氏名	朱　超原
学位（専攻分野）	博士（理学）
学位記番号	総研大甲第６０号
学位授与の日付	平成５年９月30日
学位授与の要件	数物科学研究科　機能分子科学専攻 学位規則第４条第１項該当
学位論文題目	Stokes phenomenon and two-state linear curve crossing problems
論文審査委員	主査　助教授　大峯　巖 教授　中村宏樹 助教授　松本吉泰 助教授　正畠宏祐 教授　中村勝弘（大阪市立大学）

論文内容の要旨

The Stokes phenomena of the standard second-order ordinary differential equations with the coefficient functions of the certain n-th order polynomials are investigated. Four cases of the coefficient function $q(z)$ are solved to find analytical solutions of the Stokes constants: (i) $q(z) = a_{2N}z^{2N} + \sum_{j=-\infty}^{N-1} a_j z^j$; (ii) $q(z) = a_{2N-1}z^{2N-1} + \sum_{j=-\infty}^{N-2} a_j z^j$; (iii) $q(z) = \sum_{j=0}^{4} a_j z^j$; and (iv) $q(z) = \sum_{j=0}^{3} a_j z^j$. The case (iii) can be immediately applied to the two-state linear curve crossing problems which represent the most basic models for non-adiabatic transition processes in atomic and molecular physics. The two-state linear curve crossing problems are generally classified into the following two cases: (1) the same sign of slopes of two diabatic potential curves(Landau-Zener case), and (2) the opposite sign of slopes(nonadiabatic tunneling case). The reduced scattering matrix for each case has been found to be expressed in terms of only one Stokes constant U_1, which is solved exactly and analytically in a form of convergent infinite series. This means that exact quantal solutions of the reduced scattering matrices for both cases are analytically found for the first time. Furthermore, new semiclassical solutions of the reduced scattering matrices for both cases are derived in simple compact forms. Especially, the case that the collision energy is lower than the crossing point is correctly dealt with for the first time. Both quantal and semiclassical solutions for the reduced scattering matrix are made possible by expressing the connection matrix, which is a crucial bridge to link physics and mathematics, in terms of Stokes constants. Among the fruitful results obtained, one of the most notable ones is about a derivation of a new formula to replace the widely used Landau-Zener formula for nonadiabatic transition probability. The new one is as simple as the Landau-Zener, but works much better than the latter. On the the other hand, by fully analyzing the distributions of the four transition points and the Stokes lines in complex plane for the basic equations of the two-state linear curve crossing problems, the validity conditions are made clear for the present and the other available semiclassical formulas of the reduced scattering matrices.

Chapter 1

This thesis begins with the asymptotic solutions of the second-order differential equations for the four cases mentioned above. The asymptotic solutions are found exactly in the form of infinite series, in which the recurrence relations among the coefficients are given explicitly. This is made possible by transforming the original differential equations from the complex-z plane to a new complex-ξ plane in which all the Stokes lines coincide with the real axis. At the same time, the standard asymptotic WKB solutions are introduced for convenience as reference functions to define Stokes constants. The Stokes phenomenon is reviewed and explained briefly so that physicists and chemists can get quickly an insight on the topics discussed in this thesis.

Chapter 2

A central task in the subject of Stokes phenomenon is to find analytical solutions of Stokes constants. The standard asymptotic WKB solutions are proved to be quite useful for the present type of analysis, especially for deriving the relations among Stokes constants. Actually, three independent relations for all Stokes constants U_i defined in the complex-z plane are easily established. They are very useful for many physical problems although they are not enough to have a complete. A further deduction is made by transforming the asymptotic solutions from complex-z plane to the complex-ξ plane where the Stokes constants T_i are defined. One-to-one simple correspondence is obtained between U_i and T_i. What is fascinating about the complex-ξ plane is that all Stokes constants T_i can be simply related to only one, for instance, T_1, by using a particular transformation under which the differential equation in the complex-ξ plane is invariant. The conclusions obtained up to now hold not only for the four cases mentioned above but generally. The remaining most difficult problem is how to find an analytical solution for T_1 for each case. By generalizing the coupled-wave-integral- equations method devised by Hinton, Stokes constant T_1 is finally shown to be expressed in the analytical form of a convergent infinite series as a function of the coefficients $q(z)$ for all four cases.

Chapter 3

A connection matrix presented in this chapter represents an important physical quantity i.e., scattering matrix, and bridge between the Stokes phenomenon in mathematics and the two-state linear curve crossing problems in physics. If the standard WKB solutions are used in the asymptotic region $|z| \to \infty$ of the complex plane, the connection matrix is exactly expressed in terms of the Stokes constants. This matrix can connect solutions in one asymptotic region in complex plane to solutions in another asymptotic region, such as physical important connections between two anti-Stokes lines, two Stokes lines, and one anti-Stokes and Stokes lines. What is fascinating about expressing the connection matrix in terms of Stokes constants is as follows: A physically required connection matrix sometimes can not be well-approximated by following traditional semiclassical path. It is much more flexible and versatile to try to find Stokes constants. Based on the knowledge of the distributions of transition points and Stokes lines, such a path which may not correspond to the physical connection matrix can be designed to derive the best semiclassical solution from Stokes constants. Excellent examples will be given in chapters 5 , 6 and 7 for semiclassical solutions of the reduced scattering matrices for the cases of energy lower than the crossing points. The connection problems for one transition point and two transition points are briefly reviewed, and those for three transition points and four transition points are presented in detail. The last case is mainly concerned with the curve crossing problems discussed in the subsequent chapters.

Chapter 4

The classic problems of the two-state linear curve crossing were initially discussed by Landau, Zener and Stueckelberg. As mentioned before, there are the following two cases: (1) the same sign of slopes of two diabatic potentials(Landau- Zener case), and (2) the opposite sign of slopes(nonadiabatic tunneling case). It is well known that the reduced scattering matrices for these two problems can be described in terms of the two parameters a^2(effective coupling strength) and b^2(effective collision energy). Finding the exact analytical quantal solutions for the reduced scattering matrices is very challenging and very difficult question. The answer to this question is given in this chapter. The starting point is the basic differential equation of the case (iii) mentioned before. By using the connection matrix obtained in chapter 3, the reduced scattering matrix for each case is first expressed in terms of three Stokes constants. Then by taking into account two extra conditions in addition to the unitarity of reduced scattering matrix, it is shown to be expressed finally in terms of only one Stokes constant U_1. Finally, this one Stokes constant is given exactly and analytically by a convergent infinite series which is a direct result from chapter 2. Another work reported in this chapter is a new numerical method to solve reduced scattering matrix for the nonadiabatic tunneling case. The original coupled equations suffer from very rapid oscillation asymptotically and can not give stable and reliable numerical results. New coupled equations are presented which involve ordinary sine and cosine solutions asymptotically. Numerical results of reduced scattering matrix can be obtained with any desirable accuracy.

Chapter 5

The distributions of the four transition points and the Stokes lines are fully analyzed for both Landau-Zener and nonadiabatic tunneling cases in the whole plane of the two parameters a^2 and b^2. This analysis is, of course, important in itself, but what is more significant about this is that the structure of the distributions essentially determines which path in complex plane is the best for obtaining good semiclassical solutions of the reduced scattering matrices. The semiclassical method used here and in the following chapters should be potentially useful for other problems in physics and chemistry.

Chapter 6

The semiclassical solution of the reduced scattering matrix for the Landau-Zener case is obtained in this chapter. Since the reduced scattering matrix is expressed in terms of one Stokes constant U_1 in chapter 4, question now is how to find an approximate solution for U_1. The distributions of transition points and Stokes lines analyzed in chapter 5 clearly show that there are two best choices of path to get good approximate solutions of U_1. One path corresponds to the connection on the anti-Stokes lines along which the four transition points are separated in two paris. Another path corresponds to the connection on the Stokes lines along which the four transition points are again separated in two pairs. The former(latter) corresponds to high(low) energy limit. In each limiting case, the exact connection matrix can be approximately decomposed into a product of the two matrices, each of which represents the connection matrix based on two transition points as is given in chapter 3. Finally, two new compact analytical formulas for the reduced scattering matrix are derived and compared with available ones. The $a^2 - b^2$ plane is now divided into five regions, in each one of which the best recommended formulas are proposed. The new formulas proposed are simple and explicit functions of the two parameters a^2 and b^2. Especially, a simple formula which works much better than the conventional Landau-Zener formula is obtained for nonadiabatic transition probability for one passage of crossing point.

Chapter 7

The semiclassical solution of the reduced scattering matrix for the nonadiabatic tunneling case is obtained in this chapter. The reduced scattering matrix is, of course, given in chapter 4 in terms of one Stokes constant U_1. The distributions of transition points and Stokes lines in this case are more complicated than the previous case. There are two limiting cases, $b^2 \gg 1$ and $b^2 \ll -1$, which are similar to the Landau-Zener case. Therefore, the two new formulas for reduced scattering matrix are obtained in these two limiting cases again by simple functions of the two parameters a^2 and b^2. Especially formula for $b^2 < -1$ is the first one ever obtained. The distributions of transition points and Stokes lines in the region $|b^2| \leq 1$ are very different from and have no correspondence to the former Landau-Zener case. Based on the solvable special differential equation given in chapter 3, an approximate expression for Stokes constant U_1 is found with use of a fitting procedure. Again, the $a^2 - b^2$ plane is divided into five regions and the best recommended formula for reduced scattering matrix is proposed for each region. Thus, a complete picture of the nonadiabatic tunneling case is attained.

論文の審査結果の要旨

朱超原氏は、物理、化学に於ける最も重要な問題の１つである状態間非断熱遷移に関して、１次元直線ポテンシャル交差問題の厳密解及び簡便な近似解析解を求めその多くの新しい性質を明かにする研究を行なった。

朱氏はまず基本となる微分方程式の漸近解の性質に関して、微分方程式のストークス現象の解析を行ない、３次多項式、４次多項式、特殊な２Ｎ次及び２Ｎ－１次多項式を係数として持つ４種類の２階常微分方程式のストークス定数の全てに対して解析的表現を得た。

次に、この中の４次多項式の微分方程式の漸近解を、２準位直線ポテンシャル交差問題に適用し、Landau-Zener型と非断熱型の両者について、散乱行列に対する量子力学的厳密解を導出した。また半古典的近似解の解析解を研究し、Landau-Zener型の場合、結合強度と衝突エネルギーの２つのパラメーター空間を５つの領域に分割し、各領域での半古典解を提唱した。これらは現存の他の半古典解公式より遥に精度がよく、例えば有名なLandau-Zenerの公式と同程度に簡便であるが、低いエネルギー領域でも正確な公式を求めている。非断熱型トンネルの場合にも同様に、２つのパラメーター空間を５つの領域に分割し、各領域での最良の公式を提唱した。特に交差点より下のエネルギー帯に対しては本研究によって、初めて解析近似解が求められた。

また、この直線ポテンシャル交差モデルの数値解法についても、座標交換を巧みに用いて発散の困難を取り除いた安定数値解析法を開発した。

以上、朱氏の博士論文は長年未解決の難問題として残っていた２準位直線ポテンシャル交差問題を解決した研究であり、その内容は
(1) J. Math. Phys. **33**,2697(1992), "Stokes constants for a certain class of second-order ordinary differential equations", (2) J. Chem. Phys. **97**,1892(1992), "The two-state linear curve crossing problems revisited, I. Analysis of Stokes phenomenon and expressions for scattering matrices",
(3) J. Chem. Phys. **97**, 8497(1992), "The two-state linear curve crossing problems revisited, II. Analytical approximations for Stokes constant and scattering matrix; Landau-Zener case",
(4) J. Chem. Phys. **98**,6208(1993), "The two-state linear curve crossing problems revisited,III. Analytical approximations for Stokes constant and scattering matrix; The nonadiabatic tunneling case", (5) Comput. Phys. Commun. **74**,9(1993), "Numerical methods for the two-state linear curve crossing; Nonadiabatic tunneling case"
の５報の論文とし国際誌に掲載されており、既に世界的に高い評価を受けている。審査委員会に於ても朱氏が本研究の問題の把握、意義をしかっりと理解しており、その数学的、物理的基礎も充分であることが明かであった。論文は英語で書かれており、発表、質疑応答も明確な英語で行なわれ、従って英語の学力も充分である。論文公開発表会に於ても本研究の高度な内容を、その意義、数学的展開、交差問題への応用、その結果と順序をおって明確に示し、質疑応答でも本研究の将来の発展など的確な答えを行なった。

以上、朱氏は博士論文の内容は、非常に画期的であり物理、化学の発展に大きく貢献したものと高く評価され、審査員全員で学位授与の対象として十分なものと判断した。