Theor Chem Acc (2000) 103:297–299
DOI 10.1007/s002149900026

Theoretical
Chemistry Accounts
© Springer-Verlag 2000

Perspective

Perspective on "Semiclassical theory of atom–diatom collisions: path integrals and the classical S matrix"

Miller WH (1970) J Chem Phys 53: 1949–1959

Reinhard Schinke

Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-37073 Göttingen, Germany

Received: 26 February 1999 / Accepted: 5 April 1999 /Published online: 21 June 1999

Abstract. Miller's papers on classical S-matrix theory had a profound influence on the understanding of inelastic atom–molecule collisions. This perspective discusses the historical background, the content, some applications, and new developments.

Key words: Semiclassical dynamics – Rainbows

When I joined the department for Molecular Interactions at the Max-Planck-Institut für Strömungsforschung as an undergraduate student in 1972, the head of that department, Professor J.P. Toennies, gave me a couple of papers [1, 2] to read, which had great influence on many researchers in the field of molecular dynamics; they certainly shaped my own scientific thinking for many years to come.

Around 1970 there was a flourishing interest in state-resolved scattering cross sections and at several locations crossed molecular beams apparatus were under construction; our institute was one of them. Although it was clear from the beginning that quantum mechanics is the ultimate tool for describing collisions between atoms and molecules, exact quantum mechanical calculations for realistic systems, especially for chemical reactions, were essentially impossible in those times. On the other hand, purely classical mechanics, i.e., trajectory calculations a la Karplus, Porter, and Sharma [3] (see the perspective by Schatz in this issue) were believed to be not fully adequate, since important quantum effects such as tunneling, zero-point energy, and interferences are – by definition – not incorporated. Thus, a theory was sought which amalgamates the simplicity of classical calculations with the essential concepts of quantum mechanics.

In the first of the papers mentioned above Miller established a general semiclassical theory for inelastic molecular scattering. This approach was the natural extension of the celebrated semiclassical theory for elastic atom-atom scattering [4] which had been developed about a decade before Miller's papers (see the perspective given by Miller in this issue). The basic concept of the semiclassical theory is the incorporation of quantities solely derived from the solution of the classical (Newton's or Hamilton's) equations of motion into the quantum mechanical principle of superposition of probability amplitudes (as opposed to the summation of probabilities). Building the theory on the superposition principle guarantees that the quantum mechanical effects neglected in classical mechanics are at least qualitatively included. Solving the classical equations of motion for a system with several degrees of freedom, in order to extract the necessary ingredients such as action integrals or generalized deflection functions, even three decades ago was not a problem and thus the classical S-matrix theory, as the semiclassical theory was termed, was considered to be a promising alternative to exact quantum mechanical methods for calculating state-resolved inelastic integral and differential cross sections for atom–molecule collisions. One must remember that around that time the first exact (close coupling) calculations had just appeared in the literature [5]. For a more comprehensive historical survey of semiclassical methods for bound states and scattering problems see the review articles by Miller [6, 7] or the monograph of Child [8].

While the first of the two Miller papers was a bit formal, especially for a young undergraduate student making his first steps into science, in the second paper it was demonstrated by means of a simple collinear $A+BC(n_1) \rightarrow A+BC(n_2)$ scattering system how the general theory must be applied [2]. Within the simplest version of classical S-matrix theory the probability for making a vibrational transition from an initial state n_1 to a final state n_2 is given by

$$P_{n_2,n_1} = p_1 + p_2 + 2(p_1 p_2)^{1/2} \sin(\Delta\phi) \ , \qquad (1)$$

where the

$$p_i = \left| 2\pi \frac{\mathrm{d}n_2(\bar{q}_1)}{\mathrm{d}\bar{q}_1} \right|^{-1}_{\bar{q}_1=\bar{q}_1^i} \tag{2}$$

are purely classical probabilities and $\Delta\phi$ is the difference between the action integrals along the two different classical trajectories, specified by the initial phase angles $\bar{q}_1^1$ and $\bar{q}_1^2$, which correspond to the particular $n_1 \rightarrow n_2$ transition. The particular form of Eq. (1) is only valid if there are two trajectories that – in the classical sense – contribute. The interference term $\sin(\Delta\phi)$ is the manifestation of the quantum mechanical superposition principle (addition of probability amplitudes rather than probabilities).

The connection between the classical trajectories and the quantum transition is established by the classical excitation function $n_2(\bar{q}_1)$, an example of which is depicted in Fig. 1a. $n_2(\bar{q}_1)$ is the final classical vibrational quantum number (not necessarily an integer) as a function of the initial phase of the oscillator. It is calculated by running – for a particular collision energy – trajectories with different initial phase angles $\bar{q}_1$. The particular trajectories which contribute to the probabilities in Eq. (1) are found using the equation

$$n_2 = n_2(\bar{q}_1) \ , \tag{3}$$

where $n_2 = 0, 1, \ldots$. In the particular case shown in Fig. 1 exactly two trajectories contribute when n is smaller than the maximum of the excitation function (classically allowed case).

The interference of these different roots to Eq. (3) leads to the pronounced oscillations of the quantum mechanical probability shown in Fig. 1b. In contrast to the quantum mechanical curve the classical probability is a smooth function of n_2. If n_2 is larger than the maximum of the excitation function there are no real-valued trajectories and the transition is classically forbidden. An extension of the semiclassical theory into the nonclassical regime is possible by analytical continuation and complex-valued trajectories [9–11]. If n_2 is close to $n_2^{\max}(\bar{q}_1)$ the classical probabilities become singular and the "primitive" semiclassical theory breaks down; however, this failure can be corrected on a more sophisticated (uniform) level of the semiclassical theory. Thus, the probability has three different regimes: the classically allowed region, in which the probability shows quantum interference oscillations; the classically forbidden region, in which the probability decays exponentially to zero; between these two regimes the probability shows a pronounced rainbowlike maximum.

About a decade later, the general predictions concerning the shape of transition probabilities, that naturally emerge from the semiclassical theory, were beautifully confirmed in rotational-state-resolved differential-scattering cross sections. These cross sections exhibit a classically forbidden region, a dominant rainbow maximum (rotational rainbow), and interference oscillations in the classically allowed region [12]. An experimental example, highlighting the supernumerary rotational rainbows, is shown in Fig. 2 for the He + Na_2 collision system together with the results of theoretical calculations employing an accurate potential-energy surface [13]. The rotational rainbow occurs at very small angles in this particular example and is not observable. However, the quite regular supernumerary oscillations, which are so nicely predicted by Eq. (1), are clearly observable; these oscillations are distinctively different from the rainbow oscillations observed in elastic collisions [4]. The semiclassical picture has also been found extremely helpful in understanding final product state distributions following the fragmentation

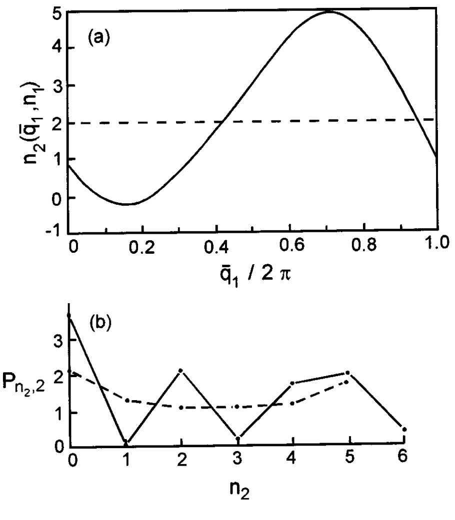

Fig. 1. a Vibrational excitation function $n_2(\bar{q}_1)$ as a function of the initial phase angle of the BC oscillator $\bar{q}_1$. Redrawn from Fig. 2 of Ref. [2]. **b** Comparison between the quantum mechanical (*solid line*) and the classical (*dashed line*) transition probabilities. Redrawn from Fig. 1 of Ref. [2]

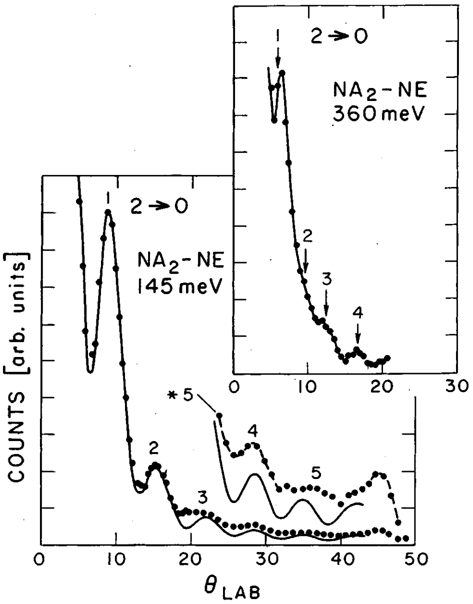

Fig. 2. Supernumerary rotational rainbow oscillations for the $j = 0 \rightarrow 2$ transition in He + Na_2 collisions. The *dots* are the experimental data and the *solid lines* are the results of quantum mechanical scattering calculations. Reproduced, with permission of the American Institute of Physics, from Ref. [13]

of polyatomic molecules, provided the dissociation is fast and direct [14]. Another, very fine application of semiclassical *S*-matrix theory has been provided by Rost in the context of electron–atom scattering, particularly the ionization of atomic hydrogen [15]. This application is especially fascinating because electrons are not considered to be well described by classical mechanics.

In the early 1970s, the semiclassical approach to inelastic scattering was mainly applied to the collinear A + BC model system defined by Secrest and Johnson [5], which included only two degrees of freedom. The emphasis at that time was mainly in testing the various implementations of the classical *S*-matrix theory. Although the agreement with the exact quantum mechanical results was excellent, applications of the semiclassical theory to more realistic and therefore necessarily more complex collision systems was sparse. The reasons why the classical *S*-matrix theory did not become a major tool for numerical calculations for realistic systems are – in my opinion – twofold. First, if more than two degrees of freedom are involved, finding the correct trajectories which lead to the desired quantum transition is "thorny" (root search problem). Second, beginning in the mid-1970s better and better numerical algorithms for solving the Schrödinger equation (the time-independent or the time-dependent one) were developed, so that today it is possible to treat any triatomic molecular system in an essentially exact quantum mechanical manner. Of course, the unforseen advances in computer technology also had an enormous impact on exact scattering calculations.

Applications of exact quantum mechanics to systems with four atoms involved is still a major numerical burden, not to mention application to even bigger systems, and so approximate methods based on the solution of the classical equations of motion are nevertheless highly desired. In this context the semiclassical initial value representation (IVR), a precursor of which had already been derived in Miller's 1970 paper [2], may turn out to become a significant tool in molecular dynamics (see Ref. [16] for a comprehensive list of recent references). In the IVR approach the quantum mechanical *S*-matrix elements are approximated by a (multi-dimensional) integral over the initial classical phase space and the integrand contains only ingredients from classical trajectories. In this way, the awkward root searching procedure is avoided. The price to be paid is that instead of a few trajectories many have to be calculated. Recent applications are very promising and show that quantum mechanical effects such as interferences, for example, are reproduced perfectly [16].

In summary, Miller's 1970 papers [1, 2] on classical *S*-matrix theory had a profound influence on the theory of molecular collisions and related topics such as photodissociation. Following earlier work on elastic scattering, they demonstrated how the results of classical mechanics can be built into a quantum mechanical framework of inelastic collisions. In my view the greatest asset of the classical *S*-matrix theory is its interpretative power. The general shape of transition probabilities or collisional cross sections can be easily understood in terms of classical trajectories and their quantum mechanical interference. Exact quantum mechanical programs are like "black boxes" and the results are often difficult to understand without the help of classical mechanics or semiclassical analyses. The new developments such as the IVR are likely to become major tools for systems consisting of many atoms.

References

1. Miller WH (1970) J Chem Phys 53: 1949
2. Miller WH (1970) J Chem Phys 53: 3578
3. Karplus M, Porter RN, Sharma RD (1965) J Chem Phys 43: 3259
4. Ford KW, Wheeler JA (1959) Ann Phys (NY) 7: 259
5. Secrest D, Johnson BR (1966) J Chem Phys 45: 4556
6. Miller WH (1974) Adv Chem Phys 25: 69
7. Miller WH (1975) Adv Chem Phys 30: 77
8. Child MS (1991) Semiclassical mechanics with molecular applications. Clarendon, Oxford
9. Miller WH (1970) Chem Phys Lett 7: 431
10. Miller WH, George TF (1972) J Chem Phys 56: 5668
11. Stine JR, Marcus RA (1972) Chem Phys Lett 15: 536
12. Korsch J, Schinke R (1980) J Chem Phys 73: 1222
13. Gottwald E, Bergmann K, Schinke R (1987) J Chem Phys 86: 2685
14. Schinke R (1993) Photodissociation Dynamics. Cambridge University Press, Cambridge
15. Rost J-M (1998) Phys Rep 297: 271
16. Skinner DE, Miller WH (1999) Chem Phys Lett 300: 20