\partial}{\partial M} E^{(-)}(\mathbf{x}). \end{aligned} \tag{4.476}$$

According to Eq. (4.474), the first quantum correction to the energy $E^{(-)}_{\rm e}$ is

$$\begin{aligned} \Delta E^{(-)}_{\rm e} &= -\int d^3x \left[-\frac{\hbar^2}{12M} \boldsymbol{\nabla}^2 V \frac{d^2}{dV^2} - \frac{\hbar^2}{24M} (\boldsymbol{\nabla} V)^2 \frac{d^3}{dV^3} \right] \\ &\qquad\qquad \times\ 2\, \frac{2}{5} \left(\frac{M}{2\pi\hbar} \right)^{3/2} \frac{1}{\Gamma(5/2)} (-V)^{5/2} \\ &= \frac{\sqrt{2M}}{12\hbar\pi^2} \int d^3x \left[(-V)^{1/2} \boldsymbol{\nabla}^2 V - \frac{1}{4} (-V)^{-3/2} (\boldsymbol{\nabla} V)^2 \right]. \end{aligned} \tag{4.477}$$

It is useful to bring the second term to a more convenient form. For this we note that by the chain rule of differentiation

$$\boldsymbol{\nabla}^2 V^{3/2} = \frac{3}{2} \boldsymbol{\nabla} \left[V^{1/2} \boldsymbol{\nabla} V \right] = \frac{3}{4} \left[V^{-1/2} (\boldsymbol{\nabla} V)^2 + 2 V^{1/2} \boldsymbol{\nabla}^2 V \right]. \tag{4.478}$$

As a consequence we find

$$\Delta E^{(-)}_{\rm e} = \frac{\sqrt{2M}}{24\hbar\pi^2} \int d^3x \left[(-V)^{1/2} \boldsymbol{\nabla}^2 V - \frac{2}{3} \boldsymbol{\nabla}^2 (-V)^{3/2} \right]. \tag{4.479}$$

This energy evaluated with the potential V determined above describes directly the lowest correction to the total energy. To prove this, consider the new total energy [recall (4.398)]

$$E^{(-)}_{\rm tot} = E^{(-)}_{\rm e} + \Delta E^{(-)}_{\rm e} - \mathcal{E}_{\varphi\varphi}[\varphi]. \tag{4.480}$$

Extremizing this in the field $\varphi(\mathbf{x})$ and denoting the new extremal field by $\varphi(\mathbf{x}) + \Delta\varphi(\mathbf{x})$, we obtain for $\Delta\varphi(\mathbf{x})$ the field equation:

$$\frac{\delta}{\delta V(\mathbf{x})} [E^{(-)}_{\rm e} + \Delta E^{(-)}_{\rm e}] + \frac{1}{e^2} \boldsymbol{\nabla}^2 [\varphi(\mathbf{x}) + \Delta\varphi(\mathbf{x})] = 0. \tag{4.481}$$

Taking advantage of the initial extremality condition (4.399), we derive the field equation

$$\frac{1}{e^2} \boldsymbol{\nabla}^2 \, \Delta\varphi(\mathbf{x}) = -\frac{\delta \Delta E^{(-)}_{\rm e}}{\delta V(\mathbf{x})}. \tag{4.482}$$

If we now expand the corrected energy up to first order in $\Delta E^{(-)}_{\rm e}$ and $\Delta\varphi(\mathbf{x})$, we obtain

$$E^{(-)}_{\rm tot} = E^{(-)}_{\rm e} + \Delta E^{(-)}_{\rm e} + \int d^3x \frac{\delta E^{(-)}_{\rm e}}{\delta V(\mathbf{x})} \Delta\varphi(\mathbf{x}) - \mathcal{E}_{\varphi\varphi}[\varphi] - \frac{1}{4\pi e^2} \int d^3x \boldsymbol{\nabla}\varphi(\mathbf{x}) \boldsymbol{\nabla}\Delta\varphi(\mathbf{x}). \tag{4.483}$$

Due to the extremality property (4.399) of the uncorrected energy at the original field $\varphi(\mathbf{x})$, the second and fourth terms cancel each other, and the correction to the total energy is indeed given by (4.479).

Actually, the statement that the energy (4.479) is the next quantum correction is not quite true. When calculating the first quantum correction in Subsection 4.10.7, we subtracted the contribution of all orbits with total energies

$$E < -\varepsilon. \tag{4.484}$$

After that we calculated in (4.459) the *exact* quantum corrections coming from the neighborhood

$$r < r_{\rm max} = Ze^2\varepsilon \tag{4.485}$$

of the origin. Thus we have to omit this neighborhood from all successive terms in the semiclassical expansion, in particular from (4.479). According to the remarks after Eq. (4.372), the energy $E_{\rm e}^{(-)}$ of electrons filling all levels up to a total energy E_F is found from (4.368) by replacing $(-V)^{D/2+1}$ by $(1-E_F\partial/E_F)(E_F-V)^{D/2+1}$. The energy level satisfying (4.484) correspond to a Fermi level E_F, so that the energy of the electrons in these levels is

$$E_{\rm e}^{(-)} = 2\,\frac{2}{5}\,E_{\rm pot\,TF}^{(-)} = -2\,\frac{2}{5}\left(\frac{M}{2\pi\hbar}\right)^{3/2}\frac{1}{\Gamma(5/2)}(1-E_F\partial_{E_F})\int d^3x[-E_F-V(\mathbf{x})]^{5/2}. \tag{4.486}$$

We therefore have to subtract from the correction (4.477) a term

$$\Delta_{\rm sub}E_{\rm e}^{(-)} = (1-E_F\partial_{E_F})\frac{\sqrt{2M}}{12\hbar\pi^2}\int d^3x\left[(-E_F-V)^{1/2}\boldsymbol{\nabla}^2V-\frac{1}{4}(-E_F-V)^{-3/2}(\boldsymbol{\nabla}V)^2\right]. \tag{4.487}$$

The true correction can then be decomposed into a contribution from the finite region outside the small sphere

$$\Delta E_{\rm outside}^{(-)} = \frac{\sqrt{2M}}{24\hbar\pi^2}\int_{r\geq r_{\rm max}} d^3x(-V)^{1/2}\boldsymbol{\nabla}^2V, \tag{4.488}$$

plus a subtracted contribution from the inside

$$\Delta E_{\rm inside}^{(-)} = \frac{\sqrt{2M}}{24\hbar\pi^2}\int_{r<r_{\rm max}} d^3x\left[(-V)^{1/2}-(1-E_F\partial_{E_F})(-E_F-V)^{1/2}\right]\boldsymbol{\nabla}^2V, \tag{4.489}$$

plus a pure gradient term

$$\Delta E_{\rm grad}^{(-)} = -\frac{\sqrt{2M}}{24\hbar\pi^2}\frac{2}{3}\left[\int d^3x\boldsymbol{\nabla}^2(-V)^{3/2}-\int_{r<r_{\rm max}} d^3x\boldsymbol{\nabla}^2(1-E_F\partial_{E_F})(-E_F-V)^{3/2}\right]. \tag{4.490}$$

The last two volume integrals can be converted into surface integrals. Either integrand vanishes on its outer surface [recall (4.452)]. At the inner surface, an infinitesimal sphere around the origin, the integrands coincide so that the energy (4.490) vanishes.

The energy (4.489) does not vanish but can be ignored in the present approximation. At the δ-function at the nuclear charge in $\boldsymbol{\nabla}^2V$, the difference $(-V)^{1/2}-(1-E_F\partial_{E_F})(-E_F-V)^{1/2}$ vanishes. In the integral, we may therefore replace $\boldsymbol{\nabla}^2V(\mathbf{x})$ by $-4\pi e^2n(\mathbf{x})$ [dropping the δ-function in (4.374)]. In the small neighborhood of the origin, the integral is suppressed by a power of $Z^{-4/3}$ as will be seen below.

Thus, only the outside energy (4.488) needs to be evaluated, where the small sphere excludes the nuclear charge, so that we may replace $\boldsymbol{\nabla}^2V(\mathbf{x})$ as in the last integral. Thus we obtain

$$\Delta E_{\rm outside}^{(-)} = -\frac{2e^2M^2M}{9\pi^3\hbar^4}\int_{r<r_{\rm max}} d^3x[-V(\mathbf{x})]^2. \tag{4.491}$$

Expressing V in terms of the screening function and going to reduced variables, the quantum correction takes the final form

$$\begin{aligned}\Delta E^{(-)}_{\rm outside} &= -\frac{8}{9\pi^2}\frac{a}{a_H}\left[\int d\xi f^2(\xi)\right] Z^{5/3}\\ &\approx -0.07971\frac{e^2}{a_H} I_2 Z^{5/3} \approx -0.04905 Z^{5/3}\frac{e^2}{a_H},\end{aligned} \tag{4.492}$$

where I_2 is the integral over $f^2(\xi)$ calculated in Eq. (4.442). We have re-extended the integration over the entire space with a relative error of order $Z^{-2/3}$, due to the smallness of the sphere. The correction factor to the leading Thomas-Fermi energy caused by this is

$$C_{\rm QM} = 1 + 0.06381\, Z^{-2/3}. \tag{4.493}$$

In the reduced variables, the order of magnitude of the ignored energy (4.489) can most easily be estimated. It reads

$$\Delta E^{(-)}_{\rm inside} = -\frac{8}{9\pi^2}\frac{a}{a_H}\int_0^{\xi_{\rm max}} d\xi \left[f^2(\xi) - \sqrt{f(\xi)-\xi/\xi_{\rm m}}\, f^{3/2}(\xi)\right] Z^{5/3}. \tag{4.494}$$

Since $\xi_{\rm max}$ and $\xi_{\rm m}$ are of the order $Z^{-2/3}$, this energy is of the relative order $Z^{-4/3}$ and thus negligible since we want to find here only corrections up to $Z^{-2/3}$.

Observe that the quantum correction (4.495) is of relative order $Z^{-2/3}$ and precisely a fraction 2/9 of the exchange energy (4.441). Both energies together are therefore

$$\Delta E^{(-)}_{\rm inside} + E^{(-)}_{\rm exch} = \frac{11}{9}\, E^{(-)}_{\rm exch} \approx -0.2699\, Z^{5/3}\frac{e^2}{a_H}. \tag{4.495}$$

The corrections of order $Z^{-2/3}$ can be collected in the expression

$$\Delta E^{(-)}_{\rm inside} + E^{(-)}_{\rm exch} = -0.7687\, Z^{7/3}\frac{e^2}{a_H} \times C_2(Z), \tag{4.496}$$

where $C_2(Z)$ is the correction factor

$$C_2(Z) = 1 + 0.3510\, Z^{-2/3} + \dots\ . \tag{4.497}$$

Including also the $Z^{-1/3}$-correction (4.463) from the origin we obtain the total energy

$$E^{(-)}_{\rm tot} = -0.7687\, Z^{7/3}\frac{e^2}{a_H} \times C_{\rm tot}(Z), \tag{4.498}$$

with the total correction factor

$$C_{\rm tot}(Z) = 1 - 0.6504\, Z^{-1/3} + 0.3510\, Z^{-2/3} + \dots\ . \tag{4.499}$$

This large-Z approximation is surprisingly accurate. The experimental binding energy of mercury with $Z = 80$ is

$$E^{\rm exp}_{\rm Hg} \approx -18130, \tag{4.500}$$

in units of $e^2/a_H = 2\,{\rm Ry}$, whereas the large-Z formula (4.498) with the correction factor (4.499) yields the successive approximations including the first, second, and third term in (4.499):

$$E_{\rm Hg} \approx -(21200,\ 18000,\ 18312) \quad \text{for} \quad C(80) = (1,\ 0.849,\ 0.868). \tag{4.501}$$

Even at the lowest value $Z = 1$, the binding energy of the hydrogen atom

$$E^{\rm exp}_{\rm H} \approx -\frac{1}{2} \tag{4.502}$$

is quite rapidly approached by the successive approximations

$$E_{\rm H} \approx -(0.7687,\ 0.2687,\ 0.5386) \quad \text{for} \quad C(1) = (1,\ 0.350,\ 0.701). \tag{4.503}$$

4.11 Classical Action of Coulomb System

Consider an electron of mass M in an attractive Coulomb potential of a proton at the coordinate origin

$$V_{\rm C}(\mathbf{x}) = -\frac{e^2}{r}. \tag{4.504}$$

If the proton is substituted by a heavier nucleus, e^2 has to be multiplied by the charge Z of that nucleon. The Lagrangian of this system is

$$L = \frac{M}{2}\dot{\mathbf{x}}^2 - \frac{e^2}{r}. \tag{4.505}$$

Because of rotational invariance, the orbital angular momentum is conserved and the motion is restricted to a plane, say $x-y$. If ϕ denotes the azimuthal angle in this plane, the constant orbital momentum is

$$l = Mr^2\dot{\phi}. \tag{4.506}$$

The conserved energy is

$$E = \frac{M}{2}(\dot{r}^2 + r^2\dot{\phi}^2) - \frac{e^2}{r}. \tag{4.507}$$

Together with (4.506) we find

$$\dot{r} = \frac{1}{M}p_E(r); \qquad p_E(r) = \sqrt{2M[E - V_{\rm eff}(r)]}, \tag{4.508}$$

where $V_{\rm eff}(r) = V_{\rm C}(r) + V_l(r)$ is the sum of the Coulomb potential and the *angular barrier* potential

$$V_l(r) = \frac{l^2}{2Mr^2}. \tag{4.509}$$

The differential equation (4.508) is solved by the integral relation

$$t = \int dr\,\frac{M}{p_E(r)}. \tag{4.510}$$

For the angle ϕ, Eq. (4.506) implies

$$\frac{d\phi}{dr} = \frac{l}{r^2 p_E(r)}, \tag{4.511}$$

which is solved by the integral

$$\phi = l\int dr \frac{1}{r^2 p_E(r)}. \tag{4.512}$$

Inserting $p_E(r)$ from (4.508) this becomes explicitly

$$\phi = l\int \frac{dr}{r}\left[2ME\left(r^2 + \frac{e^2 r}{E} - \frac{l^2}{2ME}\right)\right]^{-1/2}, \tag{4.513}$$

while (4.510) reads

$$t = M\int dr\, r\left[2ME\left(r^2+\frac{e^2 r}{E}-\frac{l^2}{2ME}\right)\right]^{-1/2}. \tag{4.514}$$

Consider now the motion for negative energies. Defining

$$\bar p_E \equiv p_{-E}(\infty)=\sqrt{-2ME}, \tag{4.515}$$

and introducing the parameters

$$a\equiv\frac{e^2}{2|E|}=\frac{Me^2}{\bar p_E^2},\quad \epsilon^2\equiv 1-\frac{l^2\bar p_E^2}{M^2e^4}=1-\frac{l^2}{aMe^2}=1-\frac{l^2v_a^2}{e^4},\quad v_a=\sqrt{\frac{e^2}{aM}}=\frac{\bar p_E}{M}, \tag{4.516}$$

we obtain

$$\phi=\frac{l}{Mv_a}\int\frac{dr}{r}\frac{1}{\sqrt{a^2\epsilon^2-(r-a)^2}}, \tag{4.517}$$

$$t=\frac{1}{v_a}\int dr\,\frac{r}{\sqrt{a^2\epsilon^2-(r-a)^2}}, \tag{4.518}$$

where v_a is the velocity associated with the momentum $\bar p_E$. The ratio

$$\omega=\frac{v_a}{a} \tag{4.519}$$

is the inverse period of the orbit, also called mean motion, which satisfies $\omega^2a^3 = e^2/M$, the third *Kepler law*. In the limit $E\to 0$, the major semiaxis a becomes infinite, and so does ω. The eccentricity vanishes and the orbit is parabolic.

Introducing the variable

$$h\equiv a(1-\epsilon^2)=\frac{l^2}{Me^2}=\frac{l^2}{\bar p_E^2 a}, \tag{4.520}$$

and observing that

$$\frac{l}{Mv_a}=a\sqrt{1-\epsilon^2}, \tag{4.521}$$

the first equation is solved by

$$\frac{h}{r}=1+\epsilon\cos(\phi-\phi_0). \tag{4.522}$$

This follows immediately from the fact that

$$\sin(\phi-\phi_0)=\frac{\sqrt{1-\epsilon^2}}{\epsilon r}\sqrt{a^2\epsilon^2-(r-a)^2}. \tag{4.523}$$

The relation (4.522) describes an ellipse with principal axes $a = h/(1-\epsilon^2)$, $b = h/\sqrt{1-\epsilon^2}$, and an eccentricity ϵ (see Fig. 4.3). In the orbital plane, the Cartesian

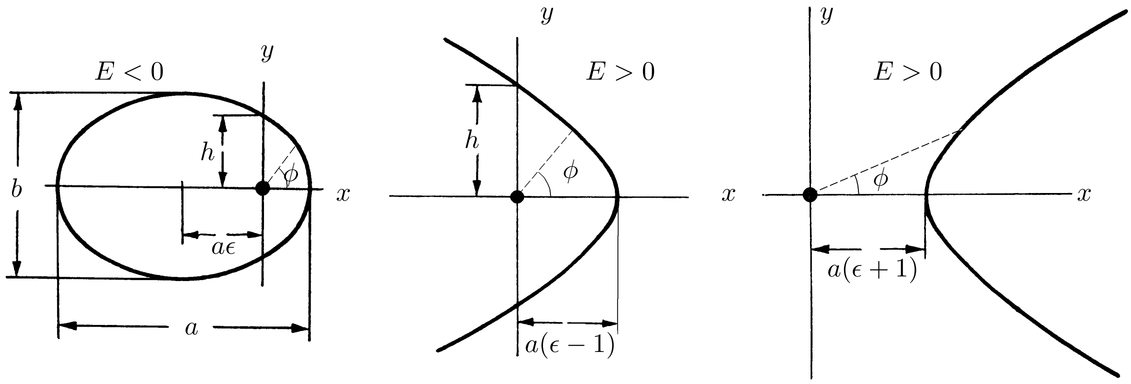

Figure 4.3 Orbits in Coulomb potential showing the parameter h and the eccentricity ϵ of ellipse ($E<0$) and hyperbola ($E>0$) in attractive and repulsive cases.

coordinates of the motion are

$$x = h\frac{\cos(\phi-\phi_0)}{1+\epsilon\sin(\phi-\phi_0)}, \qquad y = h\frac{\sin(\phi-\phi_0)}{1+\epsilon\sin(\phi-\phi_0)}. \tag{4.524}$$

For positive energy, we define a momentum

$$p_E = p_E(\infty) = \sqrt{2ME}, \tag{4.525}$$

and the parameters

$$a \equiv \frac{e^2}{2|E|} = \frac{Me^2}{p_E^2}, \quad \epsilon^2 \equiv 1+\frac{l^2p_E^2}{M^2e^4} = 1+\frac{l^2}{aMe^2} = 1+\frac{l^2v_a^2}{e^4}, \quad v_a = \sqrt{\frac{e^2}{aM}} = \frac{p_E}{M}. \tag{4.526}$$

The eccentricity ϵ is now larger than unity. Apart from this, the solutions to the equations of motion are the same as before, and the orbits are hyperbolas as shown in Fig. 4.3. The y-coordinate above the focus is now

$$h = a(\epsilon^2-1) = \frac{l^2}{Me^2} = \frac{l^2}{p_E^2 a}. \tag{4.527}$$

For a repulsive interaction, we change the sign of e^2 in the above equations. The equation (4.522) for r becomes now

$$\frac{h}{r} = -1+\epsilon\cos(\phi-\phi_0), \tag{4.528}$$

and yields the right-hand hyperbola shown in Fig. 4.3.

For later discussions in Chapter 13, where we shall solve the path integral of the Coulomb system exactly, we also note that by introducing a new variable in terms of the variable ξ, to so-called *eccentric anomaly*

$$r = a(1-\epsilon\cos\xi), \tag{4.529}$$

we can immediately perform the integral (4.518) to find

$$t = \frac{a}{v_a} \int d\xi \, (1 - \epsilon \cos \xi) = \frac{1}{\omega}(\xi - \epsilon \sin \xi), \tag{4.530}$$

where we have chosen the integration constant to zero. Using Eq. (4.528) we see that

$$x = r \cos \phi = \frac{h - r}{\epsilon} = a(\cos \xi - \epsilon), \tag{4.531}$$

$$y = r \sin \phi = \sqrt{r^2 - x^2} = a\sqrt{1 - \epsilon^2} \sin \xi = b \sin \xi. \tag{4.532}$$

Equations (4.529) and (4.530) represent a parametric representation of the orbit. From Eqs. (4.530) and (4.529) we see that

$$\frac{dt}{r} = \frac{1}{a} d(\xi/\omega), \tag{4.533}$$

exhibiting ξ/ω is a path-dependent *pseudotime*. As a function of this pseudotime, the coordinates x and y oscillate harmonically.

The pseudotime facilitates the calculation of the classical action $A(\mathbf{x}_b, \mathbf{x}_a; t_b - t_a)$, as done first in the eighteenth century by Lambert.[15] If we denote the derivative with respect to ξ by a prime, the classical action reads

$$A = \int_{\xi_a}^{\xi_b} d\xi \left[\frac{M}{2r} a\omega \left(x'^2 + y'^2 \right) + \frac{e^2}{a\omega} \right]. \tag{4.534}$$

For an elliptic orbit with principal axes a, b, this becomes

$$A = \int_{\xi_a}^{\xi_b} d\xi \left[\frac{M}{2} \omega \frac{a^2 \sin^2 \xi + b^2 \cos^2 \xi}{1 - \epsilon \cos \xi} \right] + M\omega a^2 (\xi_b - \xi_a). \tag{4.535}$$

After performing the integral using the formula

$$\int \frac{d\xi}{1 - \epsilon \cos \xi} = \frac{2}{1 - \epsilon^2} \arctan \frac{\sqrt{1 - \epsilon^2} \, \tan(\xi/2)}{1 - \epsilon}, \tag{4.536}$$

we find

$$A = \frac{M}{2} a^2 \omega \left[3(\xi_b - \xi_a) + \epsilon(\sin \xi_b - \sin \xi_a) \right]. \tag{4.537}$$

Introducing the parameters α, β, γ, and δ by the relations

$$\cos \alpha \equiv \epsilon \cos[(\xi_b + \xi_a)/2], \quad \beta \equiv (\xi_b - \xi_a)/2, \quad \gamma \equiv \alpha + \beta, \quad \delta \equiv \alpha - \beta, \tag{4.538}$$

[15] Johann Heinrich Lambert (1728–1777) was an ingenious autodidactic taylor's son who with 16 years found *Lambert's law* for the apparent motion of comets (and planets) on the sky: If the sun lies on the concave (convex) side of the apparent orbit, comet is closer to (farther from) the sun than the earth. In addition, he laid the foundations to photometry.

the action becomes

$$A = \frac{M}{2}a^2\omega\left[(3\gamma+\sin\gamma)-(3\delta+\sin\delta)\right]. \tag{4.539}$$

Using (4.530), we find for the elapsed time $t_b - t_a$ the relation

$$t_b - t_a = \frac{1}{\omega}\left[(\gamma-\sin\gamma)\mp(\delta-\sin\delta)\right]. \tag{4.540}$$

The $\mp$-signs apply to an ellipse whose short or long arc connects the two endpoints, respectively. The parameters γ and δ in the action and in the elapsed time are related to the endpoints $\mathbf{x}_b$ and $\mathbf{x}_a$ by

$$r_b + r_a + R = 4a\sin^2(\gamma/2) \equiv 4a\rho_+ , \qquad r_b + r_a - R = 4a\sin^2(\delta/2) \equiv 4a\rho_- , \tag{4.541}$$

where $r_b \equiv |\mathbf{x}_b|$, $r_a \equiv |\mathbf{x}_a|$, $R \equiv |\mathbf{x}_b - \mathbf{x}_a|$, and $\rho_\pm \in [0,1]$. Expressing the semimajor axis in (4.539) in terms of ω as $a = (e^2/M\omega^2)^{1/3}$, and ω in terms of $t_b - t_a$ we obtain the desired classical action $A(\mathbf{x}_b, \mathbf{x}_a; t_b - t_a)$.

The elapsed time depends on the endpoints via a transcendental equation which can only be solved by a convergent power series (Lambert's series)

$$t_b - t_a = \frac{1}{\sqrt{2}\omega}\sum_{j=1}^{\infty}\frac{(2j)!}{2^{2j}j!^2}\frac{1}{j^2-1/4}\epsilon^{j-1}\left(\rho_+^{j+1/2} \pm \rho_-^{j+1/2}\right). \tag{4.542}$$

In the limit of a parabolic orbit the series has only the first term, yielding

$$t_b - t_a = \frac{\sqrt{2}}{3\omega}(\rho_+^{3/2} \pm \rho_-^{3/2}). \tag{4.543}$$

We can also express a and ω in terms of the energy E as $e^2/(-2E)$ and $\sqrt{-2E/Ma^2}$, respectively, and go over to the eikonal $S(\mathbf{x}_b, \mathbf{x}_a; E)$ via the Legendre transformation (4.87). Substituting for $t_b - t_a$ the relation (4.540), we obtain for the short arc of the ellipse

$$S(\mathbf{x}_b, \mathbf{x}_a; E) = A(\mathbf{x}_b, \mathbf{x}_a; E) + (t_b - t_a)\,E = \frac{M}{2}a^2\omega\,4(\gamma-\delta). \tag{4.544}$$

For a complete orbit, the expression (4.537) yields a total action

$$A = \frac{M}{2}a^2\omega\,2\pi(1+2) = \frac{M}{2}v_a^2\frac{2\pi}{\omega}(1+2) = \frac{\bar{p}_E}{2M}\frac{2\pi}{\omega}(1+2), \tag{4.545}$$

where the numbers 1 and 2 indicate the source of the contributions from the kinetic and potential parts of the action (4.534), respectively. Since the action is the difference between kinetic and potential energy, the average potential energy is minus twice as big as the kinetic energy, which is the single-particle version of the virial theorem observed in the Thomas-Fermi approximation (4.428).

For positive energies E, the eccentricity is $\epsilon > 1$ and the orbit is a hyperbola (see Fig. 4.3). Then equations (4.529)–(4.532) become

$$r = a(\epsilon \cosh \xi - 1), \qquad t = \frac{a}{v_a}(\xi - \epsilon \sin \xi), \tag{4.546}$$

$$x = -a\epsilon(\cosh \xi - \epsilon), \qquad y = a\sqrt{\epsilon^2 - 1}\sinh \xi. \tag{4.547}$$

The orbits take a simple form in momentum space. Using Eq. (4.506), we find from (4.524):

$$p_x = -\frac{l}{h}\left[\epsilon + \sin(\phi - \phi_0)\right], \qquad p_y = \frac{l}{h}\cos(\phi - \phi_0). \tag{4.548}$$

As a function of time, the momenta describe a circle of radius

$$p_0 = \frac{l}{h} = \frac{Me^2}{l} = \frac{\bar{p}_E}{\sqrt{1-\epsilon^2}} \tag{4.549}$$

around a center on the p_y-axis with (see Fig. 4.4)

$$p_x^c = -\frac{l}{h}\epsilon = -\frac{\epsilon}{\sqrt{1-\epsilon^2}}. \tag{4.550}$$

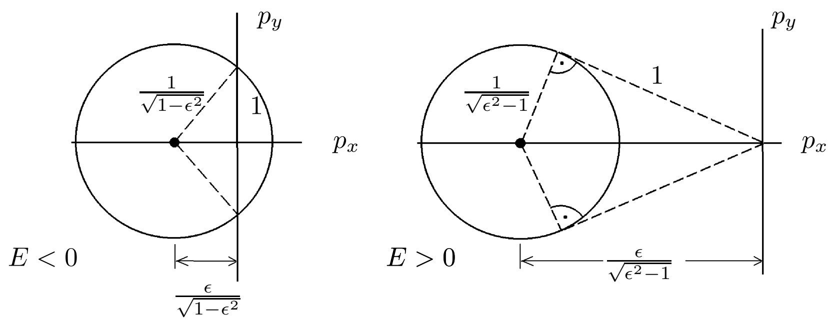

Figure 4.4 Circular orbits in momentum space in units $\bar{p}_E$ for $E < 0$ and p_E for $E > 0$.

For positive energies, the above solutions can be used to describe the scattering of electrons or ions on a central atom. For helium nuclei obtained by α-decay of radioactive atoms, this is the famous *Rutherford scattering* process. The potential is then repulsive, and e^2 in the potential (4.504) must be replaced by $-2Ze^2$, where $2e$ is the charge of the projectiles and Ze the charge of the central atom. As we can see on Fig. 4.5, the trajectories in an attractive potential are simply related to those in a repulsive potential. The momentum $\bar{p}_E$ is the asymptotic momentum of the projectile, and may be called p_∞. The impact parameter b of the projectile fixes the angular momentum via

$$l = bp_\infty = b\bar{p}_E. \tag{4.551}$$

Inserting l and $\bar{p}_E$ we see that b coincides with the previous parameter b.

The relation of the impact parameter b with the scattering angle θ may be taken from Fig. 4.5, which shows that (see also Fig. 4.4)

$$\tan\frac{\theta}{2} = \frac{p_0}{p_\infty} = \frac{1}{\epsilon^2 - 1}. \tag{4.552}$$

Thus we have

$$b = a\cot\frac{\theta}{2}. \tag{4.553}$$

The particles impinging into a circular annulus of radii b and $b + db$ come out between the angles θ and $\theta + d\theta$, with $db/d\theta = -a/2\sin^2(\theta/2)$. The area of the annulus $d\sigma = 2\pi b db$ is the differential cross section for this scattering process. The absolute ratio with respect to the associated solid angle $d\Omega \equiv 2\pi \sin\theta d\theta$ is then

$$\frac{d\sigma}{d\Omega} = \frac{b}{\sin\theta}\left|\frac{db}{d\theta}\right| = \frac{a^2}{4\sin^4(\theta/2)} = \frac{Z^2\alpha^2 M^2}{4p_\infty^4 \sin^4(\theta/2)}. \tag{4.554}$$

The right-hand side is the famous *Rutherford formula*, which arises after expressing a in terms of the incoming momentum p_∞ [recall (4.526)] as $a = Ze^2/2E = Z\alpha\hbar cM/p_\infty^2$.

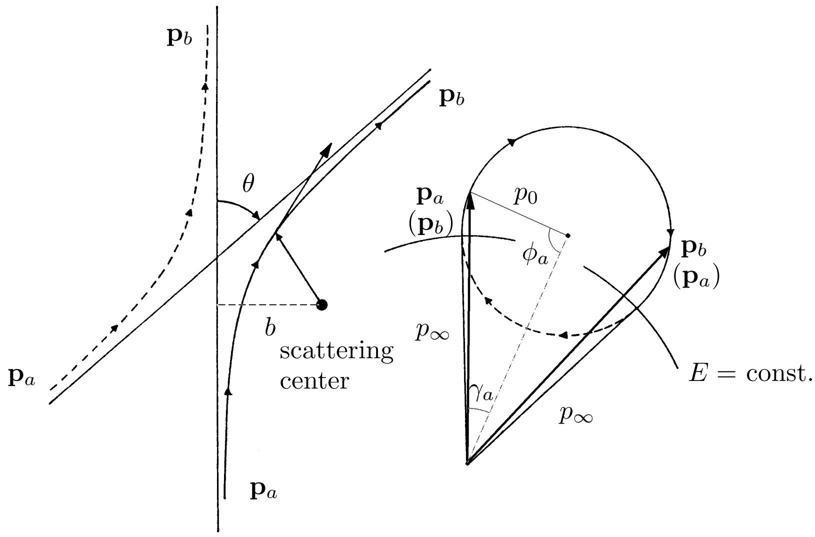

Figure 4.5 Geometry of scattering in momentum space. The solid curves are for attractive Coulomb potential, the dashed curves for repulsive (Rutherford scattering). The right-hand part of the figure shows the circle on which the momentum moves from $\mathbf{p}_a$ to $\mathbf{p}_b$ as the angle ϕ runs from ϕ_a to ϕ_b. The distance b is the impact parameter, and θ is the scattering angle.

Let us also calculate the classical eikonal in momentum space. We shall do this for the attractive interaction at positive energy. Inserting (4.524) and (4.548) we have

$$S(\mathbf{p}_b,\mathbf{p}_a;E) = -l\int_{\phi_a}^{\phi_b}\frac{d\phi}{1+\epsilon(\phi-\phi_0)}. \tag{4.555}$$

Using the formula[16]

$$\int\frac{d\xi}{1+\epsilon\cos\xi} = \frac{2}{\sqrt{\epsilon^2-1}}\log\frac{1+\epsilon+\sqrt{\epsilon^2-1}\tan(\xi/2)}{1-\epsilon-\sqrt{\epsilon^2-1}\tan(\xi/2)}. \tag{4.556}$$

Inserting $l/\sqrt{1-\epsilon^2} = Mv_a a = Me^2/p_\infty$, we find after some algebra

$$S(\mathbf{p}_b,\mathbf{p}_a;E) = -\frac{Me^2}{p_\infty}\log\frac{\zeta+1}{\zeta-1}, \qquad p_\infty = \sqrt{2ME}, \tag{4.557}$$

with

$$\zeta \equiv \sqrt{1+\frac{(p_b^2-p_\infty^2)(p_b^2-p_\infty^2)}{p_\infty^2|\mathbf{p}_b-\mathbf{p}_a|^2}}. \tag{4.558}$$

The expression (4.557) has no definite limit if the impinging particle comes in from spatial infinity where p_a becomes equal to p_∞. There is a logarithmic divergence which is due to the infinite range of the Coulomb potential. In nature, the charges are always screened at some finite radius R, after which the logarithmic divergence disappears. This was discussed before when deriving the eikonal approximation (1.502) to Coulomb scattering.

There is a simple geometric meaning to the quantity ζ. Since the force is central, the change in momentum along a classical orbit is always in the direction of the center, so that (4.555) can also be written as

$$S(\mathbf{p}_b,\mathbf{p}_a;E) = -\int_{\mathbf{p}_a}^{\mathbf{p}_b} r\,dp. \tag{4.559}$$

Expressing r in terms of momentum and total energy, this becomes for an attractive (repulsive) potential

$$S(\mathbf{p}_b,\mathbf{p}_a;E) = \pm 2Me^2\int_{\mathbf{p}_a}^{\mathbf{p}_b}\frac{dp}{p^2-2ME}. \tag{4.560}$$

Now we observe, that for $E<0$, the integrand is the arc length on a sphere of radius $1/\bar{p}_E$ in a four-dimensional momentum space. Indeed, the three-dimensional momentum space can be mapped onto the surface of a four-dimensional unit sphere by the following transformation

$$n_4 \equiv \frac{p^2-\bar{p}_E^2}{p^2+\bar{p}_E^2}, \qquad \mathbf{n} \equiv \frac{2\bar{p}_E\mathbf{p}}{p^2+\bar{p}_E^2}. \tag{4.561}$$

[16]See the previous footnote.

Then we find that

$$\frac{dp}{p^2+\bar{p}_E^2}=\frac{d\vartheta}{2\bar{p}_E}, \tag{4.562}$$

where $d\vartheta$ is the infinitesimal arc length on the unit sphere. But then the eikonal becomes simply

$$S(\mathbf{p}_b,\mathbf{p}_a;E)=\pm\frac{2Me^2}{\bar{p}_E}\vartheta_{ba}, \tag{4.563}$$

where ϑ is the angular difference between the images of the momenta $\mathbf{p}_b$ and $\mathbf{p}_a$. This is easily calculated. From (4.561) we find directly

$$\cos\vartheta_{ba}=\frac{4\bar{p}_E^2\,\mathbf{p}_b\cdot\mathbf{p}_a+(p_b^2-\bar{p}_E^2)(p_a^2-\bar{p}_E^2)}{(p_b^2+\bar{p}_E^2)(p_a^2+\bar{p}_E^2)}=1-2\frac{\bar{p}_E^2(\mathbf{p}_b-\mathbf{p}_a)^2}{(p_b^2+\bar{p}_E^2)(p_a^2+\bar{p}_E^2)}. \tag{4.564}$$

Continuing E analytically to positive energies, we may replace $\bar{p}_E$ by $ip_\infty=2ME$, and obtain

$$\cos\vartheta_{ba}=1+2\frac{p_\infty^2(\mathbf{p}_b-\mathbf{p}_a)^2}{(p_b^2-p_\infty^2)(p_a^2-p_\infty^2)}. \tag{4.565}$$

Hence ϑ becomes imaginary, $\vartheta=i\bar{\vartheta}$, with

$$\sin\frac{\bar{\vartheta}}{2}=\frac{p_\infty^2(\mathbf{p}_b-\mathbf{p}_a)^2}{(p_b^2-p_\infty^2)(p_a^2-p_\infty^2)}, \tag{4.566}$$

and the eikonal function (4.567) takes the form

$$S(\mathbf{p}_b,\mathbf{p}_a;E)=\pm\frac{2Me^2}{p_\infty}\bar{\vartheta}_{ba}. \tag{4.567}$$

This is precisely the expression (4.557) with $\zeta=1/\tanh(\bar{\vartheta}_{ab}/2)$.

4.12 Semiclassical Scattering

Let us also derive the semiclassical limit for the scattering amplitude.

4.12.1 General Formulation

Consider a particle impinging with a momentum $\mathbf{p}_a$ and energy $E=E_a=\mathbf{p}_a^2/2M$ upon a nonzero potential concentrated around the origin. After a long time, it will be found far from the potential with some momentum $\mathbf{p}_b$ and the same energy $E=E_b=\mathbf{p}_b^2/2M$. Let us derive the scattering amplitude for such a process from the heuristic formula (1.510):

$$f_{\mathbf{p}_b\mathbf{p}_a}=\frac{p_b}{M}\frac{\sqrt{2\pi\hbar M/i}^3}{(2\pi\hbar)^3}\lim_{t_b\to\infty}\frac{1}{t_b^{1/2}}e^{iE_b(t_b-t_a)/\hbar}\left[(\mathbf{p}_bt_b|\mathbf{p}_at_a)-\langle\mathbf{p}_b|\mathbf{p}_a\rangle\right]. \tag{4.568}$$

In the semiclassical approximation we replace the exact propagator in the momentum representation by a sum over all classical trajectories and associated phases, connecting $\mathbf{p}_a$ to $\mathbf{p}_b$ in the time $t_b - t_a$. According to formula (4.172) we have in three dimensions

$$(\mathbf{p}_b t_b|\mathbf{p}_a t_a) - \langle \mathbf{p}_b|\mathbf{p}_a\rangle = \frac{(2\pi\hbar)^3}{(2\pi\hbar/i)^{3/2}} \sum_{\text{class. traj.}}{}' \left|\det\left(-\frac{\partial \mathbf{x}_a}{\partial \mathbf{p}_b}\right)\right|^{1/2} e^{iA(\mathbf{p}_b,\mathbf{p}_a;t_b-t_a)/\hbar - i\nu\pi\hbar/2}. \tag{4.569}$$

The sum carries a prime to indicate that unscattered trajectories are omitted. The classical action in momentum space is

$$A(\mathbf{p}_b, \mathbf{p}_a; t_b - t_a) = \int_{\mathbf{p}_b}^{\mathbf{p}_a} \mathbf{x}\cdot\dot{\mathbf{p}} - \int_{t_a}^{t_b} H dt = S(\mathbf{p}_b, \mathbf{p}_a; E) - E(t_b - t_a), \tag{4.570}$$

where $S(\mathbf{p}_b, \mathbf{p}_a; E)$ is the eikonal function introduced in Eqs. (4.240) and (4.68).

Inserting (4.569) into (1.510) we obtain the semiclassical scattering transition amplitude

$$f_{\mathbf{p}_b\mathbf{p}_a} = \lim_{t_b\to\infty} \sum_{\text{class. traj.}}{}' \frac{p_b}{\sqrt{t_b M}} \left|\det \frac{\partial \mathbf{x}_a}{\partial \mathbf{p}_b}\right|^{1/2} e^{iS(\mathbf{p}_b,\mathbf{p}_a;E)/\hbar - i\nu\pi/2}. \tag{4.571}$$

The determinant has a simple physical meaning. To see this we rewrite

$$\left.\frac{\partial \mathbf{x}_a}{\partial \mathbf{p}_b}\right|_{\mathbf{p}_a} = \left.\frac{\partial \mathbf{p}_b}{\partial \mathbf{x}_a}\right|_{\mathbf{p}_a}^{-1}, \tag{4.572}$$

so that (4.573) becomes

$$f_{\mathbf{p}_b\mathbf{p}_a} = \lim_{t_b\to\infty} \sum_{\text{class. traj.}}{}' \frac{p}{\sqrt{t_b M}} \left|\det \frac{\partial \mathbf{p}_b}{\partial \mathbf{x}_a}\right|_{\mathbf{p}_a}^{-1/2} e^{iS(\mathbf{p}_b,\mathbf{p}_a;E)/\hbar - i\nu\pi/2}. \tag{4.573}$$

We now note that for large t_b

$$\mathbf{p}_b = \mathbf{p}(t_b) = M\mathbf{x}_b(t_b)/t_b \tag{4.574}$$

along any trajectory. Thus we find

$$f_{\mathbf{p}_b\mathbf{p}_a} = \lim_{t_b\to\infty} \sum_{\text{class. traj.}}{}' r_b \left|\det \frac{\partial \mathbf{x}_b}{\partial \mathbf{x}_a}\right|_{p_b}^{-1/2} e^{iS(\mathbf{p}_b,\mathbf{p}_a;E)/\hbar - i\nu\pi/2}, \tag{4.575}$$

where $r_b = |\mathbf{x}_b|$.

From the definition of the scattering amplitude (1.497) we expect the prefactor of the exponential to be equal to the square root of the classical differential cross section $d\sigma_{\rm cl}/d\Omega$. Let us choose convenient coordinates in which the particle trajectories start out at a point with cartesian coordinates $\mathbf{x}_a = (x_a, y_a, z_a)$ with a large negative z_a and a momentum $\mathbf{p}_a \approx p_a\hat{\mathbf{z}}$, where $\hat{\mathbf{z}}$ is the direction of the z-axis. The final points $\mathbf{x}_b$ of the trajectories will be described in spherical coordinates. If $\hat{\mathbf{p}}_b =$

$(\sin\theta_b \cos\phi_b, \sin\theta \sin\phi_b, \cos\theta_b)$ denotes the direction of the final momentum $\mathbf{p}_b = p_b\hat{\mathbf{p}}_b$, then $\mathbf{x}_b = r_b\hat{\mathbf{p}}$. Let us introduce an auxiliary triplet of spherical coordinates $\mathbf{s}_b \equiv (r_b, \theta_b, \phi_b)$. Then we factorize the determinant in (4.575) as

$$\det\frac{\partial \mathbf{x}_b}{\partial \mathbf{x}_a} = \det\frac{\partial \mathbf{x}_b}{\partial \mathbf{s}_a} \times \det\frac{\partial \mathbf{s}_b}{\partial \mathbf{x}_a} = r_b^2 \det\frac{\partial \mathbf{s}_b}{\partial \mathbf{x}_a}.$$

We further calculate

$$\det\frac{\partial \mathbf{s}_b}{\partial \mathbf{x}_a} = \begin{pmatrix} \frac{\partial r_b}{\partial x_a} & \frac{\partial r_b}{\partial y_a} & \frac{\partial r_b}{\partial z_a} \\ \frac{\partial \theta_b}{\partial x_a} & \frac{\partial \theta_b}{\partial y_a} & \frac{\partial \theta_b}{\partial z_a} \\ \frac{\partial \phi_b}{\partial x_a} & \frac{\partial \phi_b}{\partial y_a} & \frac{\partial \phi_b}{\partial z_a} \end{pmatrix}. \tag{4.576}$$

Long after the collision, for $t_b \to \infty$, a small change of the starting point *along* the trajectory dz_a will not affect the scattering angle. Thus we may approximate the matrix elements in the third column by $\partial z_a \approx \partial\phi/\partial z_a \approx 0$. After the same amount of time the particle will only wind up at a slightly more distant r_b, where $dr_b \approx dz_b$. Thus we may replace the matrix element in the right upper corner by 1, so that the determinant (4.576) becomes in the limit

$$\lim_{t_b\to\infty} \det\frac{\partial \mathbf{s_b}}{\partial \mathbf{x}_a} \approx \det\begin{pmatrix} \frac{\partial \theta_b}{\partial x_a} & \frac{\partial \theta_b}{\partial y_a} \\ \frac{\partial \phi_b}{\partial x_a} & \frac{\partial \phi_b}{\partial y_a} \end{pmatrix} = \frac{d\theta_b \mathrm{d}\phi_b}{dx_b dy_b} = \frac{d\Omega}{d\sigma}, \tag{4.577}$$

where $d\Omega = \sin\theta_b d\theta d\phi_b$ is the element of the solid angle of the emerging trajectories, and $d\sigma$ the area element in the $x - y$ -plane, for which the trajectories arrive in an element of the final solid angle $d\Omega$. Thus we obtain

$$\left[\det\frac{\partial \mathbf{x}_b}{\partial \mathbf{x}_a}\right]^{-1} \approx \frac{1}{r_b^2}\frac{d\sigma}{d\Omega}. \tag{4.578}$$

The ratio $d\sigma/d\Omega$ is precisely the classical differential cross section of the scattering process.

Combining (4.575) and (4.577), we see that the contribution of an individual trajectory to the semiclassical amplitude is of the expected form [7]

$$f_{\mathbf{p}_b\mathbf{p}_a} = \sqrt{\frac{d\sigma_{\text{cl}}}{d\Omega}} \times \sum_{\text{class. traj.}}{}' e^{iS(\mathbf{p}_b,\mathbf{p}_a;E)/\hbar - i\nu\pi/2}. \tag{4.579}$$

Note that this equation is also valid for some potentials which are not restricted to a finite regime around the origin, such as the Coulomb potentials. In the operator theory of quantum-mechanical scattering processes, such potentials always cause considerable problems since the outgoing wave functions remain distorted even at large distances from the scattering center.

Usually, there are only a few trajectories contributing to a process with a given scattering angle. If the actions of these trajectories differ by less than $\hbar$, the semiclassical approximation fails since the fluctuation integrals overlap. Examples are the light scattering causing the ordinary rainbow in nature, and glory effects seen at night around the moonlight.

We now turn to a derivation of the amplitude (4.579) from the more reliable formula (1.531) for the interacting wave function

$$\langle \mathbf{x}_b | \hat{U}_I(0,t_a)|\mathbf{p}_a\rangle = \lim_{t_a\to-\infty}\left(\frac{-2\pi i\hbar t_a}{M}\right)^{3/2}(\mathbf{x}_b t_b|\mathbf{x}_a t_a)e^{i(\mathbf{p}_a\mathbf{x}_a - p_a^2 t_a/2M)/\hbar}\Big|_{\mathbf{x}_a=\mathbf{p}_a t_a/M},$$

by isolating the factor of $e^{ip_a r_b}/r_b$ for large r_b, as discussed at the end of Section 1.16. On the right-hand side we now insert the x-space form (4.127) of the semiclassical amplitude, and use (4.87) to write

$$\begin{aligned}\langle \mathbf{x}_b | \hat{U}_I(0,t_a)|\mathbf{p}_a\rangle &= \lim_{t_a\to-\infty}\left(\frac{-t_a}{M}\right)^{3/2}\left[\det{}_3\left(-\frac{\partial \mathbf{p}_a}{\partial \mathbf{x}_b}\right)\right]^{1/2} \\ &\times\; e^{i[S(\mathbf{x}_b,\mathbf{x}_a;E_a)+i\mathbf{p}_a\mathbf{x}_a - i\nu\pi/2]/\hbar}\Big|_{\mathbf{x}_a=\mathbf{p}_a t_a/M}.\end{aligned} \tag{4.580}$$

Now we observe that

$$\left(\frac{-t_a}{M}\right)^{3/2}\left[\det{}_3\left(-\frac{\partial \mathbf{p}_a}{\partial \mathbf{x}_b}\right)\right]^{1/2} = \left[\det{}_3\left(\frac{\partial \mathbf{x}_a}{\partial \mathbf{x}_b}\right)\right]^{1/2}. \tag{4.581}$$

In Eq. (4.578) we have found that this determinant is equal to $\sqrt{d\sigma/d\Omega}/r_b$, bringing Eq. (4.580) to the form

$$\langle \mathbf{x}_b | \hat{U}_I(0,t_a)|\mathbf{p}_a\rangle = \lim_{t_a\to-\infty}\frac{1}{r_b}\sqrt{\frac{d\sigma_{\rm cl}}{d\Omega}}e^{i[S(\mathbf{x}_b,\mathbf{x}_a;E_a)+i\mathbf{p}_a\mathbf{x}_a - i\nu\pi/2]/\hbar}\Bigg|_{\mathbf{x}_a=\mathbf{p}_a t_a/M}. \tag{4.582}$$

For large $\mathbf{x}_b$ in the direction of the final momentum $\mathbf{p}_b$, we can rewrite the exponent as [recalling (4.240)]

$$S(\mathbf{x}_b,\mathbf{x}_a;E_a) + i\mathbf{p}_a\mathbf{x}_a = p_b r_b + S(\mathbf{p}_b,\mathbf{p}_a;E_a) \tag{4.583}$$

so that (4.582) consists of an outgoing spherical wave function $e^{ip_b r_b/\hbar}/r_b$ multiplied by the scattering amplitude

$$f_{\mathbf{p}_b\mathbf{p}_a} = \sqrt{\frac{d\sigma_{\rm cl}}{d\Omega}} \times \sum_{\text{class. traj.}}{}' \; e^{iS(\mathbf{p}_b,\mathbf{p}_a;E)/\hbar - i\nu\pi/2}, \tag{4.584}$$

the same as in (4.579).

4.12.2 Semiclassical Cross Section of Mott Scattering

If the scattering particle is distinguishable from the target particles, the extra phase in the semiclassical formula (4.584) does not change the classical result (4.554). A quantum-mechanical effect becomes visible only if we consider electron-electron scattering, also referred to as *Mott scattering*. The potential is repulsive, and the above Coulomb potential holds for the relative motion of the two identical particles in their center-of-mass frame. Moreover, the identity of particles requires us to add the amplitudes for the trajectories going to $\mathbf{p}_b$ and to $-\mathbf{p}_b$ [see Fig. 4.6], so that the differential cross section is

$$\frac{d\sigma_{\rm sc}}{d\Omega} = |f_{\mathbf{p}_b\mathbf{p}_a} - f_{\mathbf{p}_b,-\mathbf{p}_a}|^2. \tag{4.585}$$

The minus sign accounts for the Fermi statistics of the two electrons. For two identical bosons, we have to use a plus sign instead. Now the eikonal function $S(\mathbf{p},\mathbf{p},E)$ enters into the result. According to Eq. (4.557), this is given by

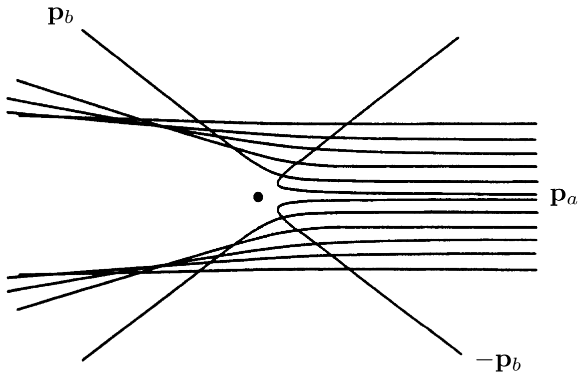

Figure 4.6 Classical trajectories in Coulomb potential plotted in the center-of-mass frame. For identical particles, trajectories which merge with a scattering angle θ and $\pi-\theta$ are indistinguishable. Their amplitudes must be subtracted from each other, yielding the differential cross section (4.585).

$$S(\mathbf{p}_b,\mathbf{p}_a;E) = -\frac{M\hbar c\alpha}{p_\infty}\log\frac{\sqrt{1+\Delta}+1}{\sqrt{1+\Delta}-1}, \tag{4.586}$$

where $p_\infty = \sqrt{2ME}$ is the impinging momentum at infinite distance, and

$$\Delta \equiv \frac{(p_b^2 - p_\infty^2)({p_a}^2 - p_\infty^2)}{p_\infty^2|\mathbf{p}_b - \mathbf{p}_a|^2}. \tag{4.587}$$

The eikonal function is needed only for momenta $\mathbf{p}_b$, $\mathbf{p}_a$ in the asymptotic regime where $p_b, p_a \approx p_\infty$, so that Δ is small and

$$S(\mathbf{p}_b,\mathbf{p}_a;E) \approx \frac{M\hbar c\alpha}{p_\infty}\log\Delta, \tag{4.588}$$

which may be rewritten as

$$S(\mathbf{p}, \mathbf{p}_a E) \approx 2\sigma_0 - \frac{M\hbar c\alpha}{p_\infty} \log(\sin^2\theta/2), \tag{4.589}$$

with

$$\sigma_0 = \frac{M\hbar c\alpha}{2p_\infty} \log\left[\frac{(p_b^2 - p_\infty^2)(p_a{}^2 - p_\infty^2)}{p_\infty^4}\right], \tag{4.590}$$

and the scattering angle determined by $\cos\theta = [\mathbf{p}_b \cdot \mathbf{p}_a / p_b p_a]$. The logarithmically diverging constant σ_0 for $p_a = p_b p_\infty$ does, fortunately, not depend on the scattering angle, and is therefore the semiclassical approximation for the phase shift at angular momentum $l = 0$. It therefore drops, fortunately, out of the difference of the amplitudes in Eq. (4.585). Inserting (4.589) with (4.590) into (4.584) and (4.585), we obtain the differential cross section for Mott scattering (see Fig. 4.7 for a plot)

$$\frac{d\sigma}{d\Omega} = \left(\frac{\hbar c\alpha}{4E}\right)^2 \left\{\frac{1}{\sin^4\theta/2} + \frac{1}{\cos^4\theta/2} \pm \frac{1}{\sin^2\theta/2\cos^2\theta/2} 2\cos\left[\frac{2\alpha Mc}{p_\infty}\log(\cot\theta/2)\right]\right\}. \tag{4.591}$$

This semiclassical result happens to be identical to the exact result. The exactness is caused by two properties of the Coulomb motion: First there is only one trajectory for each scattering angle, second the motion can be mapped onto that of a harmonic oscillator in four dimensions, as we shall see in Chapter 13.

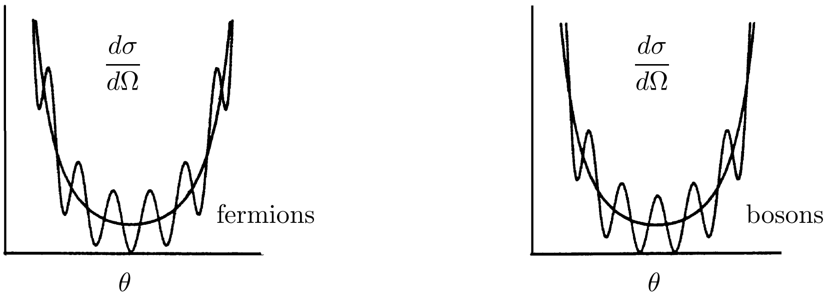

Figure 4.7 Oscillations in differential Mott scattering cross section caused by statistics. For scattering angle $\theta = 90^0$, the cross section vanishes due to the Pauli exclusion principle. The right-hand plot shows the situation for identical bosons.

Appendix 4A Semiclassical Quantization for Pure Power Potentials

Let us calculate the local density of states (4.264) for the general pure power potential $V(\mathbf{x}) = gx^p/p$ in D dimensions. For $D = 1$ and $p = 2$, we shall recover the exact spectrum of the harmonic oscillator. For $p = 4$, we shall find the energies of the purely quartic potential which can be compared with the strong-coupling limit of the anharmonic oscillator with $V(x) = \omega^2 x^2/2 + gx^4/4$ to be calculated in Section 5.16. The integrals on the right-hand side of Eq. (4.264) can be calculated using the formula

$$\int d^D x\, r^\mu [E - V(\mathbf{x})]^\nu = S_D \int_0^{r_E} dr\, r^{D-1+\mu} \left(E - \frac{g}{p} r^p\right)^\nu$$

$$= S_D \frac{\Gamma(1+\nu)\Gamma((D+\mu)/p)}{p\,\Gamma(1+\nu+(D+\mu)/p)}\left(\frac{g}{p}\right)^{-(D+\mu)/p} E^{\nu+(D+\mu)/p}\,, \quad p>0, \quad (4A.1)$$

where $r_E = (pE/g)^{1/p}$. For $p < 0$, the result is

$$\int d^D x\, r^\mu [E - V(\mathbf{x})]^\nu = S_D \frac{\Gamma(1+\nu)\Gamma(-\nu-(D+\mu)/p)}{p\,\Gamma(1-(D+\mu)/p)}\left(-\frac{g}{p}\right)^{-(D+\mu)/p} (-E)^{\nu+(D+\mu)/p}, \; p<0. \quad (4A.2)$$

Recalling (4.214), we find the total density of states for $p > 0$:

$$\begin{aligned}\rho(E) \;=\; & \frac{2}{\Gamma\left(\frac{D}{2}\right) p}\left(\frac{M}{2\hbar^2}\right)^{D/2}\left(\frac{g}{p}\right)^{-D/p} \frac{\Gamma\left(\frac{D}{p}\right)}{\Gamma\left(\frac{D}{2}+\frac{D}{p}\right)}\Bigg\{1 - \frac{\hbar^2}{24M}\left(\frac{g}{p}\right)^{2/p} \\ & \times \frac{p^2\,\Gamma\left(\frac{D-2}{p}+2\right)\Gamma\left(\frac{D}{2}+\frac{D}{p}\right)}{\Gamma\left(\frac{D-2}{2}(1+\frac{2}{p})\right)\Gamma\left(\frac{D}{p}\right)} E^{-1-2/p} + \dots\Bigg\} E^{(D/2)(1+2/p)-1}, \quad p>0, \end{aligned} \quad (4A.3)$$

and for $p < 0$:

$$\begin{aligned}\rho(E) \;=\; & -\frac{2}{\Gamma(\frac{D}{2})\,p}\left(\frac{M}{2\hbar^2}\right)^{D/2}\left(-\frac{g}{p}\right)^{-D/p} \frac{\Gamma\left(1-\frac{D}{2}-\frac{D}{p}\right)}{\Gamma\left(1-\frac{D}{p}\right)}\Bigg\{1 + \frac{\hbar^2}{24M}\left(-\frac{g}{p}\right)^{2/p} \\ & \times \frac{p^2\Gamma\left(1-\frac{D-2}{2}(1+\frac{2}{p})\right)\Gamma\left(1-\frac{D}{p}\right)}{\Gamma\left(-1-\frac{D-2}{p}\right)\Gamma\left(1-\frac{D}{2}-\frac{D}{p})\right)} (-E)^{-1-2/p} + \dots\Bigg\}(-E)^{(D/2)(1+2/p)-1}, \; p<0. \end{aligned} \quad (4A.4)$$

For a harmonic oscillator with $p = 2$ and $g = M\omega^2$, we obtain

$$\rho(E) = \frac{1}{(\hbar\omega)^D}\left\{\frac{1}{\Gamma(D)}E^{D-1} - \frac{\hbar^2\omega^2}{24}\frac{D}{\Gamma(D-2)}E^{D-3} + \dots\right\}. \quad (4A.5)$$

In one and two dimension, only the first term survives and $\rho(E) = 1/\hbar\omega$ or $\rho(E) = E/(\hbar\omega)^2$. Inserting this into Eq. (1.586), we find the number of states $N(E) = \int_0^E dE'\,\rho(E') = E/\hbar\omega$ or $E^2/2(\hbar\omega)^2$. According to the exact quantization condition (1.588), we set $N(E) = n + 1/2$ the exact energies $E_n = (n + 1/2)\hbar\omega$. Since the semiclassical expansion (4A.3) contains only the first term, the exact quantization condition (1.588) agrees with the Bohr-Sommerfeld quantization condition (4.190).

In two dimensions we obtain $\rho(E) = E/(\hbar\omega)^2$ and $N(E) = E^2/2(\hbar\omega)^2$. Here the exact quantization condition $N(E) = n + 1/2$ cannot be used to find the energies E_n, due to the degeneracies of the energy eigenvalues E_n. In order to see that it is nevertheless a true equation, let us expand the known partition function (2.407) of the two-dimensional oscillator as

$$Z = \frac{1}{[2\sinh(\hbar\beta\omega/2)]^2} = e^{-\hbar\beta\omega}\frac{1}{(1-e^{-\hbar\beta\omega})^2} = \sum_{n=0}^{\infty}(n+1)e^{-(n+1)\hbar\beta\omega}. \quad (4A.6)$$

This shows that the energies are $E_n = (n + 1)\hbar\omega$ withy $n + 1$ -fold degeneracy. The density of states is found from this by the Fourier transform (1.585):

$$\rho(E) = \sum_{n'=0}^{\infty}(n'+1)\delta(E - \hbar\omega(n'+1)). \quad (4A.7)$$

Integrating this over E yields the number of states

$$N(E) = \int_0^E dE'\,\rho(E') = \sum_{n'=0}^{\infty}(n'+1)\Theta(E - E_n). \quad (4A.8)$$

For $E = E_n$ this becomes [recall (1.313)]

$$N(E_n) = \sum_{n'=0}^{n-1}(n'+1) + (n+1)\frac{1}{2} = \frac{1}{2}(n+1)^2. \tag{4A.9}$$

This shows that the exact energies $E_n = (n+1)\hbar\omega$ of the two-dimensional oscillator satisfy the quantization condition $N(E_n) = (n+1)^2/2$ rather than (1.588).

For a quartic potential $gx^4/4$, Eq. (4A.3) becomes

$$\rho(E) = \frac{1}{2\,\Gamma(\frac{D}{2})}\frac{\Gamma(\frac{D}{4})}{\Gamma(\frac{3D}{4})}\left(\frac{g\hbar^4}{M^2}\right)^{-\frac{D}{4}}\left\{1 - \left(\frac{g\hbar^4}{M^2}\right)^{\frac{1}{2}}\frac{\Gamma(\frac{3}{2}+\frac{D}{4})\Gamma(\frac{3D}{4})E^{-\frac{3}{2}}}{3\Gamma(\frac{D}{4})\Gamma\left(\frac{3}{4}(D-2)\right)} + \ldots\right\}E^{\frac{3D}{4}-1}. \tag{4A.10}$$

Integrating this over E yields $N(E)$. Setting $N(E) = n + 1/2$ in one dimension, we obtain the Bohr-Sommerfeld energies (4.35) plus a first quantum correction. Since we have studied these corrections to high order in Subsection 4.9.6 (see Fig. 4.1), we do not write the result down here.

A physically important case is $p = -1$, $g = \hbar c\alpha$, with α of Eq. (1.505), where $V(x) = -\hbar c\alpha/r$ becomes the Coulomb potential. Here we obtain from (4A.10):

$$\begin{aligned}\rho(E) \;&=\; \frac{2}{\Gamma(\frac{D}{2})}\left(\frac{Mg^2}{2\pi\hbar^2}\right)^{D/2}\frac{\Gamma\left(1+\frac{D}{2}\right)}{\Gamma\left(1+D\right)}\\ &\times\;\left\{1 - \frac{\hbar^2}{24Mg^{-2}}\frac{p^2\,\Gamma\left(\frac{D-2}{2}\right)\Gamma\left(1+D\right)}{\Gamma\left(D-3\right)\Gamma\left(1+\frac{D}{2}\right))}E + \ldots\right\}(-E)^{(D/2)(1+2/p)-1}.\end{aligned} \tag{4A.11}$$

For $D = 1$, only the leading term survives and

$$\rho(E) = \sqrt{\frac{Mg^2}{2\hbar^2}}(-E)^{-3/2}, \tag{4A.12}$$

implying that

$$N(E) = 2\sqrt{\frac{Mg^2}{2\hbar^2}}(-E)^{-1/2}. \tag{4A.13}$$

In order to find the bound-state energies, we must watch out for a subtlety in one dimension: only the positive half-space is accessible to the particle in a Coulomb potential, due to the strong singularity at the origin. For this reason, the "surface of a sphere" S_D for $D = 1$, which is equal to 2, must be replaced by 1, so that we must equate $N(E)/2$ to $n + 1/2$. This yields the spectrum $E_n = -\alpha^2 Mc^2/2(n+1/2)^2$. The exact energies follow the same formula with n^2 instead of $(n+1/2)^2$ [7]. In contrast to the harmonic oscillator, the Bohr-Sommerfeld approximation yields here the correct energies only for large n. We have seen at the end of Section 4.1 how to correct this defect: we must go to a new variable ξ by the coordinate transformation $r = e^{\xi}$. This moves the singularity at $r = 0$ to $\xi = -\infty$ and the semiclassical result becomes *exact*.

Appendix 4B Derivation of Semiclassical Time Evolution Amplitude

Here we derive the semiclassical approximation to the time evolution amplitude (4.267). We shall do this for imaginary times $\tau = it$. Decomposing the path $\mathbf{x}(\tau)$ into path average of the ends points $\bar{\mathbf{x}} = (\mathbf{x}_b + \mathbf{x}_a)/2$ and fluctuations $\boldsymbol{\eta}(\tau)$, we calculate the imaginary-time amplitude[17]

$$(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a) = \int_{\boldsymbol{\eta}(\tau_a)=-\Delta\mathbf{x}/2}^{\boldsymbol{\eta}(\tau_b)=\Delta\mathbf{x}/2}\mathcal{D}\boldsymbol{\eta}\,\exp\left\{-\frac{1}{\hbar}\int_{\tau_a}^{\tau_b}d\tau\left[\frac{M}{2}\,\dot{\boldsymbol{\eta}}^2(\tau) + V\Big(\bar{\mathbf{x}} + \boldsymbol{\eta}(\tau)\Big)\right]\right\}\,, \tag{4B.1}$$

[17]In the mathematical literature this is a heat kernel (see Footnote 16 in Chapter 2). The expansions in (4B.16) and (4B.59) are called a *heat kernel expansions*, or *Hadamard expansions*, crediting J. Hadamard, *Lectures on Cauchy's Problem*, Yale University Press, New Haven, 1932.

where $\Delta\mathbf{x} \equiv \mathbf{x}_b - \mathbf{x}_a$. For smooth potentials we expand

$$V\Big(\bar{\mathbf{x}} + \boldsymbol{\eta}(\tau)\Big) = V(\bar{\mathbf{x}}) + \partial_i V(\bar{\mathbf{x}})\,\eta_i(\tau) + \frac{1}{2}\,\partial_i\partial_j V(\bar{\mathbf{x}})\,\eta_i(\tau)\,\eta_j(\tau) + \dots\,, \tag{4B.2}$$

where $V_{ij\dots}(\bar{\mathbf{x}}) \equiv \partial_i\partial_j \cdots V(\bar{\mathbf{x}})$, and rewrite the path integral (4B.1) as

$$\begin{aligned}(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a) \;&=\; e^{-\beta V(\bar{\mathbf{x}})}\int_{\boldsymbol{\eta}(\tau_a)=-\Delta\mathbf{x}/2}^{\boldsymbol{\eta}(\tau_b)=\Delta\mathbf{x}/2} \mathcal{D}\boldsymbol{\eta}\;\exp\left\{-\frac{1}{\hbar}\int_{\tau_a}^{\tau_b} d\tau\,\frac{M}{2}\,\dot{\boldsymbol{\eta}}^2(\tau)\right\}\\ &\times\left\{1 - \frac{1}{\hbar}\int_{\tau_a}^{\tau_b} d\tau\Big[V_i(\bar{\mathbf{x}})\,\eta_i(\tau) + \frac{1}{2}\,V_{ij}(\bar{\mathbf{x}})\,\eta_i(\tau)\,\eta_j(\tau) + \dots\Big]\right.\\ &\left.\quad + \frac{1}{2\hbar^2}\int_{\tau_a}^{\tau_b} d\tau\int_{\tau_a}^{\tau_b} d\tau'\Big[V_i(\bar{\mathbf{x}})V_j(\bar{\mathbf{x}})\,\eta_i(\tau)\eta_j(\tau')+\dots\Big]+\dots\right\}.\end{aligned} \tag{4B.3}$$

At this point it is useful to introduce an auxiliary harmonic imaginary-time amplitude

$$(\Delta\mathbf{x}/2\,\tau_b|-\Delta\mathbf{x}/2\,\tau_a) = \int_{\boldsymbol{\eta}(\tau_a)=-\Delta\mathbf{x}/2}^{\boldsymbol{\eta}(\tau_b)=\Delta\mathbf{x}/2} \mathcal{D}\boldsymbol{\eta}\,\exp\left\{-\frac{1}{\hbar}\int_{\tau_a}^{\tau_b} d\tau\,\frac{M}{2}\,\dot{\boldsymbol{\eta}}^2(\tau)\right\} \tag{4B.4}$$

and the harmonic expectation values

$$\langle F[\boldsymbol{\eta}]\rangle \equiv \frac{1}{(\Delta\mathbf{x}/2\,\tau_b|-\Delta\mathbf{x}/2\,\tau_a)}\int_{\boldsymbol{\eta}(\tau_a)=-\Delta\mathbf{x}/2}^{\boldsymbol{\eta}(\tau_b)=\Delta\mathbf{x}/2} \mathcal{D}\boldsymbol{\eta}\,F[\boldsymbol{\eta}]\exp\left\{-\frac{1}{\hbar}\int_{\tau_a}^{\tau_b} d\tau\,\frac{M}{2}\dot{\boldsymbol{\eta}}^2(\tau)\right\}, \tag{4B.5}$$

which allows us to rewrite (4B.3) more concisely as

$$\begin{aligned}(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a) &= e^{-\beta V(\bar{\mathbf{x}})}\,(\Delta\mathbf{x}/2\,\tau_b|-\Delta\mathbf{x}/2\,\tau_a)\left\{1 - \frac{1}{\hbar}\int_{\tau_a}^{\tau_b} d\tau\,V_i(\bar{\mathbf{x}})\,\langle\eta_i(\tau)\rangle\right.\\ &\left.-\frac{1}{2\hbar}\,V_{ij}(\bar{\mathbf{x}})\int_{\tau_a}^{\tau_b} d\tau\langle\eta_i(\tau)\eta_j(\tau)\rangle + \frac{1}{2\hbar^2}V_i(\bar{\mathbf{x}})V_j(\bar{\mathbf{x}})\int_{\tau_a}^{\tau_b} d\tau\int_{\tau_a}^{\tau_b} d\tau'\,\langle\eta_i(\tau)\eta_j(\tau')\rangle + \dots\right\}.\end{aligned} \tag{4B.6}$$

The amplitudes (4B.4) reads explicitly, with $\Delta\tau \equiv \tau_b - \tau_a$:

$$(\Delta\mathbf{x}/2\,\tau_b| - \Delta\mathbf{x}/2\,\tau_a) = \left(\frac{M}{2\pi\hbar\Delta\tau}\right)^{D/2}\exp\left\{-\,\frac{M}{2\hbar\Delta\tau}\,(\Delta\mathbf{x})^2\right\}, \tag{4B.7}$$

and (4B.5) can be calculated from the generating functional

$$(\Delta\mathbf{x}/2\,\tau_b|-\Delta\mathbf{x}/2\,\tau_a)[\mathbf{j}] = \int_{\boldsymbol{\eta}(\tau_a)=-\Delta\mathbf{x}/2}^{\boldsymbol{\eta}(\tau_b)=\Delta\mathbf{x}/2} \mathcal{D}\boldsymbol{\eta}\left\{-\frac{1}{\hbar}\int_{\tau_a}^{\tau_b} d\tau\left[\frac{M}{2}\,\dot{\boldsymbol{\eta}}^2(\tau) - \mathbf{j}(\tau)\,\boldsymbol{\eta}(\tau)\right]\right\}, \tag{4B.8}$$

whose explicit solution is

$$\begin{aligned}(\Delta\mathbf{x}/2\,\tau_b|-\Delta\mathbf{x}/2\,\tau_a)[\mathbf{j}] &= \left(\frac{M}{2\pi\hbar\Delta\tau}\right)^{D/2}\exp\left\{-\frac{M}{2\hbar\Delta\tau}(\Delta\mathbf{x})^2 + \frac{1}{\hbar\Delta\tau}\int_{\tau_a}^{\tau_b} d\tau(\tau-\bar{\tau})\,\Delta\mathbf{x}\,\mathbf{j}(\tau)\right.\\ &\left.+\;\frac{1}{2\hbar}\int_{\tau_a}^{\tau_b} d\tau\int_{\tau_a}^{\tau_b} d\tau'\,\frac{\Theta(\tau-\tau')(\Delta\tau-\tau)\tau' + \Theta(\tau'-\tau)(\Delta\tau-\tau')\tau}{M\Delta\tau}\,\mathbf{j}(\tau)\,\mathbf{j}(\tau')\right\}.\end{aligned}$$

The expectation values in (4B.6) and (4B.5) are obtained from the functional derivatives

$$\langle\eta_i(\tau)\rangle \;=\; \frac{1}{(\Delta\mathbf{x}/2\,\tau_b| - \Delta\mathbf{x}/2\,\tau_a)}\;\frac{\hbar\delta}{\delta j_i(\tau)}\,(\Delta\mathbf{x}/2\,\tau_b|-\Delta\mathbf{x}/2\,\tau_a)[\mathbf{j}]\bigg|_{\mathbf{j}=\mathbf{0}}\,, \tag{4B.9}$$

$$\langle\eta_i(\tau)\eta_j(\tau')\rangle \;=\; \frac{1}{(\Delta\mathbf{x}/2\,\tau_b|-\Delta\mathbf{x}/2\,\tau_a)}\;\frac{\hbar\delta}{\delta j_i(\tau)}\frac{\hbar\delta}{\delta j_j(\tau')}(\Delta\mathbf{x}/2\,\tau_b|-\Delta\mathbf{x}/2\,\tau_a)[\mathbf{j}]\bigg|_{\mathbf{j}=\mathbf{0}}. \tag{4B.10}$$

This yields the $\Delta\mathbf{x}$-dependent expectation value

$$\langle \eta_i(\tau)\rangle = (\tau-\bar\tau)\,\frac{\Delta x_i}{\Delta\tau}\,, \tag{4B.11}$$

and the $\Delta\mathbf{x}$-dependent correlation function

$$\begin{aligned}\langle \eta_i(\tau)\eta_j(\tau')\rangle &= \frac{\hbar}{M\Delta\tau}\left[\Theta(\tau-\tau')(\Delta\tau-\tau)\tau'+\Theta(\tau'-\tau)(\Delta\tau-\tau')\tau\right]\delta_{ij}\\ &+ (\tau-\bar\tau)\,(\tau'-\bar\tau)\,\frac{\Delta x_i}{\Delta\tau}\frac{\Delta x_j}{\Delta\tau}\\ &\equiv G(\tau,\tau')\delta_{ij}+H(\tau,\tau')\Delta x_i\Delta x_j\equiv G^{\Delta x}_{ij}(\tau,\tau').\end{aligned} \tag{4B.12}$$

Note that

$$\int_{\tau_a}^{\tau_b} d\tau\ \langle\eta_i(\tau)\rangle = 0, \tag{4B.13}$$

and

$$\int_{\tau_a}^{\tau_b} d\tau\int_{\tau_a}^{\tau_b} d\tau'\ \langle\eta_i(\tau)\eta_j(\tau')\rangle=\int_{\tau_a}^{\tau_b} d\tau\int_{\tau_a}^{\tau_b} d\tau'\ G^{\Delta x}_{ij}(\tau,\tau')=\frac{\hbar}{12M}\Delta\tau(\Delta\tau^2-\tau_a^2)\delta_{ij}, \tag{4B.14}$$

$$\int_{\tau_a}^{\tau_b} d\tau\ \langle\eta_i(\tau)\eta_j(\tau)\rangle=\int_{\tau_a}^{\tau_b} d\tau\, G^{\Delta x}_{ij}(\tau,\tau)=\frac{\hbar}{M}\left[\frac{\Delta\tau^2}{6}-\tau_a^2\right]\delta_{ij}+\frac{\Delta\tau}{12}\Delta x_i\Delta x_j. \tag{4B.15}$$

Thus we obtain the semiclassical imaginary-time amplitude

$$\begin{aligned}(\mathbf{x}_b\,\tau_b|\mathbf{x}_a\,\tau_a) &= \left(\frac{M}{2\pi\hbar\Delta\tau}\right)^{D/2}\exp\left\{-\frac{M}{2\hbar\Delta\tau}\Delta\mathbf{x}^2-\frac{\Delta\tau}{\hbar}V(\bar{\mathbf{x}})\right\}\\ &\times\left\{1-\frac{\Delta\tau^2}{12M}\boldsymbol{\nabla}^2V(\bar{\mathbf{x}})-\frac{\Delta\tau}{24\hbar}\left(\Delta\mathbf{x}\boldsymbol{\nabla}\right)^2V(\bar{\mathbf{x}})+\frac{\Delta\tau^3}{24M\hbar}\left[\boldsymbol{\nabla}V(\bar{\mathbf{x}})\right]^2+\dots\right\}.\end{aligned} \tag{4B.16}$$

This agrees precisely with the real-time amplitude (4.267).

For the partition function at inverse temperature $\beta=(\tau_b-\tau_a)/\hbar$, this implies the semiclassical approximation

$$\begin{aligned}Z &= \int d^Dx\,(\mathbf{x}\,\hbar\beta|\mathbf{x}\,0)\\ &\approx \left(\frac{M}{2\pi\hbar^2\beta}\right)^{D/2}\int d^D\bar{x}\left(1-\frac{\hbar^2\beta^2}{12M}\boldsymbol{\nabla}^2V(\mathbf{x})+\frac{\hbar^2\beta^3}{24M}[\boldsymbol{\nabla}V(\mathbf{x})]^2\right)e^{-\beta V(\mathbf{x})}.\end{aligned} \tag{4B.17}$$

A partial integration simplifies this to

$$\begin{aligned}Z &\approx \left(\frac{M}{2\pi\hbar^2\beta}\right)^{D/2}\int d^Dx\left(1-\frac{\hbar^2\beta^2}{24M}\boldsymbol{\nabla}^2V(\mathbf{x})\right)e^{-\beta V(\mathbf{x})}\\ &\approx \left(\frac{M}{2\pi\hbar^2\beta}\right)^{D/2}\int d^Dx\,\exp\left(-\beta V(\mathbf{x})-\frac{\hbar^2\beta^2}{24M}\boldsymbol{\nabla}^2V(\mathbf{x})\right).\end{aligned} \tag{4B.18}$$

Let us also sketch how to calculate all terms in (4B.16) proportional to $V(\bar{\mathbf{x}})$ and its derivatives. Instead of the expansion (4B.6), we evaluate

$$(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a)=e^{-\beta V(\bar{\mathbf{x}})}\,(\Delta\mathbf{x}/2\,\tau_b|-\Delta\mathbf{x}/2\,\tau_a)\left\{1-\frac{1}{\hbar}\int_{\tau_a}^{\tau_b}d\tau\ \langle V\left(\bar{\mathbf{x}}+\boldsymbol{\eta}(\tau)\right)-V(\bar{\mathbf{x}})\rangle\right\}. \tag{4B.19}$$

By rewriting $V(\bar{\mathbf{x}}+\boldsymbol{\eta})$ as a Fourier integral

$$V(\bar{\mathbf{x}}+\boldsymbol{\eta})=\int\frac{d^Dk}{(2\pi)^D}\tilde{V}(\mathbf{k})\exp\left[i\mathbf{k}\left(\bar{\mathbf{x}}+\boldsymbol{\eta}\right)\right], \tag{4B.20}$$

we obtain

$$\begin{aligned}(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a) &= (\Delta\mathbf{x}/2\,\tau_b|-\Delta\mathbf{x}/2\,\tau_a)\\ &\times\; e^{-\beta V(\bar{\mathbf{x}})}\left\{1-\frac{1}{\hbar}\int_{\tau_a}^{\tau_b}d\tau\int\frac{d^Dk}{(2\pi)^D}\tilde{V}(\mathbf{k})e^{i\mathbf{k}\bar{\mathbf{x}}}\left\langle e^{i\mathbf{k}\boldsymbol{\eta}(\tau)}-1\right\rangle\right\}.\end{aligned} \tag{4B.21}$$

The expectation value can be calculated using Wick's theorem (3.310) as

$$\int_{\tau_a}^{\tau_b}d\tau\left\langle e^{i\mathbf{k}\boldsymbol{\eta}(\tau)}\right\rangle=\int_{\tau_a}^{\tau_b}d\tau e^{-k_ik_j\langle\eta_i(\tau)\eta_j(\tau)\rangle/2}=\int_{\tau_a}^{\tau_b}d\tau e^{-k_ik_j[G(\tau,\tau)\delta_{ij}+H(\tau,\tau)\Delta x_i\Delta x_j]/2}. \tag{4B.22}$$

where the equal-time functions $G(\tau,\tau)$, $H(\tau,\tau)$ are from (4B.12):

$$G(\tau,\tau)=\frac{\hbar}{M\Delta\tau}(\Delta\tau-\tau)\tau,\qquad H(\tau,\tau)=\frac{(\tau-\bar{\tau})^2}{\Delta\tau^2}. \tag{4B.23}$$

Inserting the inverse of the Fourier decomposition (4B.20),

$$\tilde{V}(\mathbf{k})=\int d^D\eta\,V(\bar{\mathbf{x}}+\boldsymbol{\eta})\exp\left[-i\mathbf{k}\left(\bar{\mathbf{x}}+\boldsymbol{\eta}\right)\right], \tag{4B.24}$$

where $\boldsymbol{\eta}$ is now a time-independent variable of integration, we find

$$\int_{\tau_a}^{\tau_b}d\tau\left\langle e^{i\mathbf{k}\boldsymbol{\eta}(\tau)}\right\rangle=\int_{\tau_a}^{\tau_b}d\tau\int d^D\eta V(\bar{\mathbf{x}}+\boldsymbol{\eta})\int\frac{d^Dk}{(2\pi)^D}e^{-(1/2)k_iG_{ij}^{\Delta x}(\tau,\tau)k_j-ik_i\eta_i(\tau)}. \tag{4B.25}$$

After a quadratic completion of the exponent, the momentum integral can be performed and yields

$$\int_{\tau_a}^{\tau_b}d\tau\left\langle e^{i\mathbf{k}\boldsymbol{\eta}(\tau)}\right\rangle \;=\; \int d^D\eta\,V(\bar{\mathbf{x}}+\boldsymbol{\eta})\int_{\tau_a}^{\tau_b}d\tau\,\left[\det G_{ij}^{\Delta x}(\tau,\tau)\right]^{-1/2}e^{-(1/2)\eta_i[G_{ij}^{\Delta x}(\tau,\tau)]^{-1}\eta_j}. \tag{4B.26}$$

Using the transverse and longitudinal projection matrices

$$P_{ij}^T=\delta_{ij}-\frac{\Delta x_i\Delta x_j}{(\Delta x)^2},\qquad P_{ij}^L=\frac{\Delta x_i\Delta x_j}{(\Delta x)^2}, \tag{4B.27}$$

satisfying ${P^T}^2=P^T$, ${P^L}^2=P^L$, we can decompose $G_{ij}(\tau,\tau')$ as

$$G_{ij}^{\Delta x}(\tau,\tau')\equiv G(\tau,\tau')P_{ij}^T+\left[G(\tau,\tau')+H(\tau,\tau')(\Delta x)^2\right]P_{ij}^L. \tag{4B.28}$$

It is then easy to find the determinant

$$\det G_{ij}^{\Delta x}(\tau,\tau')=[G(\tau,\tau')]^{D-1}[G(\tau,\tau')+H(\tau,\tau')(\Delta x)^2], \tag{4B.29}$$

and the inverse matrix

$$[G_{ij}^{\Delta x}(\tau,\tau')]^{-1}=\frac{1}{G(\tau,\tau')}\left[\delta_{ij}-\frac{\Delta x_i\Delta x_j}{(\Delta x)^2}\right]+\frac{1}{G(\tau,\tau')+H(\tau,\tau')(\Delta x)^2}\frac{\Delta x_i\Delta x_j}{(\Delta x)^2}. \tag{4B.30}$$

Inserting (4B.26) back into (4B.21), and taking the correction into the exponent, we arrive at

$$(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a) \;=\; (\Delta\mathbf{x}/2\,\tau_b|-\Delta\mathbf{x}/2\,\tau_a)\,e^{-\int_{\tau_a}^{\tau_b}d\tau\bar{V}(\bar{\mathbf{x}},\tau)/\hbar}, \tag{4B.31}$$

where $\bar{V}(\bar{\mathbf{x}},\tau)$ is the harmonically smeared potential

$$\bar{V}(\bar{\mathbf{x}},\tau) \equiv \left[\det G^{\Delta x}_{ij}(\tau,\tau)\right]^{-1/2} \int d^D\eta\, V(\bar{\mathbf{x}}+\boldsymbol{\eta}) e^{-(1/2)\eta_i[G^{\Delta x}_{ij}(\tau,\tau)]^{-1}\eta_j}. \tag{4B.32}$$

By expanding $V(\bar{\mathbf{x}}+\boldsymbol{\eta})$ to second order in $\boldsymbol{\eta}$, the exponent in (4B.31) becomes

$$-\beta V(\bar{\mathbf{x}}) - \frac{1}{2\hbar} V_{ij}(\bar{\mathbf{x}}) \int_{\tau_a}^{\tau_b} d\tau\, G^{\Delta x}_{ij}(\tau,\tau) + \dots\ . \tag{4B.33}$$

According to Eq. (4B.15), we have

$$\int_{\tau_a}^{\tau_b} d\tau\, G^{\Delta x}_{ij}(\tau,\tau) = \frac{\hbar}{M}\frac{\Delta\tau^2}{6}\delta_{ij} + \frac{\Delta\tau}{12}\Delta x_i\, \Delta x_j, \tag{4B.34}$$

so that we reobtain the first two correction terms in the curly brackets of (4B.16)

The calculation of the higher-order corrections becomes quite tedious. One rewrites the expansion (4B.2) as $V\Big(\bar{\mathbf{x}}+\boldsymbol{\eta}(\tau)\Big) = e^{\eta_i(\tau)\partial_i} V(\bar{\mathbf{x}})$ and (4B.19) as

$$(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a) = (\Delta\mathbf{x}/2\,\tau_b|-\Delta\mathbf{x}/2\,\tau_a) \times \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left\langle \prod_{n=0}^{\infty} \int_{\tau_a}^{\tau_b} d\tau_n\, e^{\eta_i(\tau_n)\partial_i} V(\bar{\mathbf{x}}) \right\rangle. \tag{4B.35}$$

Now we apply Wick's rule (3.310) for harmonically fluctuating variables, to re-express

$$\begin{aligned} \left\langle e^{\eta(\tau)\partial_i} \right\rangle &= e^{\langle \eta_i(\tau)\eta_j(\tau)\rangle/2} = e^{G^{\Delta x}_{ij}(\tau,\tau)\partial_i\partial_j/2}, \\ \left\langle e^{\eta_i(\tau)\partial_i} e^{\eta_i(\tau')\partial_i} \right\rangle &= e^{\left[\langle \eta_i(\tau)\eta_j(\tau)\rangle\partial_i\partial_j + \left\langle \eta_i(\tau')\eta_j(\tau')\right\rangle\partial_i\partial_j + 2\left\langle \eta_i(\tau)\eta_j(\tau')\right\rangle\partial_i\partial_j\right]/2} \\ &= e^{\left[G^{\Delta x}_{ij}(\tau,\tau)\partial_i\partial_j + G^{\Delta x}_{ij}(\tau',\tau')\partial_i\partial_j + 2G^{\Delta x}_{ij}(\tau,\tau')\partial_i\partial_j\right]/2} \\ &\vdots \quad . \end{aligned} \tag{4B.36}$$

Expanding the exponentials and performing the τ-integrals in (4B.35) yields all desired higher-order corrections in (4B.16).

For $\Delta\mathbf{x} = 0$, the expansion has been driven to high orders in Ref. [8] (including a minimal interaction with a vector potential).

There exists an efficient operator method for evaluating (4B.1) and deriving (4B.16) which goes as follows. We rewrite (4B.1) in operator form as

$$(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a) = \langle \mathbf{x}_b| e^{-\Delta\tau H(\hat{p}^2,\hat{\mathbf{x}})/\hbar} |\mathbf{x}_a\rangle = \langle \mathbf{x}_b| e^{-\Delta\tau[\hat{p}^2/2M + V(\hat{\mathbf{x}})]/\hbar} |\mathbf{x}_a\rangle. \tag{4B.37}$$

With the help of formula (1.296), this can be expressed es follows:

$$(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a) \;=\; \langle \mathbf{x}_b| e^{-\Delta\tau\hat{p}^2/2M\hbar}\, \hat{T} \exp\left\{ -\int_0^{\Delta\tau} d\tau\, e^{\tau\hat{p}^2/2M\hbar} V(\mathbf{x}) e^{-\tau\hat{p}^2/2M\hbar} \right\} |\mathbf{x}_a\rangle. \tag{4B.38}$$

Now we use the Heisenberg equation (1.277) and evalaute

$$e^{\tau\hat{p}^2/2M\hbar} V(\hat{\mathbf{x}}) e^{-\tau\hat{p}'^2/2M\hbar} \equiv V(\hat{\mathbf{x}}_H(\tau)) = V(\hat{\mathbf{x}} - i\hat{\mathbf{p}}\tau/M). \tag{4B.39}$$

This allows us to recast (4B.38) to the form

$$(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a) \;=\; \langle \mathbf{x}_b| e^{-\Delta\tau\hat{p}^2/2M\hbar}\, \hat{T} \exp\left\{ -\frac{1}{\hbar}\int_0^{\Delta\tau} d\tau\, \Delta V(\hat{\mathbf{x}},\hat{\mathbf{p}},\tau) \right\} |\mathbf{x}_a\rangle e^{-\Delta\tau V(\mathbf{x}_a)/\hbar}, \tag{4B.40}$$

where

$$\Delta V(\hat{\mathbf{x}}, \hat{\mathbf{p}}, \tau) \equiv V(\hat{\mathbf{x}} - i\hat{\mathbf{p}}\tau/M) - V(\hat{\mathbf{x}}). \tag{4B.41}$$

Expressing $V(\hat{\mathbf{x}})$ by its Fourier representation, this is equal to

$$\Delta V(\hat{\mathbf{x}}, \hat{\mathbf{p}}, \tau) = \int \frac{d^D k}{(2\pi)^D} \tilde{V}(\mathbf{k}) \left(e^{i\mathbf{k}(\hat{\mathbf{x}} - i\hat{\mathbf{p}}\tau/M)} - e^{i\mathbf{k}\hat{\mathbf{x}}} \right), \tag{4B.42}$$

which is also equal to

$$\Delta V(\hat{\mathbf{x}}, \hat{\mathbf{p}}, \tau) = \int d^D x' \, V(\mathbf{x}') S(\hat{\mathbf{p}}\tau, \hat{\mathbf{x}}, \mathbf{x}'), \tag{4B.43}$$

where

$$S(\hat{\mathbf{p}}\tau, \hat{\mathbf{x}}, \mathbf{x}'; \tau) \equiv \int \frac{d^D k}{(2\pi)^D} \left(e^{i\mathbf{k}(\hat{\mathbf{x}} - \mathbf{x}' - i\hat{\mathbf{p}}\tau/M)} - e^{i\mathbf{k}(\hat{\mathbf{x}} - \mathbf{x}')} \right) \tag{4B.44}$$

is a smearing operator. Inserting now a completeness relation of the momentum states in front of the time-ordering operator in Eq. (4B.38), we find

$$(\mathbf{x}_b \tau_b | \mathbf{x}_a \tau_a) \equiv \int \frac{d^D p}{(2\pi\hbar)^D} e^{i\mathbf{p}\cdot\mathbf{x}_b/\hbar} e^{-\Delta\tau H(p, \mathbf{x}_a)\hbar} \langle \mathbf{p} | \hat{T} \exp \left\{ -\frac{1}{\hbar} \int_0^{\Delta\tau} d\tau \, \Delta V(\hat{\mathbf{x}}, \hat{\mathbf{p}}, \tau) \right\} | \mathbf{x}_a \rangle. \tag{4B.45}$$

This formula can now be evaluated by expanding the time-ordered product in powers of $\Delta V(\hat{\mathbf{x}}, \hat{\mathbf{p}}, \tau)$.

To first-order, we use the Baker-Campbell-Hausdorff formula (2.9) to re-order the exponential of the operators $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$. This leads to the matrix element

$$\begin{aligned} \langle \mathbf{p} | S(\hat{\mathbf{p}}\tau, \hat{\mathbf{x}}, \mathbf{x}') | \mathbf{x}_a \rangle &= \int \frac{d^D k}{(2\pi)^D} \langle \mathbf{p} | \left(e^{\mathbf{k}\hat{\mathbf{p}}\tau/M} e^{i\mathbf{k}(\hat{\mathbf{x}} - \mathbf{x}')} e^{-k^2\tau\hbar/2M} - e^{i\mathbf{k}(\hat{\mathbf{x}} - \mathbf{x}')} \right) | \mathbf{x}_a \rangle \\ &= \int \frac{d^D k}{(2\pi)^D} \left(e^{i\mathbf{k}(\mathbf{x}_a - \mathbf{x}' - i\mathbf{p}\tau/M)} e^{-k^2\tau\hbar/2M} - e^{i\mathbf{k}(\mathbf{x}_a - \mathbf{x}')} \right) e^{-i\mathbf{p}\mathbf{x}_a}. \end{aligned} \tag{4B.46}$$

It is now useful to introduce a softended δ-function of width $\tau M/\eta$:

$$\delta_\tau(\mathbf{x}) \equiv \int \frac{d^D k}{(2\pi)^D} e^{i\mathbf{k}\mathbf{x}} e^{-k^2\tau\hbar/2M}. \tag{4B.47}$$

It has the properties

$$\int d^D x \, \delta_\tau(\mathbf{x}) = 1, \quad \int d^D x \, x_i x_j \delta_\tau(\mathbf{x}) = \tau \frac{\hbar}{M} \delta_{ij}, \dots . \tag{4B.48}$$

With the help of this we define the smeared potential

$$V_\tau(\mathbf{x}) \equiv \int d^D x' \delta_\tau(\mathbf{x} - \mathbf{x}') V(\mathbf{x}') = \frac{1}{(2\pi\tau\hbar/M)^{D/2}} \int d^D x' \, V(\mathbf{x} - \mathbf{x}') e^{-x'^2 M/2\tau\hbar} \tag{4B.49}$$

For small τ, this has an expansion

$$V_\tau(\mathbf{x}) \equiv V_\tau(\mathbf{x}) + \frac{\tau}{2} \frac{\hbar}{M} \boldsymbol{\nabla}^2 V(\mathbf{x}) + \frac{\tau^2}{8} \left(\frac{\hbar}{M} \right)^2 \boldsymbol{\nabla}^4 V(\mathbf{x}) + \dots . \tag{4B.50}$$

Then we arrive at the first-order result

$$(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a) = \int \frac{d^Dp}{(2\pi\hbar)^D} e^{i\mathbf{p}\cdot\Delta\mathbf{x}/\hbar} e^{-\Delta\tau H(p,\mathbf{x}_a)/\hbar} \left\{1 - \frac{1}{\hbar}\int_0^{\Delta\tau} d\tau\, W_{\mathbf{p}\tau} + \ldots\right\}. \tag{4B.51}$$

where

$$W_{\mathbf{p}\tau} \equiv \langle \mathbf{p}|V_\tau(\hat{\mathbf{x}} - i\hat{\mathbf{p}}\tau/M) - V(\hat{\mathbf{x}})|\mathbf{x}_a\rangle. \tag{4B.52}$$

We now change the variable of integration from $\mathbf{p}$ to $\mathbf{p}' \equiv \mathbf{p} - iM\Delta\mathbf{x}/\tau$, and find (after omitting the prime)

$$(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a) = e^{-M\Delta\mathbf{x}^2/2\Delta\tau\hbar} \int \frac{d^Dp}{(2\pi\hbar)^D} e^{-\Delta\tau H(p,\mathbf{x}_a)/\hbar} \left\{1 - \frac{1}{\hbar}\int_0^{\Delta\tau} d\tau\, W_{\mathbf{p}\tau + iM\Delta\mathbf{x}} + \ldots\right\}. \tag{4B.53}$$

Performing the momentum integration, we errive at

$$(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a) = \frac{e^{-M\Delta\mathbf{x}^2/2\Delta\tau\hbar}}{(2\pi\Delta\tau\hbar/M)^{D/2}} e^{-\Delta\tau V(\mathbf{x}_a)/\hbar} \left\langle 1 - \frac{1}{\hbar}\int_0^{\Delta\tau} d\tau\, W_{\mathbf{p}\tau + iM\Delta\mathbf{x}} + \ldots\right\rangle_p, \tag{4B.54}$$

where the expectation value of a function $\langle f(\mathbf{p})\rangle_p$ denotes the Gaussian momentum average:

$$\langle f(\mathbf{p})\rangle_p \equiv \int \frac{d^Dp}{(2\pi\hbar)^D} f(\mathbf{p}) e^{-\Delta\tau p^2/2M\hbar} \Bigg/ \int \frac{d^Dp}{(2\pi\hbar)^D} e^{-\Delta\tau p^2/2M\hbar}. \tag{4B.55}$$

Now we expand $\Delta V_\tau(\mathbf{x}_b - i\mathbf{p}\tau/M)$ in powers of $\mathbf{p}$:

$$\Delta V_\tau(\mathbf{x}) \approx V(\mathbf{x}_b) - V(\mathbf{x}_a) + \frac{\tau}{2}\frac{\hbar}{M}\boldsymbol{\nabla}^2 V(\mathbf{x}_b) - i\frac{\tau}{M}\mathbf{p}\boldsymbol{\nabla}V(\mathbf{x}_b) - \frac{\tau^2}{2!M^2}(\mathbf{p}\boldsymbol{\nabla})^2 V(\mathbf{x}_b). \tag{4B.56}$$

The momentum averages in formula (4B.63) are calculated with the help of the integral formula (4.331) which reads here

$$\int \frac{d^Dp}{(2\pi\hbar)^D} e^{-\Delta\tau p^2/2M\hbar} \{1, p^ip^j, p^{i_1}p^{i_2}p^{i_3}p^4, \ldots\ldots, p^{i_1}p^{i_2}\cdots p^{i_{2n-1}}p^{i_{2n}}, \ldots\}$$
$$= \frac{1}{(2\pi\Delta\tau\hbar/M)^{D/2}} \left\{1, \frac{M\hbar}{\Delta\tau}\delta^{ij}, \left(\frac{M\hbar}{\Delta\tau}\right)^2 \delta^{i_1i_2i_3i_4}, \ldots, \left(\frac{M\hbar}{\Delta\tau}\right)^n \delta^{i_1i_2\ldots i_{2n-1}i_{2n}}, \ldots\right\}, \tag{4B.57}$$

with the contraction tensors (4.333). Applying these to the expression (4B.63) we obtain the low-order contributions to (4B.63)

$$(\mathbf{x}_b\tau_b|\mathbf{x}_a\tau_a) = \frac{e^{-M\Delta\mathbf{x}^2/2\Delta\tau\hbar}}{(2\pi\Delta\tau\hbar/M)^{D/2}} e^{-\Delta\tau V(\mathbf{x}_a)/\hbar}(1 + A_1 + A_2 + \ldots), \tag{4B.58}$$

where

$$A_1 = -\frac{1}{\hbar}\int_0^{\Delta\tau} d\tau \left[V(\mathbf{x}_b) - V(\mathbf{x}_a) + \left(\frac{\tau}{2} - \frac{\tau^2}{2\Delta\tau}\right)\frac{\hbar}{M}\boldsymbol{\nabla}^2 V(\mathbf{x}_b) + \ldots\right]. \tag{4B.59}$$

After integrating over τ we recover (4B.16).

To second order, the calculation becomes more complicated since we have to find the matrix element

$$\langle \mathbf{p}|S(\hat{\mathbf{p}}\tau, \hat{\mathbf{x}}, \mathbf{x}')S(\hat{\mathbf{p}}\tau', \hat{\mathbf{x}}, \mathbf{x}'')|\mathbf{x}_a\rangle = \int \frac{d^Dk}{(2\pi)^D} \int \frac{d^Dk'}{(2\pi)^D} \tag{4B.60}$$
$$\times \langle \mathbf{p}| \left(e^{\mathbf{k}\hat{\mathbf{p}}\tau/M} e^{i\mathbf{k}(\hat{\mathbf{x}}-\mathbf{x}')} e^{-k^2\tau\hbar/2M} - e^{i\mathbf{k}(\hat{\mathbf{x}}-\mathbf{x}')}\right) \left(e^{\mathbf{k}'\hat{\mathbf{p}}\tau'/M} e^{i\mathbf{k}'(\hat{\mathbf{x}}-\mathbf{x}'')} e^{-k'^2\tau\hbar/2M} - e^{i\mathbf{k}'(\hat{\mathbf{x}}-\mathbf{x}'')}\right)|\mathbf{x}_a\rangle.$$

The first term in the product need re-ordering according to the Baker-Campbell-Hausdorff formula (2.9) which states that $e^{\hat{A}}e^{\hat{B}} = e^{\hat{B}}e^{\hat{A}}e^{[\hat{A},\hat{B}]}$, so that

$$\langle \mathbf{p}| e^{\mathbf{k}\hat{\mathbf{p}}\tau/M} e^{i\mathbf{k}(\hat{\mathbf{x}}-\mathbf{x}')} e^{-k^2\tau\hbar/2M}\, e^{\mathbf{k}'\hat{\mathbf{p}}\tau'/M} e^{i\mathbf{k}'(\hat{\mathbf{x}}-\mathbf{x}')} e^{-k'^2\tau\hbar/2M}|\mathbf{x}_a\rangle$$
$$= e^{-\mathbf{k}\mathbf{k}'\tau'\hbar/M}\langle \mathbf{p}| e^{\mathbf{k}\mathbf{p}\tau/M} e^{i\mathbf{k}(\mathbf{x}_a-\mathbf{x}'')} e^{-k^2\tau\hbar/2M}\, e^{\mathbf{k}'\mathbf{p}\tau'/M} e^{i\mathbf{k}'(\mathbf{x}_a-\mathbf{x}'')} e^{-k'^2\tau\hbar/2M}|\mathbf{x}_a\rangle. \quad (4B.61)$$

The prefactor can obviously be rewritten as a differential operator:

$$e^{-\mathbf{k}\mathbf{k}'\tau'\hbar/M} = e^{(\tau'\hbar/M)\boldsymbol{\nabla}'\boldsymbol{\nabla}''}. \quad (4B.62)$$

Apart from that, the integrand consists of the product of the smeared potentials $V_\tau(\mathbf{x}' - i\mathbf{p}\tau/M)$. Thus the second-order correction in (4B.59) becomes

$$A_2 = \left\langle \frac{1}{\hbar^2}\int_0^{\Delta\tau} d\tau \int_0^{\tau} d\tau'\, W^{(2)}(\mathbf{p}) \right\rangle_p , \quad (4B.63)$$

where

$$W^{(2)}(\mathbf{p}) \equiv \left(e^{(\tau'\hbar/M)\boldsymbol{\nabla}'\boldsymbol{\nabla}''} - 1\right) V_\tau(\mathbf{x}' - i\mathbf{p}\tau/M) V_{\tau'}(\mathbf{x}'' - i\mathbf{p}\tau'/M)\Big|_{\mathbf{x}'=\mathbf{x}_a,\mathbf{x}''=\mathbf{x}_a}$$
$$+ \left[V_\tau(\mathbf{x}_b - i\mathbf{p}\tau/M) - V(\mathbf{x}_a)\right]\left[V_{\tau'}(\mathbf{x}_b - i\mathbf{p}\tau'/M) - V(\mathbf{x}_a)\right]. \quad (4B.64)$$

By evaluating this expression we can extend the expansion (4B.16) to higher orders in $\beta = \Delta\tau/\hbar$.

The expression (4B.63) can be used to derive a compact formula for the gradient expansion of the trace log of the Hamiltonian operator $\hat{H} = \hat{\mathbf{p}}^2/2M + V(\hat{\mathbf{x}})$. We insert (4B.40) into formula and (4.290), and obtain the Euclidean-time formula

$$\mathrm{Tr}\log\hat{H} \;=\; -\int d^D x \int_0^\infty \frac{d\tau}{\tau}\langle \mathbf{x}|e^{-\tau H(\hat{p},\mathbf{x}_a)/\hbar}\,\hat{T}\exp\left\{-\frac{1}{\hbar}\int_0^\tau d\tau'\,\Delta V(\hat{\mathbf{x}},\hat{\mathbf{p}},\tau')\right\}|\mathbf{x}\rangle. \quad (4B.65)$$

Appendix 4C Potential of Thomas Fermi Model

Let us expand $f(\xi) = 1 + \sum_{n=2}^\infty a_n\xi^{n/2}$, and insert this into the self-consistent Thomas-Fermi equation (4.384) to obtain

$$\sum_{k=3}^\infty a_k \frac{k(k-2)}{4}\xi^{(k-4)/2} = \xi^{-1/2}\exp\left[\tfrac{3}{2}\log(1+\sum_{k=2}^\infty a_n\xi^{n/2})\right]. \quad (4C.1)$$

This leads to a recursive determination of the coeffcients:

$$a_3 = \tfrac{4}{3},\;\; a_4 = 0,\; a_5 = \tfrac{2}{5}a_2,\;\; a_6 = \tfrac{1}{3},\;\; a_7 = \tfrac{3}{70}a_2^2,\;\; a_8 = \tfrac{2}{15}a_2,$$
$$a_9 = \tfrac{2}{27} - \tfrac{1}{252}a_2^3,\;\; a_{10} = \tfrac{1}{175}a_2^2,\;\; a_{11} = \tfrac{31}{1485}a_2 + \tfrac{1}{1056}a_2^4,\;\; \ldots\;. \quad (4C.2)$$

Inserting the slope parameter $a_2 = -s$ from Eq. (4.386), we obtain a so-called asymptotic expansion of the function $f(\xi)$. This can, however, be used to obtain the plot in Fig. 4.2 only for very small ξ, due its divergence. Only after developing the resummation technique called variational perturbation theory in Chapter 5 will we able to obtain the entire plot from the expansion.

For large ξ, the behavior of $f(\xi)$ is $f(\xi) \to f_{\rm as}(\xi) \equiv 144/\xi^3$ as verifed by direct insertion into Eq. (4.384) [recall Eq. (4.387)]. The next correction to this is

$$f(\xi) = f_{\rm as}(\xi)\left(1 + b_1 x^{-q} + b_2 x^{-2q} + \ldots\right), \quad (4C.3)$$

where

$$q = \frac{1}{2}\left(\sqrt{73} - 7\right), \quad b_2 = -\frac{9b_1^2}{2\left(7\sqrt{73} - 67\right)}. \quad (4C.4)$$

with $b_1 \approx -13.3$. Fixing this parameter is equivalent to fixing the slope paramter s in the small-ξ expansion.

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