ANNALS OF PHYSICS: 60, 401–447 (1970)

Distribution of Eigenfrequencies for the Wave Equation in a Finite Domain I. Three-Dimensional Problem with Smooth Boundary Surface

R. BALIAN AND C. BLOCH

Service de Physique Théorique, Centre d'Etudes Nucléaires de Saclay, France

Received March 20, 1970

The distribution of eigenvalues of the equation $\Delta\varphi + E\varphi = 0$ is calculated for a volume V of arbitrary shape, and for the general boundary condition $\partial\varphi/\partial n = \kappa\varphi$ on the surface S, assumed to be smooth. A time-independent Green function method is used, involving a multiple reflection expansion. In the limit of wavelengths small compared to any characteristic dimension of the system, the eigenvalue density, smoothed to eliminate its fluctuating part, is given by the asymptotic expansion:

$$\rho(E) = \frac{1}{4\pi^2}\left[Vk + S\left(\frac{\pi}{4} - \delta\right) + \frac{1}{k}\left(\frac{1}{3} + \cos^2\delta - \delta\cot\delta\right)\int d\sigma\,\frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + \cdots\right],$$

where R_1 and R_2 are the main curvature radii of S, with $\delta = \tan^{-1}\kappa/k$. Both surface and curvature terms depend on the boundary condition. The correct curvature term differs from the extrapolation of the wedge term of the parallelepiped, which has sometimes been used in nuclear physics. Neumann and Dirichlet boundary conditions are recovered for $\kappa = 0$ and $\kappa \to +\infty$. For $\kappa \to -\infty$, the density contains an additional contribution corresponding to surface states.

I. INTRODUCTION

In many branches of physics, it is necessary to know the distribution of eigenvalues of the wave equation

$$\Delta\varphi + k^2\varphi = 0, \tag{I.1}$$

where the functions φ satisfy some boundary condition on a closed surface S. The wave equation (I.1) is supposed to hold inside the volume V bounded by S. For instance, the function φ may represent a sound wave, either in three dimensions (room acoustics), or in two dimensions [1] (vibrations of a membrane). In nuclear physics, φ may be the single particle wave function in the independent particle approximation. Then Eq. (I.1) with a suitable boundary condition is an idealization

of the actual self-consistent field of a heavy nucleus, and the distribution of its eigenvalues provides a description of the nuclear properties in terms of the deformation [2]. Another problem of the same type, but with vector waves, occurs for the distribution of normal modes for electromagnetic waves in a cavity. From the resulting density of modes, it is possible, for instance, to evaluate the Casimir effect [3], considered as the sum of the energy shifts of the electromagnetic eigenmodes due to the presence of a conductor. Eq. (I.1) appears also in connection with diffusion problems. Finally, the present theory may be used for evaluating the density of electron states in small particles.[1]

The enumeration of the eigenvalues is very simple for a parallelepiped. In the limit of a large volume, one obtains, for the number of eigenfunctions with a wave number between k and $k + dk$, the expression

$$\rho(k)\, dk \sim \frac{Vk^2}{2\pi^2}\, dk. \tag{I.2}$$

We shall also use, instead of k, the variable

$$E \equiv k^2,$$

which is the energy in nonrelativistic quantum mechanics, with units such that $\hbar^2/2M = 1$. Correspondingly, one introduces the density of eigenvalues with respect to the variable E

$$\rho(E) = \rho(k)\frac{dk}{dE} = \frac{1}{2k}\rho(k) = \frac{Vk}{4\pi^2} + \cdots. \tag{I.3}$$

The theory developed here yields the density $\rho(E)$ more directly than $\rho(k)$, and we shall therefore always refer to it.

Strictly speaking, the density $\rho(E)$ is not a smooth function, but a sum of distributions $\delta(E - E_n)$, because the eigenvalues E_n are discrete. In order to write truly asymptotic expressions, mathematicians usually evaluate, rather than $\rho(E)$, its primitive $N(E)$, the number of eigenvalues whose energy is less than E. This is a sum of step functions, which behaves for a large volume V as

$$N(E) = \int_0^E dE'\, \rho(E') \sim \frac{Vk^3}{6\pi^2}. \tag{I.4}$$

The fact that expression (I.4) is asymptotically exact for a large volume V irrespective of its shape, provided the limiting surface S satisfies appropriate regularity conditions, is a famous theorem due to H. Weyl [4]. The problem of determining the asymptotic behavior of eigenvalue distributions has since raised

[1] L. N. Cooper and S. Hu, private communication.

considerable interest among mathematicians, who have studied various extensions [5] of Weyl's theorem.[2]

For physical applications, it is often necessary to consider wavelengths $2\pi/k$ which are not very short compared to the dimensions of the volume V. One then needs to improve the expression (I.4), by considering it as the beginning of an asymptotic expansion in inverse powers of $kV^{1/3}$, and evaluating corrections of next orders.

A priori, one may expect (I.4) to be the first term of an asymptotic expansion of $N(E)$ of the form:

$$N(E) = \frac{Vk^3}{6\pi^2} + ak^2 + bk + \mathcal{O}(1), \qquad (k \to \infty). \tag{I.5}$$

It is clearly impossible to go beyond these three terms since $N(E)$ increases by steps of at least one unit with E. Moreover, for many particular shapes of V the modes are degenerate and $N(E)$ may increase by much larger steps. For a spherical volume, for instance, each level of angular momentum l gives rise to a step of height $2l + 1$ in $N(E)$ at the corresponding energy. This produces *fluctuations* in $N(E)$ of amplitude proportional to k and it is therefore impossible to define in a strict asymptotic sense an expansion of $N(E)$ beyond the term in k^2. For a volume of arbitrary shape, the levels are no longer degenerate, but they may remain bunched, due to resonance effects depending on the shape.

These fluctuations give rise to very important physical effects, such as the shell structure in spherical or deformed nuclei, and we shall evaluate them in a forthcoming paper. Mathematically, their existence raises very difficult problems as long as one is interested in the function $N(E)$ itself. A natural way out of this difficulty consists in considering only averaged or *smoothed functions*, which are usually sufficient for physical applications. If the width γ of the smoothing function is sufficiently large, not only with respect to the distance between eigenvalues, but also with respect to the period of the fluctuations, it becomes possible to define asymptotic expansions not only for the smoothed $N(E)$, but even for the smoothed density itself. In this paper, we shall assume that the width γ is sufficiently large for wiping out entirely the fluctuations, in such a way that expansions such as (I.5) become valid up to the term in k for $N(E)$ or to the term in $1/k$ for $\rho(E)$. For evaluating the fluctuations, we shall later discuss how γ can be reduced as much as possible.

Various smoothing functions have been used in the literature. A first method consists in calculating the primitive of $N(E)$, and has been applied to a polyhedral volume [6]. More generally, repeated integration of $N(E)$ would further reduce the relative fluctuations. For evaluating the function $N(E)$, a log Gaussian smoothing

[2] The review article [5] contains a large number of references on this problem.

procedure has also been used [7]. In this paper we shall take a Lorentzian shape for the smoothing function. This choice, familiar to the physicist, yields relatively simple calculations.

It should be noted that, whereas the first term of expansion (I.5) is independent of the *boundary conditions*, this is no longer true for the subsequent terms. Besides the Dirichlet and Neumann boundary conditions on S:

$$\text{(A)} \qquad \varphi = 0,$$

$$\text{(B)} \qquad \frac{\partial \varphi}{\partial n} = 0,$$

already considered in the literature, we shall discuss the more general boundary condition

$$\text{(C)} \qquad \frac{\partial \varphi}{\partial n} - \kappa \varphi = 0,$$

of particular interest in nuclear physics, but which does not seem to have been studied so far. We specify the orientation of the normal to S by taking it pointing towards the interior region: when S is a sphere, $\partial/\partial n$ reduces to $-\partial/\partial r$ in spherical coordinates. In some problems (for instance in acoustics) the logarithmic derivative κ of φ may vary along the surface S. This possibility is easily included in the present theory.

For boundary conditions (A) and (B), the expansion including the surface term had already been conjectured by Weyl as:

$$\rho(E) \approx \frac{Vk}{4\pi^2} \mp \frac{S}{16\pi}, \tag{I.6}$$

where S denotes the area of the boundary surface, and where the signs $-$ and $+$ correspond respectively to (A) and (B). But, as far as we know, the surface term was not known for boundary condition (C).

The next term in the expansion clearly depends on the curvature of the surface. Surprisingly, it was derived only recently [1, 7], and only for boundary conditions (A) and (B). For three dimensions:

$$\rho(E) \approx \frac{Vk}{4\pi^2} \mp \frac{S}{16\pi} + \frac{1}{12\pi^2 k} \int d\sigma \, \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \tag{I.7}$$

where R_1 and R_2 are the two main curvature radii at each point of the boundary. This result does not seem to have been widely known. For instance [8], path integral methods have been quite recently proposed as an attempt to formulate conjectures for the surface and curvature terms in two dimensions.

Equation (I.7) applies to smooth surfaces. It is interesting to compare it with the asymptotic distribution of eigenvalues for a parallelepiped of sides L_1, L_2, L_3, which is easy to derive. For boundary condition (A), the result is:

$$\rho(E) \approx \frac{Vk}{4\pi^2} - \frac{S}{16\pi} + \frac{1}{8\pi k}(L_1 + L_2 + L_3). \tag{I.8}$$

It was then tempting [9] to consider each edge of the parallelepiped as a region with a δ-like curvature, and to extrapolate (I.8) into an expression applicable to a smooth surface. This extrapolation, which has been used in nuclear physics [10] while the correct result (I.7) was not known, yields an expansion similar to (I.7), but in which the coefficient of the last term is wrong by a factor 3/2. The existence of sharp edges is therefore pathological, and it is impossible to transpose the results valid for a smooth surface to the edges of a parallelepiped.

In this paper, we propose a systematic method for calculating the asymptotic eigenvalue density of equation (I.1), with any one of boundary conditions (A), (B), or (C) on a smooth surface S. We shall explicitly derive the first three terms of the expansion only (as in Eq. (I.7)), since it is not clear that further terms would really be useful. Moreover, the actual calculation of further terms becomes tedious, although not difficult in principle. Various extensions will be examined later, including the use of curvilinear coordinates, the effect of sharp edges, the n-dimensional case, the evaluation of fluctuations, and the problem of electromagnetic waves. A similar asymptotic method will be given for the Schrödinger equation.

Most studies of eigenvalue densities are based on the Green function technique initiated by Carleman [11], applied in various ways. Before describing the particular Green function formalism which we shall use, it may be interesting to outline a slightly different form, which has a simple intuitive interpretation showing clearly the essence of the method.

Consider the diffusion equation

$$\Delta\varphi - \frac{\partial\varphi}{\partial t} = 0 \tag{I.9}$$

inside V, with boundary condition (A) or (B) on S. In order to have a physical picture, we may consider this as a heat diffusion equation, where φ denotes the temperature.

The Green function for this heat diffusion problem satisfies the equations

$$\begin{aligned} \left(\Delta - \frac{\partial}{\partial t}\right) G(r\,r', t) &= 0, \qquad t > 0, \\ G(r\,r', 0) &= \delta(r - r'), \end{aligned} \tag{I.10}$$

together with the appropriate boundary condition on S. It is related to the orthonormalized eigenfunctions $\varphi_n(r)$ and eigenvalues k_n of (I.1) (with boundary condition (A) or (B)) by the expansion

$$G(r\,r',\,t) = \sum_n \varphi_n(r)\, e^{-k_n{}^2 t} \varphi_n(r'), \tag{I.11}$$

from which it is easy to derive the density of eigenvalues $\rho(E)$. Actually, the expression

$$\Phi(t) \equiv \int_V d^3r\; G(r\,r',\,t) = \sum_n e^{-k_n{}^2 t} = \int_0^{+\infty} dE\; e^{-Et}\rho(E) \tag{I.12}$$

is the Laplace transform of $\rho(E)$. Its singularity with the smallest real part is at $t = 0$. This singularity determines the behavior of $\rho(E)$ for large E. The problem therefore reduces to the evaluation of the Green function $G(r\,r',\,t)$ for small t.

Physically, $G(r\,r',\,t)$ describes the evolution of a heat pulse, localized at time $t = 0$ at some point r' inside V. It is clear that, for small values of t, the heat will remain concentrated within a small region around r'. Thus, provided r' is not too close to S, it is a reasonable approximation to disregard the boundary condition for t small, and to replace G by G_0, the Green function for the heat diffusion problem in infinite space:

$$\begin{aligned} G_0(r\,r',\,t) &= \frac{1}{(2\pi)^3} \int d^3p\; e^{ip\cdot(r-r')-p^2t} \\ &= \frac{1}{(4\pi t)^{3/2}}\, e^{-(r-r')^2/4t}. \end{aligned} \tag{I.13}$$

Substitution of this expression into (I.12) gives

$$\Phi_0(t) = \frac{V}{(4\pi t)^{3/2}}, \tag{I.14}$$

which is a good approximation of $\Phi(t)$ for small t.

The density of eigenvalues is given by the inverse Laplace transform:

$$\rho(E) = \frac{1}{2\pi i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} dt\; e^{Et}\Phi(t), \tag{I.15}$$

which yields, when $\Phi(t)$ is approximated by $\Phi_0(t)$, Weyl's asymptotic form indicated above

$$\rho(E) \approx \frac{V}{16\pi^{5/2} i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} dt\, \frac{e^{Et}}{t^{3/2}} = \frac{Vk}{4\pi^2}. \tag{I.16}$$

The Green function G differs very much from G_0 if the initial point r' lies near the boundary S. If this surface is sufficiently smooth, and if r' is sufficiently close to it, we may replace S by its tangent plane (Fig. 1). A better approximation to the Green function may then be obtained by using the idea of *images*. Let r_1' be the symmetrical of the point r' with respect to the tangent plane. The approximate Green function

$$G(r\,r', t) \simeq G_0(r\,r', t) \mp G_0(r\,r_1', t) \tag{I.17}$$

satisfies Eq. (I.10), together with the boundary condition (A) or (B) on the tangent plane for the sign $-$ or $+$, respectively. For t small, the reflected term $G_0(r\,r_1', t)$ is negligible unless r' is near the surface.

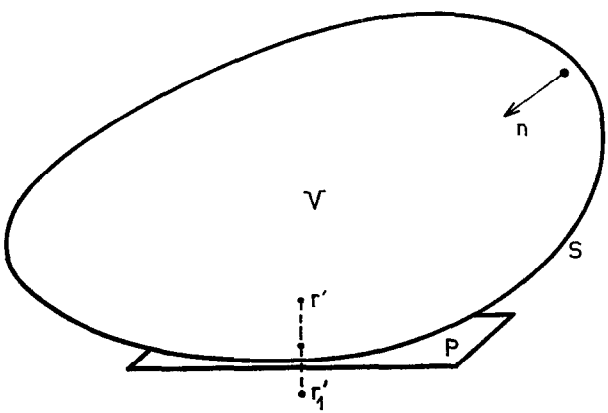

FIG. 1. The image r_1' of a point r' of V.

When the improved expression (I.17) for G is substituted into the integral (I.12) for $\Phi(t)$, this second term gives a correction if r lies within a thin layer near S. Denoting by z the distance of r to the nearest tangent plane, the correction to $\Phi(t)$ is

$$\mp \int d^3r\, G_0(r\,r_1\,, t) = \mp \frac{1}{(4\pi t)^{3/2}} \int_S d\sigma \int_0^\infty dz\, e^{-z^2/t} = \mp \frac{S}{16\pi t}, \tag{I.18}$$

since the distance between r and its image r_1 is $2z$.

The inverse Laplace transform of (I.18)

$$\mp \frac{S}{16\pi^2 i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} dt\, \frac{e^{Et}}{t} = \mp \frac{S}{16\pi} \tag{I.19}$$

yields the surface term of Eq. (I.6).

This argument shows how simply the first two terms of the asymptotic expansion of $\rho(E)$ are obtained by considering the heat diffusion problem and the idea of images. It may be given full mathematical rigor [5, 11] by using Tauberian theorems to legitimate the expansion of $\Phi(t)$ around $t = 0$ in the inverse Laplace transform (I.15). A similar method, based on the propagation equation

$$\Delta\varphi - \frac{\partial^2\varphi}{\partial t^2} = 0$$

instead of (I.9), has also been used [6]. In its physical interpretation, heat diffusion is simply replaced by wave propagation.

We find it more convenient, however, for a systematic approach, to work with *time-independent* Green functions. This type of Green functions is more directly related to the smoothed eigenvalue density, and then Tauberian theorems are not required. On the other hand, it will be possible to treat boundary condition (C), for which the method of images is not readily applicable.

In Section II, we introduce the time-independent Green function, and express it in a form which may be interpreted as a *multiple reflection expansion.* The successive terms of this expansion correspond to the propagation of a wave from an initial point r' located within the volume V to another point r inside V, after 0, 1, 2,... reflections on the boundary surface S. The essential property of this expansion is that, when the surface is smooth, the successive terms decrease rapidly. This follows from the fact that the main contributions to the smoothed eigenvalue density come from points $r = r'$ lying close to the surface S and from reflections with impacts in the neighborhood of r.

In Sections III and IV, we derive the surface and curvature contributions to the eigenvalue density, and show that they come entirely from the one- and two-reflection terms of the Green function expansion.

The results are summarized in Section V and their domains of validity are discussed as well as some limiting cases and applications.

II. The Green Function Formalism

A. *Introduction of the Time-Independent Green Function*

The time-independent Green function is defined by

$$(\Delta + z)\, G(r\, r', z) = -\delta(r - r'), \tag{II.1}$$

together with one of the boundary conditions (A), (B) or (C). This Green function may be expressed in terms of the normalized eigenfunctions $\varphi_n(r)$ and eigenvalues

k_n of the equation (I.1) with the appropriate boundary condition, by the expansion

$$G(r\,r', z) = \sum_n \frac{\varphi_n(r)\,\varphi_n(r')}{k_n^2 - z}. \tag{II.2}$$

We now have the following identity for $\epsilon \to +0$:

$$\begin{aligned}\rho(E) &\equiv \frac{1}{2i\pi}\int_V d^3r\,[G(r\,r', E + i\epsilon) - G(r\,r', E - i\epsilon)]_{r'=r} \\ &= \frac{1}{2i\pi}\sum_n \left[\frac{1}{k_n^2 - E - i\epsilon} - \frac{1}{k_n^2 - E + i\epsilon}\right] = \sum_n \delta(k_n^2 - E),\end{aligned} \tag{II.3}$$

which relates the distribution of eigenvalues to the Green function.

In order to obtain a continuous eigenvalue density, we should smooth out the function $\rho(E)$, which is a sum of δ-functions. A convenient well known procedure consists in using a smoothing function of the Lorentz type with a width γ. Let us therefore define the density $\rho_\gamma(E)$ by:

$$\begin{aligned}\rho_\gamma(E) &= \frac{\gamma}{\pi}\int_{-\infty}^{+\infty} \frac{dE'}{(E' - E)^2 + \gamma^2}\,\rho(E') \\ &= \frac{\gamma}{\pi}\sum_n \frac{1}{(k_n^2 - E)^2 + \gamma^2}.\end{aligned} \tag{II.4}$$

It should be understood that γ must be chosen as small as possible, but nevertheless sufficiently large so that the sum in the right hand side of (II.4) contains many effective contributions.

Let us now substitute in (II.4) the expression (II.3) of $\rho(E)$ in terms of the Green function. We get

$$\rho_\gamma(E) = \frac{1}{2i\pi}\int_V d^3r\,\frac{\gamma}{\pi}\int_{-\infty}^{+\infty} \frac{dE'}{(E' - E)^2 + \gamma^2}\,[G(r\,r', E' + i\epsilon) - G(r\,r', E' - i\epsilon)]_{r'=r} \tag{II.5}$$

The function $G(r\,r', E' + i\epsilon)$ is analytic in the upper half-plane of E', and the corresponding integral may be computed by closing the contour by a large half-circle in the upper half-plane. The resulting closed contour contains the unique pole $E' = E + i\gamma$. The same argument applies to the other term in the lower half-plane with the pole $E' = E - i\gamma$. Altogether we obtain:

$$\begin{aligned}\rho_\gamma(E) &= \frac{1}{2i\pi}\int_V d^3r\,[G(r\,r', E + i\gamma) - G(r\,r', E - i\gamma)]_{r'=r} \\ &= \frac{1}{\pi}\int_V d^3r\,[\mathrm{Im}\,G(r\,r', E + i\gamma)]_{r'=r}.\end{aligned} \tag{II.6}$$

It should be noted that $G(r\,r', E + i\gamma)$ becomes infinite for $r' \to r$. It is therefore necessary in (II.6) to form the difference of the two Green functions, i.e., to take the imaginary part of G, *before* setting $r' = r$. Similarly, the method of Carleman [11] was based on an identity involving the difference of the Green functions for two energies. Carleman, however, took two real negative energies whereas we use here two complex conjugate values.

In order to examine more closely the divergence occurring for $r' = r$, let us write formally the contribution to (II.6) from a single Green function. We get

$$\int_V d^3r\, G(r\,r, E + i\gamma) = \sum_n \frac{1}{k_n^2 - E - i\gamma} \approx \int_{-\infty}^{+\infty} dE' \frac{\rho(E')}{E' - E - i\gamma},$$

which is divergent for the large values of E' since $\rho(E') \sim \sqrt{E'}$. By taking the difference between the Green functions at $E + i\gamma$ and $E - i\gamma$, the denominator $E' - E - i\gamma$ is replaced by $(E' - E)^2 + \gamma^2$ and the integral in E' becomes convergent.

This remark shows that the procedure used here will not work for more than three dimensions since then $\rho(E') \sim E'^{\nu}$ for $E' \to +\infty$ with $\nu > \frac{1}{2}$. A more powerful "regularization" is then required as we shall see in part II of this work.

In the actual calculation of (II.6) it is convenient to first evaluate the contribution of the function $G(r\,r', E + i\gamma)$ and to take the imaginary part only in the end. This interchange of the order of the operations Im and $r \to r'$ may be carried out by introducing an appropriate convergence factor $\mathscr{F}(r\,r', \eta)$ into (II.6). We write therefore:

$$\rho_\gamma(E) = \lim_{\eta \to 0} \frac{1}{\pi} \operatorname{Im} \int_V d^3r\, d^3r'\, \mathscr{F}(r\,r', \eta)\, G(r\,r', E + i\gamma), \tag{II.7}$$

which will be our basic expression. The function $\mathscr{F}(r\,r', \eta)$ must be such that the integral converges and it must satisfy the limiting condition:

$$\lim_{\eta \to 0} \mathscr{F}(r\,r', \eta) = \delta(r - r').$$

The existence of such a convergence factor and its actual form for practical calculations will be discussed below.

B. *Multiple Reflection Expansion of the Green Function for Boundary Condition* (A)

We now set up a systematic procedure for calculating the Green function, for boundary conditions on an arbitrary surface S. The analysis now depends on the type of boundary conditions on S. We shall discuss here the boundary condition (A), and later the boundary condition (C), noting that (B) is a special case of (C) for $\kappa = 0$.

As in the introduction, let us first consider the Green function corresponding to the whole space. We may then replace the eigenfunctions $\varphi_n(r)$ by the usual set of plane waves normalized to a δ-function. This gives:

$$G_0(r\,r',\,E+i\gamma) = \int \frac{d^3p}{(2\pi)^3}\,\frac{e^{ip\cdot(r-r')}}{p^2-E-i\gamma} = \frac{e^{ik|r-r'|}}{4\pi\,|\,r-r'\,|}\,. \tag{II.8}$$

Here we have denoted by k the square root of $E+i\gamma$ which has a positive imaginary part:

$$k \equiv \sqrt{E+i\gamma}, \qquad \operatorname{Im} k > 0. \tag{II.9}$$

We write the Green function G as:

$$G \equiv G_0 + G_1\,, \tag{II.10}$$

where G_0 is the Green function for the infinite space given by (II.8). The correction G_1 to the Green function must satisfy the following differential equation and boundary condition:

$$(\Delta + k^2)\,G_1 = 0, \qquad \text{for } r \text{ in } V, \tag{II.11a}$$

$$G_1 = -G_0\,, \qquad \text{for } r \text{ on } S, \tag{II.11b}$$

if G is to satisfy the boundary condition (A). The determination of G_1 appears, therefore, as a somewhat generalized Dirichlet problem (it would be the Dirichlet problem for $k = 0$). We shall use for solving it the classical method of Neumann, which consists of replacing the differential equation and boundary condition (II.11) by a unique two-dimensional integral equation on S. For the particular type of boundary condition which we are considering now, this is achieved by representing the function G_1 as a *double layer potential.* For the present type of differential equation, the elementary potential is the Green function G_0 given by (II.8). We shall therefore write the function G_1 in terms of an unknown density $\mu(\alpha\,r')$ as

$$G_1(r\,r') = \int_S d\sigma_\alpha\,\frac{\partial G_0(r\,\alpha)}{\partial n_\alpha}\,\mu(\alpha\,r'). \tag{II.12}$$

For simplicity, we shall from now on omit the energy variable in the Green functions. We denote by r' the "initial" point of the Green function, by r an arbitrary point inside V, and by $\alpha, \beta, \gamma, \ldots$ arbitrary points on the surface S. The integral

in (II.12) is extended to the surface S, $d\sigma_\alpha$ being the surface differential element. Finally, $\partial/\partial n_\alpha$ denotes the normal derivative at point α, with the normal oriented towards the interior region. The problem is now to determine the double layer density $\mu(\alpha\, r')$.

The function defined by (II.12) satisfies the differential equation (II.11a) no matter what the density μ is. The density μ is therefore determined by the boundary condition (II.11b).

It is well known from potential theory that:

(a) The integral in the right-hand side of (II.12) exists when r is a point β of the surface S. Let us call its value $G_1^{(0)}(\beta\, r')$.

(b) If we denote by $G_1^{(+)}(\beta\, r')$ the limit of the right-hand side of (II.12) as r approaches a point β of S from the interior region, we have:

$$G_1^{(+)}(\beta\, r') - G_1^{(0)}(\beta\, r') = \tfrac{1}{2}\mu(\beta\, r'). \tag{II.13}$$

By definition the Green function G is continuous inside V. It must therefore vanish as r approaches the surface S from the inside. It follows that

$$G_1^{(+)}(\beta\, r') = -G_0(\beta\, r').$$

Finally, by replacing in (II.13) $G_1^{(+)}$ by this value and $G_1^{(0)}$ by its expression (II.12), we obtain the relation

$$\frac{1}{2}\,\mu(\beta\, r') = -G_0(\beta\, r') - \int_S d\sigma_\alpha \frac{\partial G_0(\beta\,\alpha)}{\partial n_\alpha}\,\mu(\alpha\, r'). \tag{II.14}$$

This is the integral equation for the determination of the density μ.

It is a classical property that the integral equation (II.14) is nonsingular and has, therefore, a well defined unique solution. The fact that makes this equation useful for the present problem is that the kernel $\partial G_0/\partial n_\alpha$ is small when the surface is smooth. More precisely, we shall see in the next section that it is of the order of $|\, 1/kR\,|$ where R is, say, the smallest radius of curvature of the surface S. When this parameter is small, the integral equation (II.14) may be solved by perturbation, and this yields for the density μ the expansion

$$\begin{aligned}\mu(\alpha\, r') = {} & -2G_0(\alpha\, r') + 2^2 \int_S d\sigma_\beta \frac{\partial G_0(\alpha\,\beta)}{\partial n_\beta}\, G_0(\beta\, r') \\ & - 2^3 \int_S d\sigma_\beta\, d\sigma_\gamma \frac{\partial G_0(\alpha\,\beta)}{\partial n_\beta} \frac{\partial G_0(\beta\,\gamma)}{\partial n_\gamma}\, G_0(\gamma\, r') + \cdots .\end{aligned} \tag{II.15}$$

By substituting this expansion into (II.12), we obtain for the complete Green function (II.10) the expansion:

$$G(r\,r') = G_0(r\,r') - 2\int_S d\sigma_\alpha \frac{\partial G_0(r\,\alpha)}{\partial n_\alpha} G_0(\alpha\,r') + 2^2 \int_S d\sigma_\alpha\, d\sigma_\beta \frac{\partial G_0(r\,\alpha)}{\partial n_\alpha} \frac{\partial G_0(\alpha\,\beta)}{\partial n_\beta} G_0(\beta\,r') - 2^3 \int_S d\sigma_\alpha\, d\sigma_\beta\, d\sigma_\gamma \frac{\partial G_0(r\,\alpha)}{\partial n_\alpha} \frac{\partial G_0(\alpha\,\beta)}{\partial n_\beta} \frac{\partial G_0(\beta\,\gamma)}{\partial n_\gamma} G_0(\gamma\,r') + \cdots . \quad \text{(II.16)}$$

This is the basic expansion for the case of the boundary condition (A). It may be described as a *multiple reflection expansion*: starting from r' the wave is reflected on S at the points $\alpha, \beta, \gamma, \ldots$ and finally goes to r.

The density of eigenvalues is obtained by substituting the expansion (II.16) into (II.7).

It is convenient here to introduce the function $F_\eta(\alpha\,\beta)$ defined for two points α and β of S by:

$$F_\eta(\beta\,\alpha) = \int_V d^3r\, d^3r'\, G_0(r\,\alpha)\, \mathscr{F}(r\,r',\eta)\, G_0(\beta\,r'). \quad \text{(II.17)}$$

We obtain then from (II.7) and (II.17) the expansion:

$$\rho_\nu(E) = \frac{kV}{4\pi^2} + \lim_{\eta\to 0} \frac{1}{\pi} \operatorname{Im}\Big[-2\int_S d\sigma_\alpha \Big\{\frac{\partial F_\eta(\beta\,\alpha)}{\partial n_\alpha}\Big\}_{\alpha=\beta} + 2^2 \int_S d\sigma_\alpha\, d\sigma_\beta \frac{\partial F_\eta(\beta\,\alpha)}{\partial n_\alpha} \frac{\partial G_0(\alpha\,\beta)}{\partial n_\beta} - 2^3 \int_S d\sigma_\alpha\, d\sigma_\beta\, d\sigma_\gamma \frac{\partial F_\eta(\gamma\,\alpha)}{\partial n_\alpha} \frac{\partial G_0(\alpha\,\beta)}{\partial n_\beta} \frac{\partial G_0(\beta\,\gamma)}{\partial n_\gamma} + \cdots\Big], \quad \text{(II.18)}$$

which holds for boundary condition (A). Here we have written explicitly the volume term, which comes from the first term of the expansion (II.16).

C. *The Case of Boundary Conditions* (B) *and* (C)

Let us now turn to the boundary condition (C). We write again the Green function in the form (II.10), but according to the standard method we now represent G_1 as a *simple layer potential*:

$$G_1(r\,r') = \int_S d\sigma_\alpha\, G_0(r\,\alpha)\, \mu(\alpha\,r'). \quad \text{(II.19)}$$

Simple layer potentials are known to be continuous near the surface S, but their normal derivatives are discontinuous. They satisfy the relation:

$$\frac{\partial G_1^{(+)}(\beta r')}{\partial n_\beta} - \frac{\partial G_1^{(0)}(\beta r')}{\partial n_\beta} = -\frac{1}{2}\mu(\beta r'), \tag{II.20}$$

where the first term in the left-hand side denotes the limiting value as r approaches a point β of S from the inside, whereas the second term denotes the value for $r = \beta$ on S. The complete Green function G to be determined is supposed to be continuous as well as its derivatives in the inside region in the neighborhood of S. Since it must satisfy the boundary condition (C), the limit of the normal derivative of G_1 as r approaches the surface must satisfy the relation:

$$\frac{\partial G_1^{(+)}(\beta r')}{\partial n_\beta} - \kappa_\beta G_1(\beta r') = -\left[\frac{\partial G_0(\beta r')}{\partial n_\beta} - \kappa_\beta G_0(\beta r')\right]. \tag{II.21}$$

This relation gives the value of the first term in the left-hand side of (II.20), whereas the second term may be expressed by means of the integral representation (II.19). Performing these substitutions, we obtain the relation

$$\frac{1}{2}\mu(\beta r') = \left(\frac{\partial}{\partial n_\beta} - \kappa_\beta\right) G_0(\beta r') + \int_S d\sigma_\alpha \left(\frac{\partial}{\partial n_\beta} - \kappa_\beta\right) G_0(\beta\,\alpha)\,\mu(\alpha r'), \tag{II.22}$$

which is the integral equation for the determination of the density μ.

Again, it is a classical result that this integral equation is nonsingular for any finite κ_β and has therefore a unique well defined solution. The kernel here contains two terms, the first of which $\partial G_0/\partial n_\beta$ is small when the surface is smooth. The second term, however, $\kappa_\beta G_0$ is not small when κ_β is finite. It is therefore not possible to use directly the integral equation (II.22) for deriving a perturbation expansion such as (II.15). For instance, even for a plane, the expansion should be resummed to all orders in κ.

We must actually take into account exactly the term in κ_β. Let us therefore rewrite the integral equation (II.22) in the following form

$$\begin{aligned}\mu(\beta r') + 2\kappa_\beta \int_S d\sigma_\alpha\, G_0(\beta\,\alpha)\,\mu(\alpha r') \\ = 2\left(\frac{\partial}{\partial n_\beta} - \kappa_\beta\right) G_0(\beta r') + 2\int_S d\sigma_\alpha \frac{\partial G_0(\beta\,\alpha)}{\partial n_\beta}\,\mu(\alpha r').\end{aligned} \tag{II.23}$$

Consider now the Green function Γ defined on the surface S by the integral equation

$$\Gamma(\beta\,\gamma) + 2\kappa_\beta \int_S d\sigma_\alpha\, G_0(\beta\alpha)\,\Gamma(\alpha\,\gamma) = \delta(\beta - \gamma), \tag{II.24}$$

corresponding to the inversion of the operator acting on $\mu(\alpha r')$ in the left-hand side of (II.23). The right-hand side of (II.24) is the two-dimensional δ-function on the surface S.

We may then rewrite (II.23) in the form:

$$\mu(\alpha r') = 2\int_S d\sigma_\beta\, \Gamma(\alpha\beta)\left(\frac{\partial}{\partial n_\beta} - \kappa_\beta\right) G_0(\beta r') + 2\int_S d\sigma_\beta\, d\sigma_\gamma\, \Gamma(\alpha\beta)\frac{\partial G_0(\beta\gamma)}{\partial n_\beta}\mu(\gamma r'). \tag{II.25}$$

This modified integral equation now has the property that the kernel is small when the surface is smooth. It may therefore, again, be solved by perturbation, which yields for μ the following expansion

$$\mu(\alpha r') = 2\int_S d\sigma_\beta\, \Gamma(\alpha\beta)\left(\frac{\partial}{\partial n_\beta} - \kappa_\beta\right) G_0(\beta r') + 2^2\int_S d\sigma_\beta\, d\sigma_\gamma\, d\sigma_\delta\, \Gamma(\alpha\delta)\frac{\partial G_0(\delta\gamma)}{\partial n_\delta}\Gamma(\gamma\beta)\left(\frac{\partial}{\partial n_\beta} - \kappa_\beta\right) G_0(\beta r') + \cdots. \tag{II.26}$$

Substituting this expansion of μ into (II.10) and (II.19), we obtain for $G(r r')$ the following *multiple reflection expansion*:

$$G(r r') = G_0(r r') + 2\int_S d\sigma_\alpha\, d\sigma_\beta\, G_0(r\alpha)\,\Gamma(\alpha\beta)\left(\frac{\partial}{\partial n_\beta} - \kappa_\beta\right) G_0(\beta r') + 2^2\int_S d\sigma_\alpha\, d\sigma_\beta\, d\sigma_\gamma\, d\sigma_\delta\, G_0(r\alpha)\,\Gamma(\alpha\delta)\frac{\partial G_0(\delta\gamma)}{\partial n_\delta}\Gamma(\gamma\beta)\left(\frac{\partial}{\partial n_\beta} - \kappa_\beta\right) G_0(\beta r') + \cdots. \tag{II.27}$$

Substitution of this expansion into (II.7) gives for the density of eigenvalues:

$$\rho_\gamma(E) = \frac{kV}{4\pi^2} + \lim_{\eta\to 0}\frac{1}{\pi}\,\mathrm{Im}\left[2\int_S d\sigma_\alpha\, d\sigma_\beta\, \Gamma(\alpha\beta)\left(\frac{\partial}{\partial n_\beta} - \kappa_\beta\right) F_\eta(\beta\alpha) + 2^2\int_S d\sigma_\alpha\, d\sigma_\beta\, d\sigma_\gamma\, d\sigma_\delta\, \Gamma(\alpha\delta)\frac{\partial G_0(\delta\gamma)}{\partial n_\delta}\Gamma(\gamma\beta)\left(\frac{\partial}{\partial n_\beta} - \kappa_\beta\right) F_\eta(\beta\alpha) + \cdots\right], \tag{II.28}$$

where we have used again the function F_η defined by (II.17).

This expansion replaces (II.18) for the boundary condition (C). In the case of the boundary condition (B), when $\kappa = 0$, the Green function Γ reduces to the δ-function, according to (II.24). The expansion (II.28) simplifies then considerably and becomes almost identical with (II.18), the only difference being that plus signs appear in front of all terms.

III. The Surface Term

A. *The Plane Approximation*

Let us consider the successive terms of the expansions of $\rho_\nu(E)$ derived in the previous section. Each term is a multiple integral involving one point of the volume V (implied in the definition of the function F_η), and a number of points on S. The basic property which is used for the evaluation of these integrals is that the functions $G_0(\alpha r)$ and $\Gamma(\alpha \beta)$ occurring in the integrands are *short range* functions. More precisely, appreciable contributions to the integrals come only from sets of points such that all the distances $| r - \alpha |$, $| \alpha - \beta |$, $| \beta - \gamma |$,... are not much larger than the ranges of G_0 and Γ. Our basic assumption is that these ranges are much smaller than the curvature radii of the surface S at all points. The idea is then to replace locally the surface S by an appropriate tangent plane. The validity of this approximation will be discussed in Section V.

The choice of the particular tangent plane suitable for a given set of points is, of course, somewhat arbitrary. To make things definite, let us call ω the middle of the segment $\alpha\beta$, where α and β are the points occurring in the function F_η in each term of the expansion (II.28). In this section, we shall replace S by its tangent plane P at ω (Fig. 2). In the next section, we shall include the lowest order infinitesimal deviations of S with respect to P.

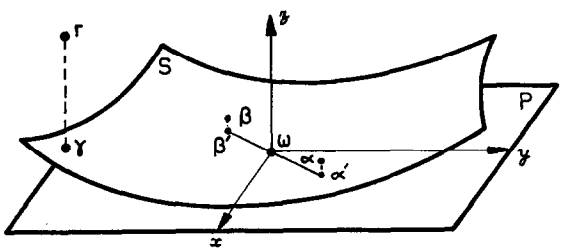

FIG. 2. The tangent plane P at a point ω of S and the associated coordinates.

The calculations will be performed by carrying out all integrations with ω fixed, the integration with respect to ω being performed last. We must therefore introduce new variables ξ and ω, replacing α and β according to

$$\xi = \alpha - \beta, \qquad \omega = \frac{\alpha + \beta}{2}. \tag{III.1}$$

The differential surface elements accordingly become in the plane approximation:

$$d\sigma_\alpha \, d\sigma_\beta = d\sigma_\xi \, d\sigma_\omega . \tag{III.2}$$

B. *The Two-Dimensional Fourier Transform*

The functions G_0, Γ, and F_η occurring in the integrands depend, in the present approximation, on two points of P and they are invariant by translation in this plane (we assume here that the convergence factor $\mathcal{F}(r\,r', \eta)$ occurring in F_η is invariant under translations parallel to P). It is therefore convenient to introduce the *two-dimensional Fourier transformation* in the plane P.

We shall use a frame of reference ωxyz, with the x and y axes in the tangent plane P, and the z-axis normal to the surface and oriented towards the interior region. In what follows we shall use bold-faced letters for the two-dimensional vectors in the plane P.

For any function $f(\boldsymbol{\alpha})$, where $\boldsymbol{\alpha}$ is a point of P with coordinates α_x, α_y, we define the Fourier transformation by

$$\begin{aligned} \hat{f}(\mathbf{p}) &= \int e^{-i\mathbf{p}\cdot\boldsymbol{\alpha}} f(\boldsymbol{\alpha})\, d\sigma_\alpha\,, \\ f(\boldsymbol{\alpha}) &= \frac{1}{(2\pi)^2} \int e^{i\mathbf{p}\cdot\boldsymbol{\alpha}} \hat{f}(\mathbf{p})\, d^2p, \end{aligned} \tag{III.3}$$

where $\mathbf{p}$ is a two-dimensional vector of coordinates p_x, p_y. In the exponential function, the scalar product denotes:

$$\mathbf{p} \cdot \boldsymbol{\alpha} = p_x\alpha_x + p_y\alpha_y\,.$$

The transform of G_0 is readily found to be:[3]

$$\hat{G}_0(p) = \frac{1}{2a(p)}\,, \tag{III.4}$$

where we have introduced the notation:

$$a(p) \equiv \sqrt{p^2 - k^2}, \qquad \operatorname{Re} a(p) > 0. \tag{III.5}$$

It should be remembered here that k^2 has a positive imaginary part. The function $a(p)$ is therefore a continuous univalued function for p real. The determination chosen in (III.5) goes from $-ik$ to $+\infty$ following the contour indicated in Fig. 3, as p varies from 0 to $+\infty$. The values of $a(p)$ for p varying from 0 to $+\infty$ have a positive real part and a negative imaginary part.

[3] This should not be confused with the usual momentum representation of the Green function $1/(p^2 - k^2)$ which is the three-dimensional Fourier transform of $G_0(r)$, occurring, for instance, in (II.8).

Consider now the plane approximation to the function Γ. It is determined by the integral equation (II.24) where α, β, and γ are supposed to be in P. We shall also assume that κ_α varies sufficiently slowly on S so that we may replace it in the equation by its value at ω. We shall discuss the effect of the variation of κ_α later on.

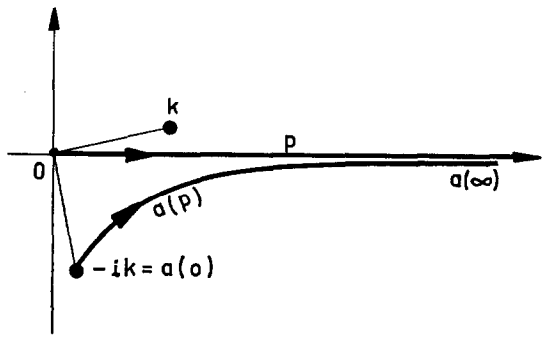

FIG. 3. The integration paths for p and $a(p)$.

Under the transformation (III.3), the integral equation (II.24) becomes

$$\hat{\Gamma}_\omega(p) + 2\kappa_\omega \hat{G}_0(p)\, \hat{\Gamma}_\omega(p) = 1, \tag{III.6}$$

where the subscript ω in $\hat{\Gamma}_\omega$ recalls that this function approximates $\hat{\Gamma}$ in the tangent plane P at ω. It follows from (III.4) that

$$\hat{\Gamma}_\omega(p) = \frac{a(p)}{\kappa_\omega + a(p)}. \tag{III.7}$$

C. *Evaluation of* $\hat{F}_\eta$

Let us now evaluate the function $F_\eta(\alpha\,\beta)$ defined by (II.17), again in the plane approximation. We rewrite the Fourier representation (II.8) of G_0 as:

$$G_0(r\,\alpha) = \int \frac{d^2p\; dq}{(2\pi)^3} \frac{e^{ip\cdot(\gamma-\alpha)+iqz}}{a^2 + q^2}, \tag{III.8}$$

where γ denotes the projection of r on P, z its distance to P (Fig. 2), and a the function of p defined by (III.5).

It is convenient to define the two-dimensional Fourier transform $\hat{G}_0(p\,z)$ of $G_0(r\,\alpha)$ with respect to $\gamma - \alpha$, keeping z fixed. Comparison of (III.3) and (III.8) shows that:

$$\hat{G}_0(p\,z) = \int_{-\infty}^{+\infty} \frac{dq}{2\pi} \frac{e^{iqz}}{a^2 + q^2}. \tag{III.9}$$

This function generalizes (III.4) to which it reduces for $z = 0$.

Let us now specify a particular choice of the convergence factor $\mathcal{F}(r\,r',\eta)$ occurring in (II.17) which simplifies the calculation of F_η as much as possible. We shall assume that in the neighborhood of a point ω of S the function $\mathcal{F}$ is a δ-function in the direction orthogonal to S and invariant under translations and rotations parallel to S:

$$\mathcal{F}(r\,r',\eta) = \delta(z - z')\,\mathcal{F}_{//}(|\gamma - \gamma'|,\eta), \tag{III.10}$$

where z and z' are the distances of r and r' to P, γ and γ' the projections of r and r' on P. Let us denote by $\hat{\mathcal{F}}_\eta(p)$ the two-dimensional Fourier transform of $\mathcal{F}_{//}$. The limiting condition for the convergence factor reads now:

$$\lim_{\eta\to 0} \hat{\mathcal{F}}_\eta(p) = 1. \tag{III.11}$$

It is not a priori obvious that a convergence factor of the form (III.10) is sufficient to ensure convergence of the integrals which we have to evaluate. We shall see that this is actually achieved provided $\hat{\mathcal{F}}_\eta(p)$ for any given η decreases sufficiently rapidly as $p \to \infty$.

Returning now to $F_\eta(\alpha\,\beta)$, we may consider it as a two-dimensional convolution integral in γ of two functions G_0 and the convergence factor $\hat{\mathcal{F}}_\eta$, combined with an integration over z from 0 to $z_{\max}$. This maximum value of z is the distance between ω and the nearest point at which the normal ωz cuts again S. At large distances, the function G_0 becomes small because k has a positive imaginary part as a result of the smoothing operation of Section II, A [see Eqs. (II.8) and (II.9)]. If we assume that

$$z_{\max}\,\mathrm{Im}\,k \gg 1, \tag{III.12}$$

the function G_0 becomes negligible for $z > z_{\max}$ and we may replace the upper limit $z_{\max}$ by $+\infty$.

The two-dimensional Fourier transform of $F_\eta(\alpha\,\beta)$ is then given by:

$$\begin{aligned}\hat{F}_\eta(p) &= \hat{\mathcal{F}}_\eta(p) \int_0^{+\infty} dz[\hat{G}_0(p\,z)]^2 \\ &= \hat{\mathcal{F}}_\eta(p) \int_0^{+\infty} dz \int_{-\infty}^{+\infty} \frac{dq\,dq'}{(2\pi)^2} \frac{e^{i(q+q')z}}{(a^2+q^2)(a^2+q'^2)}.\end{aligned}$$

An elementary integration finally yields:

$$\begin{aligned}\hat{F}_\eta(p) &= \hat{\mathcal{F}}_\eta(p) \int_0^{+\infty} dz\, \frac{e^{-2az}}{4a^2} \\ &= \frac{1}{8[a(p)]^3}\,\hat{\mathcal{F}}_\eta(p).\end{aligned} \tag{III.13}$$

D. *Evaluation of* $\partial \hat{F}_\eta / \partial n$

We also need the normal derivatives of the function F_η. For reasons of symmetry, we have:

$$\frac{\partial F_\eta(\alpha\,\beta)}{\partial n_\alpha} = \frac{\partial F_\eta(\alpha\,\beta)}{\partial n_\beta} = \frac{1}{2}\left(\frac{\partial}{\partial n_\alpha} + \frac{\partial}{\partial n_\beta}\right) F_\eta(\alpha\,\beta). \tag{III.14}$$

In the plane approximation, the normal derivative is identical with the derivative with respect to the z-coordinate:

$$\frac{\partial}{\partial n} \approx \frac{\partial}{\partial z}. \tag{III.15}$$

We also note that since $G_0(\alpha\, r)$ is invariant by translation, derivatives with respect to coordinates of r are equal and opposite to the corresponding derivatives with respect to coordinates of α. Thus:

$$\frac{\partial G_0(\alpha\, r)}{\partial n_\alpha} \approx \frac{\partial G_0(\alpha\, r)}{\partial z_\alpha} = -\frac{\partial G_0(\alpha\, r)}{\partial z}. \tag{III.16}$$

We now introduce the definition (II.17) of F_η into (III.14), taking into account (III.16). Moreover we separate, as above, the integration over r into a two-dimensional integration over the projection γ of r on P, and an integration over z, the distance of r to P, extended from 0 to $+\infty$. This yields, taking into account the fact that for the particular choice (III.10) of the convergence factor, the points r, r' have the same z-coordinate:

$$\begin{aligned}
&\frac{\partial F_\eta(\alpha\,\beta)}{\partial n} \\
&= \frac{1}{2}\int_V d^3r\, d^3r' \left[\frac{\partial G_0(\alpha\, r)}{\partial n_\alpha}\, G_0(r'\beta) + G_0(\alpha\, r)\,\frac{\partial G_0(r'\beta)}{\partial n_\beta}\right] \mathscr{F}(r\, r',\, \eta) \\
&\approx -\frac{1}{2}\int d\sigma_\gamma\, d\sigma_{\gamma'} \int_0^{+\infty} dz \left[\frac{\partial G_0(\alpha\, r)}{\partial z}\, G_0(r'\beta) + G_0(\alpha\, r)\,\frac{\partial G_0(r'\beta)}{\partial z}\right] \mathscr{F}_{//}(\gamma - \gamma',\, \eta) \\
&= -\frac{1}{2}\int d\sigma_\gamma\, d\sigma_{\gamma'} \int_0^{+\infty} dz\, \frac{\partial}{\partial z}\left[G_0(\alpha\, r)\, G_0(r'\beta)\right] \mathscr{F}_{//}(\gamma - \gamma',\, \eta) \\
&= \frac{1}{2}\int d\sigma_\gamma\, d\sigma_{\gamma'}\, G_0(\alpha\gamma)\, G_0(\gamma'\beta)\, \mathscr{F}_{//}(\gamma - \gamma',\, \eta).
\end{aligned} \tag{III.17}$$

This expression is simply the two-dimensional convolution integral of two functions G_0 and the convergence factor. The two-dimensional Fourier transform of $\partial F_\eta / \partial n$ is therefore:

$$\frac{\partial \hat{F}_\eta(p)}{\partial n} = \frac{1}{2}\left[\hat{G}_0(p)\right]^2 \hat{\mathscr{F}}_\eta(p) = \frac{1}{8[a(p)]^2}\, \hat{\mathscr{F}}_\eta(p). \tag{III.18}$$

E. *The Surface Contribution to the Density*

We now have all the elements necessary for the evaluation of the surface term. We consider therefore the second term of the expansion (II.28), replace the variables α and β by ξ and ω defined by (III.1) and express the functions by their Fourier transforms. This gives:

$$\frac{2}{\pi}\operatorname{Im}\int_S d\sigma_\omega \int d\sigma_\xi\, \Gamma_\omega(\xi)\left(\frac{\partial}{\partial n}-\kappa_\omega\right)F_\eta(-\xi)$$
$$=\frac{2}{\pi(2\pi)^2}\operatorname{Im}\int_S d\sigma_\omega \int d^2p\,\hat{\Gamma}_\omega(p)\left[\frac{\partial \hat{F}_\eta(p)}{\partial n}-\kappa_\omega \hat{F}_\eta(p)\right].$$

By introducing the expressions (III.7), (III.13), and (III.18) of the Fourier transforms derived above, we obtain for the surface term the expression

$$\frac{1}{2(2\pi)^2}\operatorname{Im}\int_S d\sigma_\omega \int_0^{+\infty}\frac{p\,dp}{[a(p)]^2}\,\frac{a(p)-\kappa_\omega}{a(p)+\kappa_\omega}\,\mathscr{F}_\eta(p), \tag{III.19}$$

where we have carried out the angular integration over the directions of p.

The integral (III.19) simplifies considerably if we take a defined by (III.5) as a new integration variable replacing p. Taking into account

$$p\,dp = a\,da,$$

we see that (III.19) becomes:

$$\frac{1}{8\pi^2}\int_S d\sigma_\omega \operatorname{Im}\int_{-ik}^{+\infty}\frac{da}{a}\,\frac{a-\kappa_\omega}{a+\kappa_\omega}\,\mathscr{F}_\eta[p(a)]. \tag{III.20}$$

We notice here that in the absence of a convergence factor ($\mathscr{F}_\eta = 1$), the integral in a would be logarithmically divergent. Let us take for instance:

$$\mathscr{F}_\eta = 1 \qquad \text{for} \quad p < 1/\eta,$$
$$\mathscr{F}_\eta = 0 \qquad \text{for} \quad p > 1/\eta.$$

Integration of (III.20) with respect to a gives:

$$\frac{1}{8\pi^2}\int_S d\sigma_\omega \operatorname{Im}[\log(-ik) - 2\log(\kappa_\omega - ik) - \log\eta + \mathcal{O}(\eta)], \tag{III.21}$$

where the determinations of the log are such that their imaginary parts lie between $-\pi$ and 0. As expected, the divergent part of the integral is purely real and we get in the limit $\eta \to 0$ the finite expression:

$$\frac{1}{4\pi^2}\int_S d\sigma_\omega\left[\frac{\pi}{4} - \tan^{-1}\frac{\kappa_\omega + k_i}{k_r} + \frac{1}{2}\tan^{-1}\frac{k_i}{k_r}\right], \tag{III.22}$$

which is the surface contribution to $\rho_\gamma(E)$. In (III.22) k_r and k_i denote the real and the imaginary parts of $k = \sqrt{E + i\gamma}$, respectively. Note that k_r and k_i are by definition both positive. In (III.22) the determinations of the $\tan^{-1}$ are such that

$$\left| \tan^{-1} \frac{\kappa_\omega + k_i}{k_r} \right| < \frac{\pi}{2}, \qquad 0 < \tan^{-1} \frac{k_i}{k_r} < \frac{\pi}{2}. \tag{III.23}$$

IV. The Curvature Term

A. *The First-Order Corrections in the Curvature*

We consider again, as in the previous section, the tangent plane P at some point ω of S. Let us assume that ωx and ωy are the curvature axes of S at ω (Fig. 2). The equation of S in the frame of reference ωxyz reads:

$$z = \frac{1}{2}\left(\frac{x^2}{R_1} + \frac{y^2}{R_2}\right) + \cdots, \tag{IV.1}$$

where the omitted terms are at least of third order in x and y. In (IV.1) R_1 and R_2 are the main radii of curvature of the surface S at the point ω.

We shall now calculate the corrections to the density of eigenvalues which are linear in $1/R_1$ and $1/R_2$. We must therefore evaluate all contributions to the expansion (II.28), originating from corrections which are linear in z.

We shall continue to denote by $\alpha, \beta, \ldots$ points on S, and we shall call $\alpha', \beta', \ldots$ the projections of these points on the tangent plane P. Let us now examine the various origins of corrections to the plane approximation, which consists of identifying $\alpha, \beta, \ldots$ with their projections $\alpha', \beta', \ldots$ (Fig. 2).

Consider first a function such as $G_0(\alpha\beta)$ which depends only on the distance $r = |\alpha - \beta|$ of two points of S. If we call $r' = |\alpha' - \beta'|$ the distance of the projections of these two points, we have:

$$r = r' + \frac{z^2}{2r'} + \cdots \approx r'. \tag{IV.2}$$

We see that the first correction is already quadratic in z and therefore negligible in the present approximation. Thus, we may write:

$$G_0(\alpha\beta) \approx G_0(\alpha'\beta'), \qquad \Gamma(\alpha\beta) \approx \Gamma(\alpha'\beta'). \tag{IV.3}$$

Similarly, no linear correction in the curvature is introduced by the differential surface elements, and we may again write:

$$d\sigma_\alpha \approx d\sigma_{\alpha'}. \tag{IV.4}$$

B. *The Curvature Correction to $\partial G/\partial n$*

Consider now the operator $\partial/\partial n$. The relation (III.15) no longer holds because the normal vector to S at a point xyz is not exactly parallel to the z-axis. From (IV.1) we see that the components of the normal vector to S are in first approximation equal to $(1, -x/R_1, -y/R_2)$, and therefore:

$$\frac{\partial}{\partial n} \approx \frac{\partial}{\partial z} - \frac{x}{R_1}\frac{\partial}{\partial x} - \frac{y}{R_2}\frac{\partial}{\partial y}. \tag{IV.5}$$

In particular, when applied to the function $G_0(\alpha\beta)$, where α and β are two points of S, this expression gives, up to the first order in the curvature:

$$\frac{\partial G_0(\alpha\beta)}{\partial n_\alpha} \approx -\left[\frac{\alpha_x(\alpha_x - \beta_x)}{R_1} + \frac{\alpha_y(\alpha_y - \beta_y)}{R_2}\right]\frac{1}{r}\frac{\partial G_0(r)}{\partial r}, \tag{IV.6}$$

where α_x, α_y and β_x, β_y are the first two coordinates of the points α and β. This relation plays a central role in the method of approximation described here. The successive terms of all the expansions given in Section II contain increasing numbers of functions $\partial G_0/\partial n$, and give therefore contributions of higher and higher order in the curvatures. Thus, for the determination of the correction linear in the curvature, it is not necessary to go beyond the third term of the expansion (II.28).

For the purpose of carrying out first-order calculations in the curvature, the expression (IV.6) may be simplified, since in the integrand in (II.28) it is multiplied by a function of α and β which actually depends only on the distance between α and β. We may therefore symmetrize the expression (IV.6) with respect to α and β:

$$\begin{aligned}\frac{\partial G_0(\alpha\beta)}{\partial n_\alpha} &\to \frac{1}{2}\left[\frac{\partial G_0(\alpha\beta)}{\partial n_\alpha} + \frac{\partial G_0(\alpha\beta)}{\partial n_\beta}\right] \\ &= -\frac{1}{2}\left[\frac{(\alpha_x - \beta_x)^2}{R_1} + \frac{(\alpha_y - \beta_y)^2}{R_2}\right]\frac{1}{r}\frac{\partial G_0(r)}{\partial r},\end{aligned}$$

and then average out with respect to the orientation of the vector $\alpha - \beta$ using the relation:

$$\overline{(\alpha_x - \beta_x)^2} = \overline{(\alpha_y - \beta_y)^2} = \tfrac{1}{2}r^2.$$

This yields the simplified expression:

$$\frac{\partial G_0(\alpha\beta)}{\partial n} \approx -\frac{r}{2R_\omega}\frac{\partial G_0(r)}{\partial r} = -\frac{1}{2R_\omega}(\mathbf{r}\cdot\nabla_r)\,G_0(r), \tag{IV.7}$$

where R_ω is the *mean curvature radius* at ω defined by

$$\frac{1}{R_\omega} = \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right). \tag{IV.8}$$

We now need the two-dimensional Fourier transform of this expression. We notice that in the Fourier transformation (III.3) the operators $\mathbf{r}$ and ∇_r are transformed into:

$$\mathbf{r} \to i\nabla_p, \qquad \nabla_r \to i\mathbf{p}. \tag{IV.9}$$

Thus, we have:

$$\frac{\partial \hat{G}_0(p)}{\partial n} = \frac{1}{2R_\omega}(\nabla_p \cdot \mathbf{p})\,\hat{G}_0(p) = \frac{1}{2R_\omega}\left(2 + p\,\frac{\partial}{\partial p}\right)\hat{G}_0(p),$$

and by using the expression (III.4) of $\hat{G}_0$ we obtain in terms of the function $a(p)$ defined by (III.5):

$$\frac{\partial \hat{G}_0}{\partial n} = \frac{a^2 - k^2}{4R_\omega a^3}. \tag{IV.10}$$

C. *The Curvature Contribution from the Two Reflection Term*

We are now in a position to evaluate, to the lowest order in the curvature, the third term of the expansion (II.28), corresponding to two reflections. By using the plane approximation for all the factors of the integrand other than $\partial G_0/\partial n$, we get the following contribution to $\rho(E)$:

$$\frac{4}{\pi(2\pi)^2}\,\mathrm{Im}\int_S d\sigma_\omega \int d^2p\,\frac{\partial \hat{G}_0(p)}{\partial n}\,\hat{\Gamma}_\omega^2(p)\left(\frac{\partial}{\partial n} - \kappa_\omega\right)\hat{F}_\eta(p)$$

$$= \frac{1}{16\pi^2}\,\mathrm{Im}\int_S \frac{d\sigma_\omega}{R_\omega}\int_{-ik}^{+\infty} da\,\frac{(a^2 - k^2)(a - \kappa_\omega)}{a^3(a + \kappa_\omega)^2}\,\hat{\mathscr{F}}_\eta. \tag{IV.11}$$

D. *The Curvature Corrections to $\partial F_\eta/\partial n$ and F_η*

We must now evaluate the curvature correction to the second term of the expansion (II.28), which was calculated in Section III in the plane approximation only. As we have seen above, the function Γ entering the integrand of this term has no correction linear in the curvature. The curvature corrections come therefore only from the functions $\partial F_\eta/\partial n$ and F_η.

The function $\partial F_\eta/\partial n$ was evaluated in Section III, D by using the approximation (III.15) to the normal derivative. We have seen above that this operator should be replaced by the expression (IV.5). It is easily seen that the first term in $\partial/\partial z$

gives the plane approximation with no linear curvature correction. The two other terms, however, give the following curvature correction to $\partial F_\eta/\partial n$:

$$\delta \frac{\partial F_\eta(\alpha\beta)}{\partial n_\alpha} = -\left[\frac{\alpha_x(\alpha_x - \beta_x)}{R_1} + \frac{\alpha_y(\alpha_y - \beta_y)}{R_2}\right] \frac{1}{r} \frac{\partial F_\eta(r)}{\partial r}.$$

By the same argument as used in Section IV, B for simplifying the expression (IV.6), we may symmetrize this correction and average it over the orientations of $\boldsymbol{\alpha} - \boldsymbol{\beta}$. This yields

$$\delta \frac{\partial F_\eta(r)}{\partial n} = -\frac{1}{2R_\omega} r \frac{\partial F_\eta(r)}{\partial r} = -\frac{1}{2R_\omega} (\mathbf{r} \cdot \nabla_r) F_\eta(r),$$

whose two-dimensional Fourier transform is:

$$\delta \frac{\partial \hat{F}_\eta(p)}{\partial n} = \frac{1}{2R_\omega} (\nabla_p \cdot \mathbf{p}) \hat{F}_\eta(p) = \frac{1}{2R_\omega} \left(2 + p \frac{\partial}{\partial p}\right) \hat{F}_\eta(p) = -\frac{a^2 + 3k^2}{16R_\omega a^5} \hat{\mathscr{F}}_\eta, \tag{IV.12}$$

where we have used the expression (III.13) of $\hat{F}_\eta(p)$. In (IV.12) we have assumed that the convergence factor $\hat{\mathscr{F}}_\eta(p)$ varies sufficiently slowly with p so that we may neglect the term containing its derivative with respect to p.

Finally, we must evaluate the curvature correction to $\hat{F}_\eta$ defined by (II.17). If we compare the value of the integral (II.17) with the actual boundary S and with the plane P taken as an approximate boundary, we see that this substitution introduces two types of corrections. First of all, the points α and β are now at distances z_α and z_β from the plane P, instead of being on the plane P. This gives the correction:

$$z_\alpha \frac{\partial F_\eta(\alpha\beta)}{\partial n_\alpha} + z_\beta \frac{\partial F_\eta(\alpha\beta)}{\partial n_\beta} = \frac{1}{2} \int d\sigma_\gamma \, d\sigma_{\gamma'} (z_\alpha + z_\beta) \, G_0(\alpha\gamma) \, G_0(\gamma'\beta) \, \mathscr{F}_{//}(\boldsymbol{\gamma} - \boldsymbol{\gamma}', \eta), \tag{IV.13}$$

where we have used the expression (III.17) for $\partial F_\eta/\partial n$. Secondly, when we integrate over r in (II.17), the domain of variation of its third component z starts at $z = z_\gamma$ given by (IV.1) instead of $z = 0$. There is therefore a missing contribution to the integral, which gives the following correction:

$$-\int d\sigma_\gamma \, d\sigma_{\gamma'} \, z_\gamma G_0(\alpha\gamma) \, G_0(\gamma'\beta) \, \mathscr{F}_{//}(\boldsymbol{\gamma} - \boldsymbol{\gamma}', \eta).$$

Altogether we obtain for the curvature correction to F the expression:

$$\delta F(\alpha\beta) = \frac{1}{2} \int d\sigma_\gamma \, d\sigma_{\gamma'} \, (z_\alpha + z_\beta - 2z_\gamma) \, G_0(\alpha\gamma) \, G_0(\gamma'\beta) \, \mathscr{F}_{//}(\boldsymbol{\gamma} - \boldsymbol{\gamma}', \eta). \tag{IV.14}$$

We must now express z_α, z_β, z_γ in terms of the positions of the points α, β, γ by means of the equation (IV.1) of the surface S. By the argument used in Section IV, B we may, again, replace expression (IV.14) by its average over all orientations of the vector $\boldsymbol{\alpha} - \boldsymbol{\beta}$ in the plane P, and use the simplified expression:

$$z \approx \frac{r^2}{2R_\omega}, \qquad (r^2 = x^2 + y^2).$$

Then, the bracket in (IV.14) becomes:

$$z_\alpha + z_\beta - 2z_\gamma \to \frac{1}{2R_\omega}[(\boldsymbol{\omega} - \boldsymbol{\alpha})^2 + (\boldsymbol{\omega} - \boldsymbol{\beta})^2 - 2(\boldsymbol{\omega} - \boldsymbol{\gamma})^2],$$

where it should be recalled that ω, the origin in the plane P, is the mid point between α and β [see (III.1)]. It is then easy to see that

$$z_\alpha + z_\beta - 2z_\gamma \to \frac{1}{2R_\omega}[(\boldsymbol{\alpha} - \boldsymbol{\beta})^2 - (\boldsymbol{\gamma} - \boldsymbol{\alpha})^2 - (\boldsymbol{\gamma} - \boldsymbol{\beta})^2]. \qquad \text{(IV.15)}$$

Thus we may rewrite (IV.14) as

$$\delta F_\eta(\alpha\beta) = \frac{1}{4R_\omega}\int d\sigma_\gamma\, d\sigma_{\gamma'}\,[(\boldsymbol{\alpha} - \boldsymbol{\beta})^2 - (\boldsymbol{\gamma} - \boldsymbol{\alpha})^2 - (\boldsymbol{\gamma} - \boldsymbol{\beta})^2]$$
$$\times\, G_0(\alpha\gamma)\, G_0(\gamma'\beta)\, \mathscr{F}_{//}(\boldsymbol{\gamma} - \boldsymbol{\gamma}', \eta). \qquad \text{(IV.16)}$$

From (III.17), we see that the first term in the bracket simply gives the contribution:

$$\frac{r^2}{2R_\omega}\frac{\partial F_\eta(r)}{\partial n}, \qquad r = |\,\alpha - \beta\,|.$$

The second and third terms appear as convolution integrals between the following two functions:

$$r_1^2 G_0(r_1), \qquad G_0(r_2), \qquad r_1 = |\,\gamma - \alpha\,|, \qquad r_2 = |\,\gamma - \beta\,|.$$

We now go over to the Fourier transforms, remembering that convolution integrals simply give rise to products, and that the operator r^2 is transformed according to

$$r^2 \to -(\nabla_p)^2.$$

Thus, neglecting again the derivative of $\hat{\mathscr{F}}_\eta$, we have:

$$\begin{aligned}\delta\hat{F}_\eta(p) &= \frac{1}{2R_\omega}\left[-(\nabla_p)^2\frac{\partial\hat{F}_\eta(p)}{\partial n} + \hat{G}_0(p)(\nabla_p)^2\,\hat{G}_0(p)\,\hat{\mathscr{F}}_\eta(p)\right] \\ &= \frac{1}{16R_\omega}\left[-(\nabla_p)^2\frac{1}{a^2} + \frac{2}{a}(\nabla_p)^2\frac{1}{a}\right]\hat{\mathscr{F}}_\eta \\ &= -\frac{1}{8R_\omega}\left(\nabla_p\frac{1}{a}\right)^2\hat{\mathscr{F}}_\eta = -\frac{a^2+k^2}{8R_\omega a^6}\hat{\mathscr{F}}_\eta\,, \qquad \text{(IV.17)}\end{aligned}$$

where we have used the expressions (III.4) and (III.18) for $\hat{G}_0$ and $\partial\hat{F}_\eta/\partial n$. Collecting the expressions (IV.12) and (IV.17), we obtain

$$\delta\left(\frac{\partial}{\partial n} - \kappa_\omega\right)\hat{F}_\eta(p) = \frac{1}{16R_\omega a^6}\left[2\kappa_\omega(a^2+k^2) - a(a^2+3k^2)\right]\hat{\mathscr{F}}_\eta\,. \qquad \text{(IV.18)}$$

E. *The Curvature Correction from the One-Reflection Term*

We may now express the curvature correction to the second term of the expansion (II.28) in the form:

$$\begin{aligned}&\frac{2}{\pi(2\pi)^2}\,\mathrm{Im}\int_S d\sigma_\omega\int d^2p\;\hat{\Gamma}(p)\;\delta\left(\frac{\partial}{\partial n} - \kappa_\omega\right)\hat{F}_\eta(p) \\ &= \frac{1}{16\pi^2}\,\mathrm{Im}\int_S\frac{d\sigma_\omega}{R_\omega}\int_{-ik}^{+\infty} da\,\frac{2\kappa_\omega(a^2+k^2) - a(a^2+3k^2)}{a^4(a+\kappa_\omega)}\hat{\mathscr{F}}_\eta\,. \qquad \text{(IV.19)}\end{aligned}$$

F. *The Complete Curvature Contribution*

Finally, the complete curvature contribution is the sum of (IV.11) and (IV.19), equal to:

$$\frac{1}{8\pi^2}\,\mathrm{Im}\int_S\frac{d\sigma_\omega}{R_\omega}\int_{-ik}^{+\infty} da\,\frac{a^2(\kappa_\omega^2 - 2k^2) + k^2\kappa_\omega^2}{a^4(a+\kappa_\omega)^2}\hat{\mathscr{F}}_\eta\,. \qquad \text{(IV.20)}$$

The integral in a converges even for $\hat{\mathscr{F}}_\eta = 1$, and an elementary integration yields:

$$\frac{1}{4\pi^2}\int_S\frac{d\sigma_\omega}{R_\omega}\,\mathrm{Im}\left[\frac{i}{3k} - \frac{k}{\kappa_\omega(k+i\kappa_\omega)} - \frac{1}{\kappa_\omega}\log\frac{k+i\kappa_\omega}{k}\right]. \qquad \text{(IV.21)}$$

By introducing explicitly the real and imaginary parts of k, we obtain the final expression of the curvature contribution to $\rho_\nu(E)$:

$$\frac{1}{4\pi^2}\int_S\frac{d\sigma_\omega}{R_\omega}\left[\frac{1}{3}\frac{k_\mathrm{r}}{k_\mathrm{r}^2+k_\mathrm{i}^2} + \frac{k_\mathrm{r}}{k_\mathrm{r}^2+(\kappa_\omega+k_\mathrm{i})^2} - \frac{1}{\kappa_\omega}\left(\tan^{-1}\frac{\kappa_\omega+k_\mathrm{i}}{k_\mathrm{r}} - \tan^{-1}\frac{k_\mathrm{i}}{k_\mathrm{r}}\right)\right], \qquad \text{(IV.22)}$$

with the same notations as in (III.22) and where determinations of the $\tan^{-1}$ are again defined by (III.23).

V. Results and Discussion

The results of the previous sections, given by Eqs. (III.22, 23) and (IV.22), can be summarized by the following expression for the *smoothed density*:

$$\rho_\gamma(E) = \frac{1}{4\pi^2}\left\{Vk_r + \int_S d\sigma_\omega \left[\frac{\pi}{4} - \tan^{-1}\frac{\kappa_\omega + k_i}{k_r} + \frac{1}{2}\tan^{-1}\frac{k_i}{k_r}\right]\right.$$
$$+ \int_S \frac{d\sigma_\omega}{R_\omega}\left[\frac{1}{3}\frac{k_r}{k_r^2 + k_i^2} + \frac{k_r}{k_r^2 + (\kappa_\omega + k_i)^2}\right.$$
$$\left.\left. - \frac{1}{\kappa_\omega}\left(\tan^{-1}\frac{\kappa_\omega + k_i}{k_r} - \tan^{-1}\frac{k_i}{k_r}\right)\right] + \cdots\right\} \tag{V.1}$$

where we recall that k_r and k_i denote the real and imaginary parts of $k = \sqrt{E + i\gamma}$, chosen with the positive determination.

A. *The Effects of the Variation of κ_ω on S*

In all the previous calculations, we have assumed that κ_ω could be considered as constant in a sufficiently large neighborhood of each point ω of S. It is clearly possible to carry out a Taylor expansion of this function around each point of S. Let us briefly discuss what would be the effect of the first-order term of this expansion, in $\partial\kappa_\omega/\partial x$ and $\partial\kappa_\omega/\partial y$.

We may notice that the surface term comes from contributions which are invariant under a rotation around the point ω in the plane P. It follows immediately that there will be no contribution from the linear terms in the first derivatives of κ_ω.

The curvature terms involve particular directions at each point ω, namely, the principal axes of the surface. We would therefore expect terms proportional to

$$\left(\frac{1}{R_1} - \frac{1}{R_2}\right)\left(\frac{\partial\kappa_\omega}{\partial x} - \frac{\partial\kappa_\omega}{\partial y}\right),$$

since we recover isotropy when $R_1 = R_2$. Such terms will be smaller than the mean curvature term retained here, and it is therefore consistent with the present approximation to disregard them.

B. *Convergence of the Multiple Reflection Expansion*

Although this may not be of great practical significance for evaluating the accuracy of the expansions derived above, it is interesting to show that the multiple reflection expansion converges for any given value of k_r when the imaginary part k_i of k is sufficiently large. The argument follows the well-known procedure used for integral equations with bounded kernel and we shall only outline it.

We consider the general boundary condition (C). We have seen in Section II that for carrying out actual calculations with this type of boundary condition, it was necessary to introduce the Green function Γ defined by (II.24). For setting up a convergence argument, however, it is more convenient not to introduce Γ, but to use directly the expansion resulting from the integral equation (II.22). Let us denote by $K(\alpha\beta)$ the kernel of this integral equation:

$$K(\alpha\beta) = 2\left(\frac{\partial}{\partial n_\alpha} - \kappa_\alpha\right) G_0(\alpha\beta), \tag{V.2}$$

and by $K^{(n)}(\alpha\beta)$ the iterated kernels defined by the relations:

$$\begin{aligned} K^{(n)}(\alpha\beta) &= \int_S d\sigma_\gamma\, K^{(n-1)}(\alpha\gamma)\, K(\gamma\beta), \\ K^{(0)}(\alpha\beta) &= \delta(\alpha - \beta), \end{aligned} \tag{V.3}$$

for $n = 0, 1, 2, \ldots$. Iteration of the integral equation (II.22) yields for $\mu(\alpha r)$ the expansion:

$$\mu(\alpha r) = 2\sum_{n=0}^{\infty} \int_S d\sigma_\beta\, K^{(n)}(\alpha\beta)\left(\frac{\partial}{\partial n_\beta} - \kappa_\beta\right) G_0(\beta r). \tag{V.4}$$

Finally, according to (II.7), (II.10), and (II.19), the expansion of $\rho_\nu(E)$ is given in terms of the expression:

$$\begin{aligned} \int_V d^3r\, G_1(r\,r) &= \int_V d^3r \int_S d\sigma_\alpha\, G_0(r\,\alpha)\, \mu(\alpha r), \\ &= \sum_{n=0}^{\infty} \int_S d\sigma_\alpha\, d\sigma_\beta\, K^{(n)}(\alpha\beta)\, Q(\beta\alpha), \end{aligned} \tag{V.5}$$

where

$$Q(\beta\alpha) = 2\int_V d^3r \left(\frac{\partial}{\partial n_\beta} - \kappa_\beta\right) G_0(\beta r)\, G_0(r\,\alpha). \tag{V.6}$$

The proof of the convergence of the expansion (V.5) may be divided into two parts.

1. Let us first show that for given κ_α and k_r, the kernel $K(\alpha\beta)$ defined by (V.2) satisfies the inequality

$$\int_S d\sigma_\beta \mid K(\alpha\beta)\mid < \lambda < 1, \tag{V.7}$$

for all α on S, provided k_i is sufficiently large. In (V.7) λ is a fixed number independent of α.

From the definition of G_0 we have:

$$\mid K(\alpha\beta)\mid < \frac{e^{-k_i\mid\alpha-\beta\mid}}{2\pi\mid\alpha-\beta\mid}\left[\kappa + (k_i + k_r)\mid\cos\theta\mid + \frac{\mid\cos\theta\mid}{\mid\alpha-\beta\mid}\right], \tag{V.8}$$

where κ denotes the upper bound of $\mid\kappa_\alpha\mid$, and θ is the angle between the vector $\beta - \alpha$ and the normal to S at the point α.

We introduce a "small" distance l which will be specified later, and define the "neighborhood" $S_1(\alpha)$ of α as the set of points β of S such that:

$$S_1(\alpha): \mid\beta - \alpha\mid < l.$$

The rest of the surface S will be denoted by $S_2(\alpha)$. We must now make some assumptions about the smoothness of the surface S. Namely, we assume that there exist three constants A, B, C and a length R independent of α, such that the inequalities:

$$\begin{aligned}
&\int_{S_1(\alpha)} \frac{d\sigma_\beta}{\mid\alpha-\beta\mid} < Al,\\
&\int_{S_1(\alpha)} \frac{d\sigma_\beta}{\mid\alpha-\beta\mid}\mid\cos\theta\mid < B\frac{l^2}{R},\\
&\int_{S_1(\alpha)} \frac{d\sigma_\beta}{\mid\alpha-\beta\mid^2}\mid\cos\theta\mid < C\frac{l}{R},
\end{aligned} \tag{V.9}$$

hold for any l. It is clearly the requirement that the inequalities (V.9) hold no matter how small l is, which imposes smoothness restrictions on S. In the limit $l \to 0$, it appears that R is of the order of the smallest radius of curvature of S. From (V.8) and (V.9) it follows that:

$$\begin{aligned}
\int_S d\sigma_\beta \mid K(\alpha\beta)\mid < &\frac{1}{2\pi}\left[\kappa Al + (k_i + k_r)\,B\frac{l^2}{R} + C\frac{l}{R}\right]\\
&+ \frac{e^{-k_i l}}{2\pi l}\left[\kappa + k_i + k_r + \frac{1}{l}\right]S,
\end{aligned} \tag{V.10}$$

where the two terms in the right-hand side come from the integration over $S_1(\alpha)$ and $S_2(\alpha)$, respectively. In the last term, S denotes the area of the boundary surface.

The right-hand side of (V.10) goes to zero, when $k_1 \to \infty$ and $l \to 0$ in such a way that $k_1 \sim 1/l^\alpha$ where $1 < \alpha < 2$. It follows that if k_1 is sufficiently large, it is possible to find a value of l such that the right-hand side of (V.10) is bounded by a given number $\lambda < 1$. This proves the existence of the bound (V.7).

From (V.7) follow corresponding inequalities for the iterated kernels:

$$\int_S d\sigma_\beta \mid K^{(n)}(\alpha\beta)\mid < \lambda^n. \tag{V.11}$$

2. Next, we show that for any given set of k and κ_α, there is a bound C independent of α and γ for the following integral:

$$\left| \int_S d\sigma_\beta K(\alpha\beta)\, Q(\beta\gamma)\right| < C \qquad \text{(for all } \alpha, \gamma). \tag{V.12}$$

From the definition (V.6) of the function $Q(\beta\gamma)$, we see that the expression (V.12) is given by the multiple integral with respect to r and β over a finite domain, of an integrand which is bounded except when any of the pairs of points $\alpha\beta$, βr, or $r\gamma$ coalesce. It is therefore necessary to examine how the integrals behave in the neighborhood of these singularities.

Consider first the function $Q(\beta\gamma)$. When β and γ are at a finite distance from each other, the integral with respect to r is singular when r approaches β or γ, where the integrand has singularities of the type

$$\frac{1}{\mid r-\beta\mid^2}, \qquad \frac{1}{\mid r-\gamma\mid},$$

respectively. These singularities are integrable in the three-dimensional domain for r, and therefore $Q(\beta\gamma)$ is finite for $\beta \neq \gamma$.

We must still look at what happens when $\beta \to \gamma$. Consider first the term in κ_β which is proportional to:

$$F(\beta\gamma) \equiv \int_V d^3r\, G_0(\beta r)\, G_0(r\gamma) \sim \int_V \frac{d^3r}{\mid r-\beta\mid\mid r-\gamma\mid},$$

where the right-hand side indicates the nature of the singularity. It is easy to check that this integral remains finite as $\beta \to \gamma$.

Consider next the term involving a normal derivative. According to (III.17) (with the convergence factor $\mathscr{F}_\eta$ replaced by a δ-function) we have:

$$\frac{\partial F(\beta\gamma)}{\partial n_\beta} \equiv \int_V d^3r \frac{\partial G_0(\beta r)}{\partial n_\beta} G_0(r\gamma) \sim \int_S d\sigma_\delta \, G_0(\beta\delta)\, G_0(\delta\gamma)$$

$$\sim \int_S \frac{d\sigma_\delta}{|\delta-\beta||\delta-\gamma|}.$$

The singularity is stronger here since the integral is only two-dimensional, and it is easy to see that it behaves as $\log|\beta-\gamma|$ when $\beta \to \gamma$. Thus, we see that the function $Q(\beta\gamma)$ is bounded everywhere except when $\beta \to \gamma$, where

$$Q(\beta\gamma) \sim \log|\beta-\gamma|, \qquad (\beta \to \gamma). \tag{V.13}$$

Finally, we consider the integral (V.12). It is singular when β is near α or γ, but it obviously converges when α and γ are at a finite distance from one another. When $\alpha \to \gamma$, the integral (V.12) is singular as:

$$\int_S \frac{d\sigma_\beta}{|\alpha-\beta|} \log|\beta-\gamma| \qquad \text{or} \qquad \int_S \frac{d\sigma_\beta\,|\cos\theta|}{|\alpha-\beta|^2} \log|\beta-\gamma|,$$

where we have used the bound (V.8) for $K(\alpha\beta)$. If S is sufficiently smooth, these integrals converge even when $\alpha = \gamma$, and this shows the existence of a constant C such that the inequality (V.12) is satisfied.[4]

We can now prove the convergence of the expansion (V.5). Considering the nth term of this expansion, we may write:

$$\left|\int_S d\sigma_\alpha\, d\sigma_\beta\, K^{(n)}(\alpha\beta)\, Q(\beta\alpha)\right| = \left|\int_S d\sigma_\alpha\, d\sigma_\beta\, d\sigma_\gamma\, K^{(n-1)}(\alpha\gamma)\, K(\gamma\beta)\, Q(\beta\alpha)\right| < C\lambda^{n-1}, \tag{V.14}$$

where we have used (V.11) and (V.12). Since $\lambda < 1$, summation over n of (V.14) yields a convergent series.

C. *Asymptotic Validity Conditions of the Expansion*

By means of the upper bound (V.8) of the kernel (V.2), we have derived above sufficient conditions for convergence of the multiple reflection expansion. This procedure is very crude, since it takes into account only the modulus of the

[4] The functions $F(\alpha\beta)$, $\partial F(\alpha\beta)/\partial n_\beta$, and the integral (V.12) are evaluated for the plane approximation in the Appendix [Eqs. (A. 6, 7, 10)]. The singularities of the exact functions are clearly the same as for the plane approximation.

integrands and their exponential decrease at large distances. The rapid oscillations of the integrands produce an additional reduction of the integrals.

On the other hand, we have studied the true convergence of the expansion. In practice asymptotic convergence is sufficient.

Finally, the form (II.28) of the multiple reflection expansion which we have used results from the expansion (V.5) studied above by a partial summation leading to the introduction of the function Γ defined by (II.24). Its convergence follows from the same arguments as in section V,B. The fact however that the kernel of (II.28) vanishes with the curvature suggests that this equation directly provides an asymptotic expansion in powers of the curvature.

We thus reconsider the calculations of Sections III and IV and discuss the approximations which we have made. The essential feature of the multiple reflection expansion (II.27) which makes it useful is the short range of the integrands. The asymptotic expansion (V.1) was thus obtained by taking into account the short range contributions to the integrals only. The long range contributions were neglected in view of the exponential decrease of the integrand. For instance, in Section III,C, the calculation of $F_\eta(\alpha\,\beta)$ involved an integration over the distance z of the point r to the surface, which varies from 0 to $z_{\max}$. In Eq. (III.13) the integral over z is evaluated approximately by replacing the upper bound $z_{\max}$ by $+\infty$. The integrand behaves as e^{-2az}, and this replacement amounts to neglecting corrections to $F_\eta(\alpha\,\beta)$ of relative order

$$e^{-2az_{\max}}. \tag{V.15}$$

In the calculations of Sections III and IV based on the plane approximation, a is integrated over the contour of Fig. 3, and $z_{\max}$, which is the length of the normal to the surface S at the point ω, remains larger than the length L of the shortest normal. It is therefore reasonable to neglect contributions of the order of (V.15) in the calculation of $F_\eta(\alpha\,\beta)$ provided[5]

$$e^{-2k_i L} \ll 1. \tag{V.16}$$

In another paper, we shall drop condition (V.16) and evaluate more precisely the corresponding corrections. Let us simply remark here that the oscillatory behavior of (V.15) gives rise to contributions to $\rho_\nu(E)$ oscillating as $\exp[2ik_r L]$ with an amplitude of the order of $\exp[-2k_i L]$. Condition (V.16) is thus clearly related to the smoothing out of the fluctuations in the eigenvalue density.

[5] Here and in the following, we shall write conditions such as (V.16) to express that a quantity is very small not only compared to finite quantities, but also to the small dimensionless quantities such as $1/k_r V^{1/3}$ or its powers, which enter in the asymptotic expansion (V.1), and which will be determined more precisely in section V,D. This ensures that terms proportional to (V.16) are negligible with respect to all terms retained in the expansion.

Although somewhat qualitative, the above argument, which we shall make more precise when studying the fluctuations, is quite general. If we want to apply it to a term of the multiple reflection expansion, we must essentially take into account the long range exponential decrease of the integrand in (II.28), which is a product of functions G_0, $\partial G_0/\partial n$, and Γ. As shown in the Appendix, $\Gamma(\alpha\beta)$ decreases at large distances as $\exp(-k_1 \mid \alpha - \beta \mid)$ if $\kappa_\omega \geqslant 0$ everywhere, in the same way as G_0 or $\partial G_0/\partial n$. Condition (V.16) is then sufficient to allow the systematic replacement of upper bounds of integration by $+\infty$. For $\kappa_\omega < 0$, $\Gamma(\alpha\beta)$ has a longer tail. It decreases however at least as fast as $\exp(-q_1 \mid \alpha - \beta \mid)$ where $q^2 = \kappa^2 + k^2$, $q_1 = \operatorname{Im} q > 0$, and κ is the minimum of $\kappa_\omega < 0$. This range $1/q_1$, which is larger than $1/k_1$, must again be short compared to L:

$$e^{-2q_1 L} \ll 1 \qquad (\kappa < 0). \tag{V.17}$$

In conclusion, we see that *in order to write an asymptotic expansion for $\rho_\gamma(E)$, we must wipe out the fluctuations, by taking a smoothing width γ large enough so that the conditions* (V.16) *for $\kappa \geqslant 0$ or* (V.17) *for $\kappa < 0$ are satisfied.*

D. *Expansion Parameters*

The asymptotic expansion (V.1) comes from the short range contributions to the first terms of the multiple reflection expansion. By studying the structure of these terms, we shall exhibit now the dimensionless small parameters which are involved in the asymptotic expansion.

The integrand is a product of the short range functions

$$G_0(r\,r') = \frac{e^{ik|r-r'|}}{4\pi \mid r - r' \mid}, \tag{V.18}$$

$\partial G_0/\partial n$ and $\Gamma(\alpha\beta)$ which, as shown in the Appendix (Eq. (A.16)), behaves as

$$\Gamma(\alpha\beta) \sim \frac{ike^{ik|\alpha-\beta|}}{2\pi\kappa_\omega \mid \alpha - \beta \mid^2} + \theta_-(\kappa_\omega)\frac{\kappa_\omega{}^2 e^{iq|\alpha-\beta|+(i\pi/4)}}{(2\pi q \mid \alpha - \beta \mid)^{1/2}} \tag{V.19}$$

when the distance $\mid \alpha - \beta \mid$ is large compared with $\mid 1/k \mid$, $\mid k/\kappa_\omega{}^2 \mid$, and $\mid 1/q \mid$ (but short compared with the mean curvature radius R_ω). In (V.19) we have used the step function:

$$\begin{aligned} \theta_-(x) &= 0 \qquad (x \geqslant 0), \\ \theta_-(x) &= 1 \qquad (x < 0). \end{aligned} \tag{V.20}$$

As seen in Section IV in the special case of the curvature term, the successive terms of the multiple reflection expansion depend on the surface S through a factor containing increasing powers of the inverse curvature radii $1/R_1$ and $1/R_2$

of S at any point ω, and also of higher order derivatives of the equation (IV.1) defining S. Let us call R some typical length, of the same order of magnitude as the local curvature radii R_1 and R_2, and as lengths characterizing the higher order infinitesimal structure of the surface, such as $R_1{}^3\partial^3 z(x, y)/\partial x^3$ or $| R_1 \nabla R_1 | \cdots$. The n-reflection term in (II.27) or (II.28) contains at least $n - 1$ factors $1/R_1$ or $1/R_2$, which come from the normal derivatives $\partial G_0(\delta\, \gamma)/\partial n_\delta$. Other factors of order $1/R$ may also arise from expanding the surface equation, exactly as in Section IV,E. Thus, in order to obtain all terms of the smoothed eigenvalue density depending on the surface S through a factor of order $1/R^n$, it is sufficient to consider a number of reflections at most equal to $n + 1$.

Besides this factor $1/R^n$, Eq. (II.27) involves a convolution integral over the surface S for a product of functions $G_0(\alpha - \beta)$, $\nabla G_0(\alpha - \beta)$, $F(\alpha\, \beta)$, and $\Gamma(\alpha\, \beta)$, possibly multiplied by powers of lengths such as $| \alpha - \beta |^p$ coming from the expansion of the surface equation. Examples of such integrals have been calculated in detail in Sections III and IV. From Eqs. (IV.18, 19) it is clear that the result depends mainly on the exponential decrease and on the oscillations at large distance of G_0 and Γ, which behave as e^{ikr} or e^{iqr} (for $\kappa_\omega < 0$). Since the real parts of k and q are both positive, the oscillations always add, and thus contribute to reduce the integral. On the whole, the convolution integral is proportional to some inverse power of k or q, which for dimensional reasons must be equal to n.

The multiple reflection expansion thus provides under the conditions (V.16) or (V.17) an asymptotic expansion for the smoothed eigenvalue density $\rho_\gamma(E)$ in powers of the dimensionless parameters $1/| k | R$, and $1/| q | R$ for $\kappa_\omega < 0$. For instance, the curvature contribution (IV.21) or (IV.22) to $\rho_\gamma(E)$ exhibits in its first and last terms the parameter $1/| k | R$; its second term contains $1/| k + i\kappa_\omega | R$, which is equivalent to $1/| q | R$.

The method thus fails for k small, and when $\kappa_\omega < 0$ for q small, that is, for $k \sim -i\kappa_\omega$. In terms of the energy E and the smoothing width γ, these values correspond to $E \sim \gamma \sim 0$, and in addition when $\kappa_\omega < 0$ to $E \sim -\kappa_\omega{}^2$, $\gamma \sim 0$. These values may be characterized as the thresholds for the spectrum. It was a priori evident that no asymptotic expansion for the eigenvalue density could be valid near a threshold.

If the surface is sufficiently smooth, R is of the same order of magnitude as $V^{1/3}$ and $S^{1/2}$. The average distance between eigenvalues is for large E approximately equal to $1/\rho_\gamma(E)$:

$$D \simeq \frac{4\pi^2}{V\sqrt{E}}. \tag{V.21}$$

The order of magnitude of the first expansion parameter for positive E is therefore:

$$\frac{1}{| k | R} \propto \frac{1}{\sqrt{E}\, V^{1/3}} \propto \left(\frac{D}{E}\right)^{1/3}. \tag{V.22}$$

The second expansion parameter $1/|q|R$ may become larger than the first one only when $\kappa_\omega < 0$ and for E negative. In order to simplify the discussion, let us assume that κ_ω is constant over S. We shall see in Section V,E that the region $-\kappa^2 < E < 0$ contains eigenvalues with a density approximately equal to $S/4\pi$. Thus, in this region

$$D \simeq 4\pi/S, \tag{V.23}$$

and the two expansion parameters are respectively of the following order:

$$\begin{aligned} \frac{1}{|k|R} &\propto \frac{1}{\sqrt{-E}\,S^{1/2}} \propto \left(\frac{D}{|E|}\right)^{1/2} \\ \frac{1}{|q|R} &\propto \frac{1}{\sqrt{E+\kappa^2}\,S^{1/2}} \propto \left(\frac{D}{E+\kappa^2}\right)^{1/2}. \end{aligned} \tag{V.24}$$

In all cases, *the expansion parameters of* (V.1) *are therefore powers of the ratio between the average level separation D, and the distance to the spectrum thresholds* $E = 0$ *and* $E = -\kappa^2$.

E. *Smoothing with the Smallest Possible Width*

In order to approach as much as possible the actual eigenvalue density (II.3), we are led to take the smoothing width γ as small as possible. However, we are limited by the fact that the asymptotic expansion of $\rho_\gamma(E)$ looses its validity if γ is too small. We must therefore look for the smallest value $\gamma_{\min}$ of γ consistent with the conditions (V.16, 17). Three different situations occur:

1. *Positive Energies.* When the expansion parameter $1/|k|R$ is sufficiently small, $\gamma_{\min}$ satisfying the validity conditions is such that $\gamma_{\min}/E \ll 1$. The validity condition (V.16), with $k_1 \simeq \gamma_{\min}/2k$, $k \simeq \sqrt{E}$ reduces to

$$e^{-\gamma_{\min} L/k} \ll 1, \tag{V.25}$$

(the second validity condition (V.17) follows from (V.25)).

On the other hand, since $\gamma_{\min}/E \ll 1$, the asymptotic expansion (V.1) of $\rho_\gamma(E)$ is practically independent of γ for $\gamma \simeq \gamma_{\min}$ and thus equal to its limit for $\gamma = 0$:

$$\begin{aligned} \rho_{\gamma_{\min}}(E) \simeq \rho_0(E) &= \frac{1}{4\pi^2}\left\{Vk + \int_S d\sigma_\omega \left(\frac{\pi}{4} - \tan^{-1}\frac{\kappa_\omega}{k}\right)\right. \\ &\quad \left. + \int_S \frac{d\sigma_\omega}{R_\omega}\left(\frac{1}{3k} + \frac{k}{k^2+\kappa_\omega^2} - \frac{1}{\kappa_\omega}\tan^{-1}\frac{\kappa_\omega}{k}\right)\right\} \\ &= \frac{1}{4\pi^2}\left\{Vk + \int_S d\sigma_\omega \left(\frac{\pi}{4} - \delta_\omega\right)\right. \\ &\quad \left. + \frac{1}{k}\int_S \frac{d\sigma_\omega}{R_\omega}\left(\frac{1}{3} + \cos^2\delta_\omega - \delta_\omega \cot\delta_\omega\right) + \cdots\right\}, \end{aligned} \tag{V.26}$$

where we have introduced the angle δ_ω defined by:

$$\delta_\omega = \tan^{-1} \frac{\kappa_\omega}{k} \qquad |\, \delta_\omega \,| < \frac{\pi}{2}\,. \tag{V.27}$$

This expression $\rho_0(E)$ is, in the domain considered here, a good approximation to the exact density of eigenvalues smoothed with a width of the order of $\gamma_{\min}$.

When κ varies from $-\infty$ to $+\infty$, the coefficient of the surface term in $4\pi^2\rho_0(E)$ continuously decreases from $3\pi/4$ to $-\pi/4$; it is equal to $+\pi/4$ for $\kappa = 0$ (Neumann boundary condition). The curvature term is less sensitive to the boundary conditions : it is an even function of κ, and takes the same maximum value 1/3 for both Neumann and Dirichlet boundary conditions ($\kappa = 0, \kappa = \pm\infty$); it attains its minimum value $-$ .0218 if $|\,\kappa\,|/k = 1.83$, and it is negative for $1.31 < |\,\kappa\,|/k < 2.62$.

2. *Below the Spectrum.* When $\kappa_\omega \geqslant 0$ everywhere, this means $E < 0$. When the lower bound κ of κ_ω is negative, this means $E < -\kappa^2$. In these regions, it is easily seen that the validity conditions (V.16, 17) may be satisfied even for $\gamma = 0$. They reduce then to

$$\begin{aligned} \exp(-2L(-E)^{1/2}) &\ll 1 \qquad (\kappa \geqslant 0), \\ \exp(-2L(-E-\kappa^2)^{1/2}) &\ll 1 \qquad (\kappa < 0). \end{aligned} \tag{V.28}$$

If E is sufficiently far below the threshold of the spectrum, the expansion parameters $1/(\sqrt{-E}\,R)$ or $1/(\sqrt{-E-\kappa^2}\,R)$ are small, and the conditions (V.28) are satisfied. We obtain then from (V.1) the obvious result:

$$\rho_0(E) = 0. \tag{V.29}$$

3. *Region of the Surface States.* Finally, when κ is negative and sufficiently large, the spectrum extends to negative energies in the range $-\kappa^2 < E < 0$. More precisely, if κ_ω is a sufficiently slowly varying function, and if $|\,\kappa\,|\,R$ is large, there exists a domain of energy between $-\kappa^2$ and 0 such that both expansion parameters $1/(\sqrt{-E}\,R)$ and $1/(\sqrt{E+\kappa^2}\,R)$ are small. Then, $\gamma_{\min}$ is negligible compared to $|\,E\,|$ and $E + \kappa^2$. The validity condition (V.17) to be satisfied by $\gamma_{\min}$ reduces to

$$\exp(-\gamma_{\min} L(E+\kappa^2)^{-1/2}) \ll 1. \tag{V.30}$$

(Condition (V.16) reduces to $\exp(-2L\sqrt{-E}) \ll 1$.) The smoothed eigenvalue density $\rho_{\gamma_{\min}}(E)$ is then approximately equal to

$$\begin{aligned} \rho_{\gamma_{\min}}(E) \simeq \rho_0(E) = \frac{1}{4\pi} \Big\{ \int_S d\sigma_\omega\, \theta_-(\sqrt{-E} + \kappa_\omega) \\ + \int_S \frac{d\sigma_\omega}{R_\omega} \Big[\frac{\theta_-(\sqrt{-E}+\kappa_\omega)}{\kappa_\omega} + \delta(\sqrt{-E}+\kappa_\omega) \Big] + \cdots \Big\}. \end{aligned} \tag{V.31}$$

The existence of negative energy levels is quite natural for $\kappa < 0$: they correspond to *surface states*. Eigenfunctions φ_n localized near the surface exist in the region of S where κ_ω is negative. If $| \kappa_\omega R_\omega |$ is large and κ_ω slowly varying, we may use the plane approximation and write these eigenfunctions in the form

$$\varphi_n(r) \simeq \kappa_\omega e^{\kappa_\omega z} \psi_n(\omega) \qquad (\kappa_\omega < 0), \tag{V.32}$$

where z is the distance of r to S, and ω its projection on S. A function of this form is clearly localized near S and satisfies the boundary condition (C) and Eq. (I.1) provided the function $\psi_n(\omega)$ satisfies the *two-dimensional wave equation*

$$(\Delta_2 + E_n + \kappa_\omega^2)\, \psi_n(\omega) = 0. \tag{V.33}$$

Let us denote by $S(E)$ the area of the region of S where $\kappa_\omega^2 > -E$. In the first approximation the density of eigenvalues for Eq. (V.33) is equal to

$$\frac{S(E)}{4\pi} = \frac{1}{4\pi} \int_S d\sigma_\omega\, \theta_-(\sqrt{-E} + \kappa_\omega). \tag{V.34}$$

Thus we recover the first term of (V.31). The other terms are curvature corrections which will be discussed in part II of this work.

We conclude this section with a remark on the order of magnitude of γ. The minimum value of γ for the validity of the asymptotic expansion (V.26, 29, 31) is $\gamma_{\min}$. On the other hand, the minimum value of γ required for defining a smooth eigenvalue density is $\gamma \gtrsim D$, the mean eigenvalue spacing. It is easy to see that

$$\gamma_{\min} \gg D.$$

In the domain $D < \gamma < \gamma_{\min}$, there exists a smoothed eigenvalue density, which however is not represented by the asymptotic expansion derived here. It exhibits fluctuations, which we shall study elsewhere. In the domain $\gamma > \gamma_{\min}$, the fluctuations are washed out, and the expansion (V.1) holds.

F. *The γ Dependence of the Smoothed Eigenvalue Density*

The definition (II.4) of $\rho_\gamma(E)$ in terms of the true density $\rho(E')$ implies a well defined dependence on γ since γ occurs only in the Lorentz smoothing function. Although the limit $\rho_0(E)$ of the asymptotic expansion (V.1) has nothing to do with the true density of eigenvalues (which is a sum of δ-functions), it is interesting to ask whether $\rho_\gamma(E)$ may be reconstructed from $\rho_0(E)$ by a Lorentzian smoothing of the form:

$$\rho_\gamma(E) = \frac{\gamma}{\pi} \int_{-\infty}^{+\infty} \frac{dE'}{(E' - E)^2 + \gamma^2}\, \rho_0(E'). \tag{V.35}$$

Let us show that this is actually the case, as a consequence of the analytic structure of the asymptotic expansion. The Green function G_0 defined by (II.8, 9)

is an analytic function in the upper half-plane (excluding the real axis) of the complex variable $z = E + i\gamma$. The function Γ which was evaluated exactly in the plane approximation has the same analyticity properties. The various terms of the asymptotic expansions considered here are obtained as multiple integrals of finite products of G_0 and Γ. They have again the same analyticity properties. In conclusion we see from (II.28) that $\rho_\gamma(E)$ is of the form

$$\rho_\gamma(E) = \operatorname{Im} \Phi(E + i\gamma), \tag{V.36}$$

where $\Phi(z)$ is analytic in the upper half-plane. Moreover it may be seen that at infinity:

$$\frac{\Phi(z)}{z} \to 0 \qquad (|z| \to \infty). \tag{V.37}$$

The explicit form of $\Phi(z)$ for the first three terms (V.1) of the expansion is:

$$\Phi(z) = \frac{1}{4\pi^2}\left\{-V\sqrt{-z} + \int_S d\sigma_\omega \left[\frac{1}{2}\log\sqrt{-z} - \log(\kappa_\omega + \sqrt{-z})\right]\right.$$
$$\left. + \int_S \frac{d\sigma_\omega}{R_\omega}\left[\frac{1}{3\sqrt{-z}} - \frac{\sqrt{-z}}{\kappa_\omega(\kappa_\omega + \sqrt{-z})} - \frac{1}{\kappa_\omega}\log\frac{\kappa_\omega + \sqrt{-z}}{\sqrt{-z}}\right] + \cdots\right\}. \tag{V.38}$$

The plane of the complex variable z should be cut from 0 to $+\infty$ along the real axis, and $\sqrt{-z}$ defined as positive for z on the negative real axis. The determinations of the log are real for $z \to -\infty$. When κ_ω takes negative values, the cut extends from $-\kappa^2$ to $+\infty$, where κ denotes the minimum of κ_ω. Thus, as stated above, $\Phi(z)$ is analytic, in particular, in the upper half-plane, and satisfies (V.37) at infinity.

Consider now the effect of a Lorentzian smoothing on $\rho_0(E)$, following (V.35). From (V.36) we get:

$$\frac{\gamma}{\pi}\int_{-\infty}^{+\infty} \frac{dE'}{(E' - E)^2 + \gamma^2}\rho_0(E') = \operatorname{Im}\frac{\gamma}{\pi}\int_{-\infty}^{+\infty}\frac{dE'}{(E' - E)^2 + \gamma^2}\Phi(E' + i0).$$

According to (V.37), the contour in this integral may be closed by a large half-circle in the upper half-plane. As $\Phi(z)$ is analytic in the upper half-plane, the integrand has only one pole at $E' = E + i\gamma$ and by taking the residue we obtain:

$$\frac{\gamma}{\pi}\int_{-\infty}^{+\infty}\frac{dE'}{(E' - E)^2 + \gamma^2}\rho_0(E') = \operatorname{Im}\Phi(E + i\gamma) = \rho_\gamma(E),$$

which proves the property (V.35).

It should be emphasized that the integral (V.35) involves the values of $\rho_0(E)$ at *all energies*, whereas we have seen in Section V,E that the asymptotic expansion is not valid near $E = 0$ and, when $\kappa_\omega < 0$ near the lower end of the spectrum

$E = -\kappa^2$. Actually, near these values, $\rho_0(E)$ is not a continuous function, but rather an integrable distribution. For instance, if $\kappa_\omega = \kappa < 0$ is constant over S, we see from (V.31) that $\rho_0(E)$ has a δ-like singularity at $E = -\kappa^2$. Of course, the distribution $\rho_0(E)$ should not be confused with the true distribution $\rho(E)$ which is a sum of δ-functions (II.3). *The connection between the distributions $\rho(E)$ and $\rho_0(E)$ is that they give the same smoothed density $\rho_\gamma(E)$ if γ is taken larger than $\gamma_{\min}$ defined above.*

G. *The Dirichlet and Neumann Boundary Conditions as Limiting Cases of* (C)

We have focused our attention mainly on the more general boundary condition (C). Let us discuss here how the Dirichlet and Neumann conditions (A) and (B) may be obtained as limiting cases of (C).

The Neumann boundary condition (B) is obtained simply by setting $\kappa_\omega = 0$, corresponding to $\delta_\omega = 0$. Then (V.26) reduces to:

$$\rho_0(E) = \frac{1}{4\pi^2}\left[Vk + \frac{\pi}{4}S + \frac{1}{3k}\int_S \frac{d\sigma_\omega}{R_\omega} + \cdots\right], \qquad \text{(B)} \quad \text{(V.39)}$$

which is identical with (I.7).

The Dirichlet boundary condition (A) is more delicate to obtain. When $\kappa = \infty$, the condition (C) reduces to (A) provided $\partial\varphi/\partial n$ remains finite. This is not a trivial restriction, and we may therefore expect to find for $\kappa \to \infty$ additional solutions to the wave equation, which do not satisfy the boundary condition (A). Note also that the basic integral equations given in Section II for condition (C) become singular when $\kappa \to \infty$. The treatment of (C) was based on a simple layer representation, whereas we have seen that the natural method for (A) consists in using a double layer representation. Nevertheless, since the calculation is exact as far as the κ dependence is concerned, we should be able to obtain correctly the limit $\kappa \to \infty$.

Actually, for $\kappa \to +\infty$, corresponding to $\delta = \pi/2$, the expansion (V.26) reduces to

$$\rho_0(E) = \frac{1}{4\pi^2}\left[Vk - \frac{\pi}{4}S + \frac{1}{3k}\int_S \frac{d\sigma_\omega}{R_\omega} + \cdots\right], \qquad \text{(A).} \quad \text{(V.40)}$$

This expression identical with (I.7) would also be obtained from the direct treatment of boundary condition (A) based on (II.18).

For $\kappa \to -\infty$, corresponding to $\delta = -\pi/2$, the limit is:

$$\rho_0(E) = \frac{1}{4\pi^2}\left[Vk + \frac{3\pi}{4}S + \frac{1}{3k}\int_S \frac{d\sigma_\omega}{R_\omega} + \cdots\right], \qquad (\kappa \to -\infty). \quad \text{(V.41)}$$

As compared with (V.40) this expression has an additional contribution equal to $S/4\pi$ which, according to (V.34), is precisely the density of surface states.

Consider finally the density of eigenvalues for $E < 0$. From (V.31) it is seen that $\rho_0\,(E < 0)$ vanishes for $\kappa \to +\infty$, whereas for $\kappa \to -\infty$:

$$\rho_0\,(E < 0) = \frac{S}{4\pi}, \qquad (\kappa \to -\infty).$$

Thus, when $\kappa \to -\infty$, we have at all energies from $-\infty$ to $+\infty$ an additional contribution to the eigenvalue density equal to $S/4\pi$, the density of surface states.

H. *The Geometrical Coefficients for Some Particular Surfaces*

The various geometrical quantities depending on the boundary surface S, occurring in the expansion of the eigenvalue density, have particularly simple expressions for the surfaces generated by the rotation of a plane curve $\mathscr{C}$ with no multiple points, around an axis z located in the plane of $\mathscr{C}$. The curve $\mathscr{C}$ may be a closed curve which does not meet the z-axis as in Fig. 4(a). The surface S is then

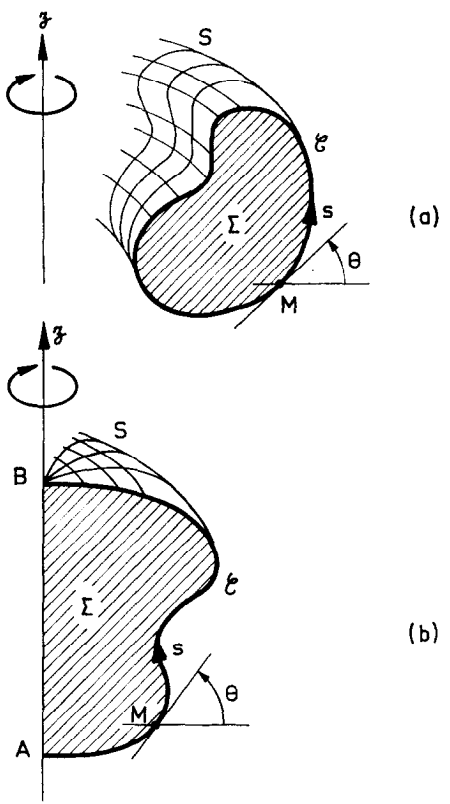

FIG. 4. Generation of a surface S by the motion of a curve $\mathscr{C}$ around a rotation axis z.

a generalized torus. The curve $\mathscr{C}$ may also be an arc cutting the z-axis at two and only two points A and B as shown in Fig. 4(b). This generates an axially symmetrical surface S topologically equivalent to a sphere. In order to avoid conical points, the curve $\mathscr{C}$ should be orthogonal to the axis z at A and B. We assume in this section that κ is constant over S.

Let us call L the length of $\mathscr{C}$, and Σ the area delineated by $\mathscr{C}$ (completed by the z-axis in case b). We define three mass-centers by the following relations:

$$\begin{aligned}
\vec{G}_\Sigma &= \frac{1}{\Sigma}\int_\Sigma d\sigma\, \vec{M}, \\
\vec{G}_L &= \frac{1}{L}\int_{\mathscr{C}} ds\, \vec{M}, \\
\vec{G}_\theta &= \frac{1}{2\pi}\int_{\mathscr{C}} d\theta\, \vec{M}, \qquad \text{(a)} \\
&= \frac{1}{\pi}\int_A^B d\theta\, \vec{M}, \qquad \text{(b)}
\end{aligned} \tag{V.42}$$

The first point is the mass-center of the area Σ, the second one is the mass-center of the curve $\mathscr{C}$. In the corresponding integral ds denotes the differential element of length along $\mathscr{C}$. In the definition of the third mass-center, θ denotes the angle of the tangent to $\mathscr{C}$ at point $\vec{M}$ measured from some direction in the plane of the curve. The total rotation of the tangent when $\vec{M}$ describes $\mathscr{C}$ is equal to 2π in case (a), and to π in case (b).

When the plane rotates around z, each of these points describes a circle. Let us denote by l_Σ, l_L, l_θ the lengths of these circles. It is then easy to show that the geometrical coefficients occurring in the first three terms of the expansion of the eigenvalue density are given by:

$$\begin{aligned}
V &= \Sigma l_\Sigma, \\
S &= L l_L, \\
\int_S \frac{d\sigma}{R} &= \pi l_\theta, \qquad \text{(a)} \\
&= \pi\left[|AB| + \frac{l_\theta}{2}\right]. \qquad \text{(b)}
\end{aligned} \tag{V.43}$$

The same type of consideration applies to a much more general family of surfaces introduced by Monge, who called them "surfaces moulures." Such surfaces are generated by the motion of a plane closed curve $\mathscr{C}$, supposed to remain indeformable. The motion is restricted by the condition that the instantaneous axis of rotation remains in the plane of the curve. This generalizes the case (a) discussed

above, since now the z-axis can move with respect to $\mathscr{C}$ within the plane of this curve, without, of course, ever cutting it. Then the curve $\mathscr{C}$ generates a kind of tube which may have a complicated shape. For a surface of this type, the expressions (V.43) remain unchanged, l_Σ, l_L, and l_θ denoting now the lengths of the curves described by the three mass-centers (V.42).

When the curve $\mathscr{C}$ has a center of symmetry, the three mass-centers defined by (V.42) become identical with the center of symmetry. Then, the three lengths l_Σ, l_L, and l_θ become equal, and may be called the length of the tube. It is remarkable that all three coefficients (V.43) occurring in the expansion (V.1) of $\rho_\gamma(E)$ depend only on the cross section $\mathscr{C}$ of the tube and its length l. It follows that if the tube is twisted in such a way that its length remains constant, the density of eigenvalues $\rho_\gamma(E)$ remains invariant, at least to the approximation considered here.

APPENDIX. Behavior of $\Gamma(\alpha\beta)$, $F(\alpha\beta)$, and of Some Related Functions

In Section III, we have evaluated in the plane approximation the Fourier transforms of the functions $\Gamma(\alpha\beta)$, $F_\eta(\alpha\beta)$, and $\partial F_\eta(\alpha\beta)/\partial n$, which enter the expansions (II.27, 28). The behavior of these functions on the surface S, although not needed in the calculations of Sections III, IV, is necessary for discussing the validity of the multiple reflection expansion. We evaluate these functions here, remaining in the plane approximation which is valid when $r \equiv |\alpha - \beta| \ll R_\omega$. For simplicity, we drop the convergence factor $\mathscr{F}$ in $F(\alpha\beta)$.

A. *Two-Dimensional Fourier Transforms of* $(p^2 - k^2)^{-n/2}$

All functions G_0, $\partial G_0/\partial n$, F, $\partial F/\partial n$, and their convolutions are expressed, by means of Eqs. (III.3, 4, 13, 18) and (IV.10), as Fourier transforms of negative powers of the function $a(p) = (p^2 - k^2)^{1/2}$.

First consider the odd negative powers of $a(p)$. From the two-dimensional Fourier transform (III.4) of G_0, we know that

$$\frac{1}{(2\pi)^2}\int d^2p\, e^{-i\mathbf{p}\cdot\mathbf{r}}\,\frac{1}{a(p)} = \frac{e^{ikr}}{2\pi r}. \tag{A.1}$$

By differentiating (A.1) n times with respect to k^2, we obtain

$$\frac{1}{(2\pi)^2}\int d^2p\, e^{-i\mathbf{p}\cdot\mathbf{r}}\,\frac{1}{[a(p)]^{2n+1}} = \frac{1}{1.3.\cdots(2n-1)}\left(\frac{1}{k}\frac{\partial}{\partial k}\right)^n \frac{e^{ikr}}{2\pi r}. \tag{A.2}$$

In particular

$$\frac{1}{(2\pi)^2}\int d^2p\, e^{-i\mathbf{p}\cdot\mathbf{r}}\,\frac{1}{[a(p)]^3} = \frac{ie^{ikr}}{2\pi k}. \tag{A.3}$$

In the same way, we deduce the Fourier transforms of the even negative powers from the simplest one:

$$\frac{1}{(2\pi)^2}\int d^2p\, e^{-i\mathbf{p}\cdot\mathbf{r}}\frac{1}{[a(p)]^2}=\frac{1}{2\pi}\int_0^\infty \frac{p\,dp}{p^2-k^2}J_0(pr)=\frac{1}{2\pi}K_0(-ikr), \quad \text{(A.4)}$$

where J_0 and K_0 are Bessel functions. By differentiating (A.4) n times with respect to k^2 we obtain:

$$\begin{aligned}\frac{1}{(2\pi)^2}\int d^2p\, e^{-i\mathbf{p}\cdot\mathbf{r}}\frac{1}{[a(p)]^{2n+2}}&=\frac{1}{n!}\left(\frac{1}{2k}\frac{\partial}{\partial k}\right)^n\frac{1}{2\pi}K_0(-ikr)\\&=\frac{1}{2\pi n!}\left(\frac{ir}{2k}\right)^n K_n(-ikr).\end{aligned} \quad \text{(A.5)}$$

B. *Behavior of the Functions F, $\partial F/\partial n$ and of their Convolutions with G_0 and $\partial G_0/\partial n$ over the Surface S*

From the expressions (III.13) and (III.18) of the Fourier transforms $\hat{F}(p)$ and $\partial\hat{F}(p)/\partial n$, and from Eqs. (A.3) and (A.4), we obtain immediately, in the plane approximation, the following expressions for $F(r)$ and $\partial F(r)/\partial n$:

$$F(r)=\frac{ie^{ikr}}{16\pi k}, \quad \text{(A.6)}$$

$$\frac{\partial F(r)}{\partial n}=\frac{1}{16\pi}K_0(-ikr). \quad \text{(A.7)}$$

At large distances, these functions decrease exponentially as $\exp[-k_1 r]$ and oscillate as G_0 itself. At short distances, $F(r)$ remains bounded, whereas $\partial F/\partial n$ tends to infinity as $|\log r|/16\pi$, in accordance with the argument of Section V,B,2 (Eq. (V.13)).

It is also easy to write in the plane approximation the complete expression of the function

$$Q^{(1)}(\alpha)=\int_S d\sigma_\beta\, K(\alpha-\beta)\,Q(\beta), \quad \text{(A.8)}$$

introduced in Section V,B,2. For instance, the term

$$\int_S d\sigma_\beta\, G(\alpha-\beta)\frac{\partial F(\beta)}{\partial n}=\frac{ie^{ikr}}{32\pi k}, \quad \text{(A.9)}$$

where $r=|\alpha|$, is the Fourier transform (A.3) of $1/16a^3$. Altogether, the function (A.8) results from Eqs. (III.4, 13, 18) and (V.2, 6), which give:

$$Q^{(1)}(r)=\frac{\kappa_\omega}{8i\pi k}\left[e^{ikr}-\frac{\kappa_\omega r}{2}K_1(-ikr)\right], \quad \text{(A.10)}$$

an expression which is clearly finite for $r \to 0$. Curvature corrections have not been written in (A.10), but it is easy to see that they are also finite for $r \to 0$.

C. *Behavior of the Function $\Gamma(r)$*

1. *Large Values of r.* The function $\Gamma(r)$ is given by Eqs. (III.3, 7), in which we drop for simplicity the index ω:

$$\begin{aligned}\Gamma(r) &= \frac{1}{(2\pi)^2}\int d^2p\, e^{-ip\cdot r}\,\frac{(p^2-k^2)^{1/2}}{\kappa+(p^2-k^2)^{1/2}}\\ &= \delta^2(r) - \frac{\kappa}{(2\pi)^2}\int d^2p\, e^{-ip\cdot r}\,\frac{1}{\kappa+(p^2-k^2)^{1/2}}\\ &= \delta^2(r) - \frac{\kappa}{2\pi}\int_0^\infty dp\, J_0(pr)\,\frac{p}{\kappa+(p^2-k^2)^{1/2}}.\end{aligned} \tag{A.11}$$

The determination of $(p^2-k^2)^{1/2}$ is defined by

$$\mathrm{Re}(p^2-k^2)^{1/2} > 0.$$

We substitute for J_0 the expression

$$J_0(x) = \frac{i}{\pi}\,[K_0(ix) - K_0(-ix)]. \tag{A.12}$$

Replacing p by $-p$ in the term in $K_0(-ipr)$, we get

$$\Gamma(r) = \delta^2(r) + \frac{\kappa}{2i\pi^2}\int_{-\infty}^{+\infty} dp\, K_0(ipr)\,\frac{p}{\kappa+(p^2-k^2)^{1/2}}, \tag{A.13}$$

where the contour goes under the singularity of the function K_0 at $p=0$ (in the complex plane of p, K_0 has a cut extending from 0 to $+i\infty$).

In the lower half-plane of p, $K_0(ipr)$ decreases exponentially; the integrand in (A.13) has a branch point at $p=-k$. We therefore introduce a cut extending from $p=-k$ to $-i\infty$. When $\kappa<0$, the integrand has also a pole at $p=-q$, where q is defined by

$$q^2 = k^2+\kappa^2, \qquad \mathrm{Im}\, q > 0. \tag{A.14}$$

Closing now the contour by a large half-circle in the lower half-plane, we get an integral along the cut, plus, when $\kappa<0$, a contribution from the pole. The final result is

$$\Gamma(r) = \delta^2(r) + \theta_-(\kappa)\,\frac{\kappa^2}{\pi}\,K_0(-iqr) - \frac{\kappa}{\pi^2}\int_{-ik}^{\infty} da\, K_0(ar)\,\frac{a(a^2+k^2)^{1/2}}{a^2+q^2}. \tag{A.15}$$

Here we have introduced the integration variable $a = ip$, which describes the contour of Fig. 3. The determination of the square root in the integrand is defined by

$$\mathrm{Re}(a^2 + k^2)^{1/2} > 0.$$

For $r \to \infty$, we may replace in (A.15) the functions K_0 by their asymptotic forms. This yields

$$\Gamma(r) = \theta_-(\kappa)\,\kappa^2 \frac{e^{iqr+i\pi/4}}{(2\pi qr)^{1/2}}\left[1 + \mathcal{O}\left(\frac{1}{|qr|}\right)\right] + \frac{i\kappa k}{\pi^{3/2}} e^{ikr} \int_0^\infty dx\, e^{-x} \frac{\sqrt{x}}{\kappa^2 r^2 - 2ikrx}\left[1 + \mathcal{O}\left(\frac{1}{|kr|}\right)\right]. \tag{A.16}$$

The second term may be further simplified if $\kappa^2 r^2 \gg kr$ or if $\kappa^2 r^2 \ll kr$.

2. *Small Values of r.* We use the expression (A.11) and expand the integrand according to

$$\frac{1}{\kappa + (p^2 - k^2)^{1/2}} = \frac{1}{(p^2 - k^2)^{1/2}} - \frac{\kappa}{p^2 - k^2} + \frac{\kappa^2}{p^2 - k^2} \frac{1}{\kappa + (p^2 - k^2)^{1/2}}. \tag{A.17}$$

The last term gives an integral in p which converges for all r, including $r = 0$. The singularities come only from the first two terms, and a short calculation using Eqs. (A.1, 4) yields

$$\Gamma(r) = \delta^2(r) - \frac{\kappa}{2\pi r} - \frac{\kappa^2}{2\pi} \log r + \mathcal{O}(1). \tag{A.18}$$

Acknowledgment

The authors wish to thank Professor J. Leray for a most stimulating discussion, and for valuable information on the earlier work on the subject.

References

1. Å. Pleijel, *Ark. Mat.* **2** (1952), 553; 12 *Skand. Mat. Kongr.* (1953), 222.
2. D. L. Hill and J. A. Wheeler, *Phys. Rev.* **89** (1953), 1102.
3. H. B. G. Casimir, *Kon. Ned. Acad. Wetensch.* **B51** (1948), 793.
4. H. Weyl, *Nachr. Akad. Wiss. Göttingen* (1911), 110.
5. C. Clark, *SIAM Rev.* **9** (1967), 627.
6. B. V. Fedossov, *Dokl. Akad. Nauk SSSR, Ser. Mat. Fiz.* **157** (1964), 536.
7. F. H. Brownell, *J. Math. Mech.* **6** (1957), 119.

8. M. KAC, *Amer. Math. Monthly* **73** (1966), 1; M. E. FISHER, *J. Combinatorial Theory* **1** (1966), 105.
9. G. M. ROE, *J. Acoust. Soc. Amer.* **13** (1941), 1; D. L. HILL AND J. A. WHEELER, *Phys. Rev.* **89** (1953), 1124.
10. W. D. MYERS AND W. J. SWIATECKI, *Nucl. Phys.* **81** (1966), 1; M. GAUDIN AND A. M. SAJOT, *J. Physique* **30** (1969), 857.
11. T. CARLEMAN, *Huitième Congr. Math. Scand. à Stockholm*, 1934, p. 34.