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Connor J N L & Marcus R A. Theory of semiclassical transition probabilities for inelastic and reactive collisions. II. Asymptotic evaluation of the S matrix. *J. Chem. Phys.* 53:5636-43, 1971.
[Noyes Chemical Laboratory, University of Illinois, Urbana, IL]

The uniform asymptotic evaluation of an oscillating integral with two coalescing saddle points is discussed in a straightforward and general way. This key problem arises in the semiclassical theory of atomic and molecular collisions. A short and simple derivation is also given for a semiclassical integral representation of a scattering matrix element. [The *SCI*® indicates that this paper has been cited in more than 140 publications.]

Uniform Semiclassical Collision Theory

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I spent the years 1969 to 1971 at the University of Illinois, working as a postdoc with Rudolf A. Marcus. Before that, I had obtained my D. Phil. degree in molecular collision theory at the University of Oxford.

Semiclassical theories of molecular collisions were of particular interest in the early 1970s. A semiclassical theory uses real (and also complex valued) solutions of classical mechanics (Hamilton's equations) to construct an asymptotic (semiclassical) approximation to the Schrödinger equation. A semiclassical approximation is often very accurate and provides excellent physical insight. I already had a good background in asymptotic techniques from my D. Phil. research. (See, e.g., reference 1.)

I wrote paper number II in this series of six, after studying and discussing paper number I with Marcus.[2] Paper number II has two parts: the first part presents a simpler and shorter derivation of number I's main result: a semiclassical integral representation using action-angle variables for an element of the scattering (or S) matrix. Paper number II's second (and main) part concerns the uniform asymptotic evaluation of oscillating integrals with two coalescing saddle points, using the method of C. Chester, B. Friedman, and F. Ursell (CFU).[3] Although M.V. Berry[4] had earlier applied the CFU technique to a specific problem (atomic rainbow scattering), the power of the CFU method was not widely known in the chemical physics literature. In paper number II, we presented the CFU method in an accessible, yet general, way. All equations necessary for applications were given explicitly, making it easy to apply the CFU theory to concrete problems. Our presentation of the CFU method was soon reproduced in reviews and books, so the uniform theory became more widely known and appreciated.

Paper number II seems to be referenced by three groups of authors: (a) those who cite it as an example of semiclassical research done in the 1970s; (b) those who use the S matrix integral representation; and (c) those who apply the uniform asymptotic theory to integrals arising in their own research (the paper is then often cited together with reference 4). Later applications of the uniform theory using the equations given in paper number II include: rotational rainbows in atom-molecule and molecule-surface scattering, analysis of vibrational transitions, the theory of chemical reactions, electron detachment in negative ion collisions, Penning ionization, the pressure broadening of spectral lines, and the analysis of quasimolecular orbital X-ray spectra.

In 1971, I joined the University of Manchester. I generalized the uniform treatment of paper number II to many (i.e., 3,4,...) coalescing saddles and also made extensions of the theory to multidimensional integrals. The treatment of these individual cases can be unified with the help of singularity (catastrophe) theory.[5] More recently, I have developed new numerical techniques that allow the uniform formalism for 3,4,... coalescing saddles to be applied in practice. I have reviewed these recent developments in reference 6, which contains many references. There is still much interesting and important research to be done in this area; the whole subject is a fascinating mixture of abstract mathematics, numerical analysis, and practical applications.

For this and other research, I have received the Royal Society of Chemistry's Meldola Medal, Marlow Medal, and Award in Theoretical Chemistry. Marcus moved to the California Institute of Technology in 1978. He has received the American Chemical Society's Langmuir, Gibbs, and Debye Awards, the Wolf Prize in Chemistry (Israel), and the US National Medal of Science.

1. Connor J N L. On the semiclassical description of molecular orbiting collisions. *Mol. Phys.* 15:621-31, 1968.
2. Marcus R A. Theory of semiclassical transition probabilities (S matrix) for inelastic and reactive collisions. *J. Chem. Phys.* 54:3965-79, 1971. (Cited 190 times.)
3. Chester C, Friedman B & Ursell F. An extension of the method of steepest descents. *Proc. Cam. Philol. Soc.* 53:599-611, 1957. (Cited 165 times.)
4. Berry M V. Uniform approximation for potential scattering involving a rainbow. *Proc. Phys. Soc. London* 89:479-90, 1966. (Cited 120 times.)
5. Connor J N L. Catastrophes and molecular collisions. *Mol. Phys.* 31:33-55, 1976.
6. ---------. Practical methods for the uniform asymptotic evaluation of oscillating integrals with several coalescing saddle points. (Wong R, ed.) *Asymptotic and computational analysis.* New York: Marcel Dekker, 1990. p. 137-73.

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