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SEMICLASSICAL DESCRIPTIONS OF ATOMIC AND NUCLEAR COLLISIONS

Editors

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SEMICLASSICAL DESCRIPTIONS OF ATOMIC AND NUCLEAR COLLISIONS

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PREFACE

The connection between quantum theory and classical physics was always one of the main themes in the work of Niels Bohr. One may think of the correspondence principle which played such a central role in his - and his pupils' - development of quantum physics, but also of his later works, where he introduced semiclassical methods in the treatment of atomic penetration and e.g. of nuclear fission. It was therefore felt appropriate to use this subject for the first in a series of conferences held celebrating the Niels Bohr Centennial.

Recent years have seen a very fruitful development in the theory of the classical limit of quantum theory. This has had an impact on the description of a large group of phenomena. The papers presented at this symposium deal with theoretical aspects of these approximations as well as applications to nuclear and atomic or molecular collisions, including chemical reactions and penetration phenomena. In these fields also experimental research, partly inspired by the semiclassical descriptions, has recently developed in interesting directions.

It was therefore natural to take the symposium as an occasion to bring together theoreticians and experimentalists from nuclear and atomic physics to promote a fruitful cross-breeding of ideas and experience in these fields.

The proceedings contain the manuscripts submitted by the invited speakers in the sequence in which they were presented at the conference. F. Zachariasen was unable to attend the symposium, but his manuscript is included. We are especially grateful to those contributors (G. Billing, P. Braun-Munzinger, M.S. Child and J.P. Dahl) who were kind enough to produce their articles at very short notice.

We wish to thank the staff members of the Niels Bohr Institute for their help in organizing this conference and Mary Carpenter (North-Holland Physics Publishing) for her help in preparing the camera-ready copy.

Jens Bang
Jorrit de Boer
Copenhagen, May 1985

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ON THE HISTORY OF THE SO-CALLED WKB-METHOD FROM 1817 TO 1926

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The mathematical approximation method which, since the breakthrough of quantum mechanics, is usually called the WKB-method, has really been known for a very long time. The method describes various kinds of wave motion in an inhomogeneous medium, where the properties change only slightly over one wavelength, and also provides the connection between classical mechanics and quantum mechanics. To a surprisingly large extent it can be found already in an investigation by Carlini (1817) on the motion of a planet in an unperturbed elliptic orbit. After that the method was independently developed and used by many people. The important connection formulas were, however, missing until Rayleigh (1912) very implicitly and Gans (1915) somewhat more explicitly derived one of them, later rediscovered independently by Jeffreys (1923), who also derived another connection formula (although not in quite correct form), and by Kramers (1926).

In 1817 Carlini[1] treated an important problem in celestial mechanics. He considered the motion of a planet in an elliptic orbit around the sun, with the perturbations from all other gravitating bodies neglected. Using a polar coordinate system in the plane of the planetary motion, with the origin at the sun, one can then express the polar angle as $2\pi t/T$ plus an infinite series containing sines of multiples of $2\pi t/T$, where t is the time counted from a perihelion position, i.e. from a moment when the planet is closest to the sun, and T is the time for one revolution of the planet in its orbit. The problem treated by Carlini was to determine the asymptotic behaviour of the coefficients of the sines in this series for large values of the summation index. In his treatment of this problem Carlini had to investigate a function s of a variable x. This function, which Carlini defined by a power series in x, is proportional to the function which is now called a Bessel function of the first kind, with the index p and the argument proportional to px. Carlini, who needed a useful approximate formula for this function when its argument is smaller than its order p, which tends to infinity, showed that $s(x)$ satisfies a linear, second-order differential equation containing the large parameter p. In this differential equation Carlini introduced a new dependent variable y by putting

$$s = \exp\left(\tfrac{1}{2}p \int^{x} y \, dx\right) \quad . \qquad (1)$$

Then he expanded the function y in inverse powers of p . When he introduced this expansion into the differential equation for y and identified terms containing the same power of $1/p$, Carlini obtained recursive formulas which give what is now usually called the WKB-approximation, with higher-order terms included, for the solution of the differential equation satisfied by $s(x)$. In explicit form he gave essentially the second-order WKB-approximation for the solution in a classically forbidden region. If we express Carlini's result for the function $s(x)$ in terms of the Bessel function $J_p(\xi)$, where ξ is proportional to p , we obtain the result

$$J_p(\xi) = \frac{\xi^p}{2^p\, p!} \exp\left\{p\left[\left(1-\frac{\xi^2}{p^2}\right)^{\frac{1}{2}} - 1 - \ln\frac{1+(1-\xi^2/p^2)^{\frac{1}{2}}}{2}\right]\right.$$

$$\left. -\frac{1}{2}\ln\left(1-\frac{\xi^2}{p^2}\right)^{\frac{1}{2}} + \frac{1}{p}\left[\frac{1}{12}+\frac{1}{8\,(1-\xi^2/p^2)^{\frac{1}{2}}} - \frac{5}{24\,(1-\xi^2/p^2)^{\frac{3}{2}}}\right] + \ldots\right\} \quad (2)$$

where $0 \leqslant \xi < p$, ξ/p is independent of p , and p (>0) is large. Formula (2) is essentially equivalent to the next lowest order of the asymptotic formula derived in 1909, i.e. almost a century later, by Debye[17] for the Bessel function $J_p(\xi)$ when $0 \leqslant \xi < p$, ξ/p is independent of p , and $p \to \infty$. We also remark that if one follows in essential respects Carlini's procedure to derive (2), but uses modern developments of phase-integral technique, one can in a simple way obtain asymptotic formulas, essentially equivalent to those derived by Debye with the aid of the more complicated method of steepest descents.

Using the language of quantum mechanics, one can say that in the part of the work by Carlini, which has been described above, Carlini obtained an approximate expression for the solution of the radial Schrödinger equation in the classically forbidden region, in the absence of a physical potential. Because of the way in which the large parameter p appears in the differential equation for the function $s(x)$, Carlini's solution remains valid at $x = 0$ in any order of approximation. Carlini thus achieved automatically in any order of approximation the result which Kramers[26] achieved in the first-order WKB -approximation by replacing $l(l+1)$ by $(l+\frac{1}{2})^2$, where l is the orbital angular momentum quantum number.

In connection with a heat conduction problem, Liouville[2] in 1837 treated an ordinary, linear, second-order differential equation which he transformed into a differential equation of the Schrödinger type by means of what one now calls a Liouville transformation. Then he arrived at what one in quantal language now usually calls the first-order WKB-approximation in a classically allowed region.

In 1837 Green[3] considered the motion of waves in a non-elastic fluid confined in a canal with infinite extension in the x-direction and with small breadth and depth, both of which may vary slowly in an unspecified way. The problem is described by a partial differential equation which is of the second order both with respect to the coordinate x and the time t . Green obtained an approximate solution which, for the particular case when its time-dependence is described by a sine or cosine function, reduces essentially to the first--order WKB-approximation in a classically allowed region.

The famous astronomer Encke, after whom a comet is named, drew Jacobi's attention to Carlini's work, and in 1849 Jacobi[4] published a paper concerning improvements and corrections to Carlini's work. In this paper Jacobi characterized Carlini's work as excellent and instructive, and he considered the problem treated in the main part of Carlini's publication as one of the most difficult problems of its class. Although Jacobi pointed out and corrected mistakes made by Carlini, he also pointed out that all the essential difficulties in the solution of the problem already had been vanquished by Carlini in 1817 and that Carlini's final result would have been correct if he had not made trivial mistakes in his calculations.

In 1850 Jacobi published a translation into German, with critical comments and extensions, of Carlini's investigation[5]. In this publication Jacobi again emphasized that, although the work by Carlini of 1817 contains many mistakes, and the final results are incorrect, this work, because of the method used there and the boldness of its composition, yet belongs indisputably to the most important works concerning the determination of the values of functions of large numbers. More than three decades after the original publication of Carlini's work, Jacobi thus considered it highly desirable to republish it with the necessary improvements and extensions included.

The problem in celestial mechanics, which Carlini had treated by starting from a formula given by Lagrange, was later solved more generally and in much simpler ways in 1856 by Scheibner[6,7], who attacked the problem from quite different starting points. In his first paper, Scheibner[6] used a peculiar and very general method, which recommends itself by the brevity and ease of the calculations. In his second paper, Scheibner[7] used Cauchy's powerful theory of complex integration. As an indication of the importance of Scheibner's papers we mention that, almost a quarter of a century after they had first been published, the first paper[6] , originally written in English, was republished in German translation[8], and the second paper[7], originally written in German, was republished in abbreviated form[9]. Scheibner thus solved the actual problem in celestial mechanics much simpler and more satisfactorily than Carlini, but the more complicated investigation by Carlini yielded the very fundamental result which is now called the WKB-approximation of arbitrary order. We mention Scheibner's work only to illuminate Carlini's treatment. The methods used by Scheibner are otherwise not related to the history of the so-called WKB-approximation.

In the second edition, published in 1895, of his well-known book on hydrodynamics, Lamb[10] treated (on pp. 291-296) the propagation of waves in a canal of gradually varying section on the basis of the investigation by Green[3].

Apparently unaware of the results obtained earlier by other authors, de Sparre[11] derived in 1898 essentially what is now called the second-order WKB-approximation for a second-order differential equation.

From a purely mathematical point of view, Horn[12,13] in 1899 considered, for real values of the independent variable, the asymptotic solution of a linear, second-order differential equation containing a large parameter. In 1906 and 1907 Schlesinger[14,15] generalized Horn's mathematical investigations by treating, for complex values of the independent variable, a linear system of first-order differential equations containing a large parameter. Referring to the method used by Green[3], Birkhoff[16] in 1908 continued Horn's and Schlesinger's work by investigating mathematically the asymptotic character of the solutions of certain arbitrary-order linear differential equations containing a large parameter.

In a paper concerning the propagation of waves through a stratified medium, Rayleigh[18] in 1912 treated the one-dimensional time-independent wave equation by writing the solution as an amplitude times a phase factor. He found the exact relation between amplitude and phase [his eq. (73)], but he did not point out the great importance of this relation, which since 1930 has been used with great success by several authors. Rayleigh obtained what is now generally known as the first-order WKB-approximation in a classically allowed region. By pursuing the approximations he also obtained the next correction to the amplitude (in approximate form) and to the phase. Considering then the case of total reflection due to a turning point, Rayleigh introduced into the wave equation a linear approximation in a certain region around the turning point and was thus able to obtain an approximate solution expressed by an Airy function in that region. When he used asymptotic approximations for the Airy function, he obtained a result which is closely related to a connection formula for the WKB-approximation.

On the basis of Maxwell's electromagnetic theory, Gans[19] in 1915 treated the propagation of light in an inhomogeneous medium, where the index of refraction depends only on one cartesian coordinate. He obtained the first-order

WKB-approximation for the solution of the one-dimensional wave equation. Considering total reflection, Gans approximated the square of the index of refraction by a linear function in the region around the turning point which gives rise to the total reflection. He was thus able to express the solution on each side of the turning point approximately in terms of Hankel functions of the order 1/3. Matching these approximate solutions at the turning point, and using asymptotic approximations for the Hankel functions on both sides of the turning point, Gans obtained a result [see in Ref. 19 eqs. (69) and p. 726] which, although not in quite explicit form, is equivalent to the connection formula for the first-order WKB-approximation which starts from the exponentially small wave function in the region into which the light penetrates only as an evanescent wave.

In a paper dealing with certain hypotheses as to the internal structure of the earth and moon, Jeffreys[20] in 1915 obtained (on pp. 211-213) essentially the first-order WKB-approximation for the solution of a linear, second-order differential equation.

In an investigation concerning the aerodynamics of a spinning shell, Fowler, Gallop, Lock and Richmond[21] in 1921 treated a system of two coupled ordinary, linear differential equations containing a large parameter, one of the equations being inhomogeneous and of the second order, the other being homogeneous and of the first order. Referring to the papers by de Sparre[11], Horn[12,13], Schlesinger[14,15] and Birkhoff[16], Fowler et al.[21] investigate the asymptotic expansion of the solution of the above-mentioned system of differential equations for large values of the parameter. In connection with this problem, the authors consider in particular a homogeneous, linear differential equation of the second order which they solve by writing the solution as the product of an amplitude and a phase factor. Finding the exact relation between amplitude and phase, they express the phase in terms of the amplitude which they obtain as an asymptotic expansion in inverse powers of the square of the large parameter. The authors make the important remark that by separating the solution correctly into the product of an amplitude and a phase factor they gain the advantage over other methods that they obtain in one step a solution with the error inversely proportional to the square of the large parameter, whereas this requires two steps in the usual procedures.

Referring to the above-mentioned previous work by Green, Lamb, Horn, Jeffreys and Fowler et al., Jeffreys[22] in 1923 derived what is now usually called the WKB-approximation for the solution of an ordinary, homogeneous, linear differential equation of the second order. In the region of a turning point Jeffreys, like Rayleigh and Gans, introduced a linear approximation in the differential equation and was thus able to express the solution there approximately in terms of Bessel functions of the order 1/3. Using asymptotic approximations for these functions, Jeffreys obtained the previously mentioned connection formula and another connection formula which was, however, not given in quite correct form. The question of the one-directional nature of the connection formulas was not clarified until later.

Obviously unaware of the existence of the work by the previous authors, Brillouin[23,24], Wentzel[25] and Kramers[26] in 1926 introduced analogous considerations in quantum mechanics. Brillouin established, for a system of particles, the connection between the Schrödinger equation of quantum mechanics and the Hamilton-Jacobi equation of classical mechanics, while Wentzel and Kramers introduced for the radial Schrödinger equation the main results obtained in the course of the developments described above. These results turned out to be extremely useful in applications of the new quantum theory and became known under the name of the WKB-method. However, Brillouin, Wentzel and Kramers contributed hardly anything new to the mathematical approximation method that had already been found by previous authors, as described in this short historical review.

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SEMICLASSICAL METHODS IN CHEMICAL DYNAMICS

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A general semiclassical (multidimensional WKB-type) approximation to quantum mechanics is reviewed. The principal feature of the approach is that it is able to incorporate the exact classical mechanics of the system and also the quantum principle of superposition. Applications to inelastic and reactive scattering, and to statistical mechanics and reaction rates are discussed.

1. Introduction

The use of semiclassical methods in chemical and molecular problems has become so pervasive over the last twenty years that it is somewhat intimidating to attempt a short review with the present title.[1] Since a comprehensive review is impossible, I have chosen several examples which illustrate the variety of quantum phenomena that semiclassical theory is able to describe correctly.

Perhaps the most dramatic quantum phenomenon is that of quantization itself, the fact that only discrete values of the energy are allowed for a system whose motion is bounded. The grandfather of all semiclassical descriptions of quantization is the Bohr model of the hydrogen atom and its generalization which became known as the Old Quantum Theory.[2] For a diatomic molecule with potential function V(r), for example, the Bohr-Sommerfeld (or WKB) quantization condition is

$$(n+\tfrac{1}{2})\pi = \int_{r_1}^{r_2} dr \sqrt{\frac{2\mu}{\hbar^2}\left[E-V(r)-\frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}\right]} \quad , \qquad (1.1)$$

where (r_1,r_2) are the two classical turning points in the effective potential (V(r) plus the centrifugal term. Eq. (1.1) is an implicit equation for the energy levels $E(n,\ell)$ in terms of the vibrational and rotational quantum numbers.

For molecular systems, i.e., diatomic molecules, Eq. (1.1) is actually quite accurate: ground-state energies are given to better than 1% accuracy even for