Molecular Physics
Vol. 110, Nos. 9–10, 10–20 May 2012, 513–516

INVITED ARTICLE

At the birth of modern semiclassical theory

Rudolph A. Marcus*

Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena CA 91125, USA

(*Received 13 February 2012; final version received 29 February 2012*)

The rapid development of the semiclassical theory of Miller and Marcus and its applications in the 1970s was an exciting experience. Some of these developments and the issues involved are described in the present overview.

Keywords: semiclassical theory; action-angle variables; theory of Miller and Marcus; collision dynamics; unimolecular dissociation

The 1970s were heady times when Bill and I were developing semiclassical theory [1–20] that would sometimes later be known as the theory of Miller and Marcus. On this occasion of Bill's 70th birthday some 40 years later, I would like to recount some of that history and its background. These impressions are intended as a bird's eye view rather than attempting to provide a detailed history. Several reviews appeared at the time [8,9,20].

This modern version of semiclassical theory has several roots. One of them that I believe particularly influenced Bill was Feynman's propagator and its application by Phil Pechukas in 1969 to collisions [21]. My own work was based instead on the short wavelength approximation to wave mechanics, the Wentzel–Kramers–Brillouin theory developed in 1926. This approximation was extensively used to treat the many wave mechanical properties in elastic collisions [22–24].

In both Bill's and my approaches classical action-angle variables [25,26] played a major role. They too have a quantum history, being an essential part of 'old quantum theory' in the 1910–1920s [26], and having a pre-quantum history in classical mechanics and celestial mechanics. However, after old quantum theory gave way to quantum or wave mechanics, those variables largely disappeared from the atomic literature.

My students and I used them in the late 1960s to treat collisional rotational-translational, vibrational-translational energy transfer, and reactive collisions [27–32]. They provided a way of understanding 'vibrational adiabaticity' in the classical mechanics of in a $H + H_2$ exchange reaction [30–32]. Both classical trajectory and quantum mechanical results for the latter on the effect of vibrational energy on the reaction probability were shown to be quantitatively understood by a vibrationally adiabatic approximation. A rich source of information about action-angle variables and their use and implications, I found, was in the astronomy library. There is another side to their usage, related to the dissociative and other behavior of isolated molecules, which we comment on later.

In the new semiclassical period of the 1970s many topics were approached in rapid succession for inelastic and reactive collisions. Both a semiclassical stationary phase approximation ('primitive semi-classical') and an integral formulation, the 'initial value representation' [2] were used. They included classically forbidden and classically allowed transitions [3,15], nuclear tunneling, electronic transitions [10], Clebsch–Gordan coefficients [8], selection rules in rotational-translational energy transfer [12], resonances in chemical reactions [18], and uniform approximations of the Airy type [2,13] and, when the collision was nearly elastic, of the Bessel type [17]. Uniform approximations avoided the singularities (infinities) of the primitive semiclassical approximation at any classical 'turning point' of a trajectory (reflection from a caustic). Two methods were used to introduce a uniform approximation, one being to infer it from the primitive semiclassical solution [2] and another being to deduce it from an integral representation [13]. Treatment of the problem starting from the primitive semiclassical [2] paved the way for deriving them more rigorously from an integral representation [13]. They can differ somewhat because a primitive

*Email: ram@caltech.edu

ISSN 0026-8976 print/ISSN 1362-3028 online

http://dx.doi.org/10.1080/00268976.2012.672772
http://www.tandfonline.com

semiclassical expression can be the limit of more than one uniform approximation. Numerical results for the two Airy uniform approximations were only slightly different, however [13]. In any case, for multi-dimensional systems only an integral representation appears to be practical and some form of it is the one in use today, including some form of the Herman–Kluk integral expression. An attempt to use the primitive semiclassical to treat a collisional rotational-translational energy transfer problem provided an interesting nightmare in finding the points of stationary phase in the integral and the phases associated with each of them to capture the interferences [19].

In these articles there are many examples of Bill's intuitive feel for a problem and his ingenuity. His evaluation of an integral for use in a generating function and treating Clebsch–Gordan coefficients was a tour de force [8]. In his seminal work on an integral representation for the S matrix for collisions he recognized that an integral for the S-matrix should not have a time-varying integrand. The angle variables w_i appearing in it often vary with time. He introduced a 'vibrational phase shift' [2] by subtracting from the w_i's at large separation distances R a quantity $R\ \nu_i/V$, where V is $\mathrm{d}R/\mathrm{d}t$ of the trajectory and ν_i is a frequency $\mathrm{d}w_i/\mathrm{d}t$. He then obtained an integral expression, the 'initial value representation', containing a time-independent expression for the semiclassical S-matrix in this clever and intuitive way.

Intrigued by this finding I wondered whether there was a more rigorous way of obtaining it or indeed obtaining some alternative expression. In particular, could one start from, say, an exact expression for the S-matrix in Goldberger and Watson's admirable book [33] in terms of the inner product $[<\Psi\oplus^{\uparrow}((-))\mathrm{mE}'|\Psi^{\uparrow}((+))nE>\delta(E-E')$ of an exact ingoing wave in state n $\Psi^{(+)}(nE)$ and time-reversed wave $\Psi^{(-)}(mE')$ in state m, then introduce a semiclassical expression for them and obtain the initial value representation for the transition $n\text{-}>m$. In brief, I found that, based on the exact Hamiltonian for the system, one could introduce a canonical transformation that transformed the separation distance R into a time variable and any time-varying angle variables into constants [14,16]. Subsequent integration over time gave a delta function that cancelled the delta function in the other side of the equation [14,16].

For an initial value representation the result turned out to be the same as that the one that Bill arrived at intuitively. A different canonical transformation, again based on the exact Hamiltonian, led to a 'final value representation,' and another different transformation led to what was termed 'a turning point representation' [14] that satisfied microscopic reversibility but was discontinuous on the turning point manifold.

A second active area in the semiclassical field in the 1970s and somewhat beyond was the quantization of the energy levels of a molecule. Because in part of time limitations I will simply refer the reader to some of the reviews at the time, [8,9,20] and focus on one of the central issues for the topic. In 'old quantum theory'. quantization was largely for systems permitting separation of variables and, using classical mechanical perturbation theory, one could treat approximately nonseparable systems. However, Einstein raised a potential roadblock [34]. He pointed out that in principle one could quantize nonseparable systems if the action variables existed for those systems. Their existence depends on whether the mechanical system is quasi-periodic or chaotic, and the famous KAM theorem (Kolmogorov, Arnold, Moser) [35] relates to this question. The existence of action variables was guaranteed when the underlying classical mechanical motion was quasiperiodic. For chaotic systems Einstein knew there would be a problem. Some methods, such as those that rely on locating caustics, can be expected to fail in a chaotic system but other methods, methods that neglect the multiple overlapping avoided crossings of the energy levels in chaotic systems, may give approximate answers for the eigenvalues, though the individual identity of the states may be lost, e.g. [20] and references cited therein. Inasmuch as action-angle variables played such a major role major in semiclassical theory, an early example of their introduction for collision theory [27] is shown in Figure 1.

Although it is a digression from the main theme of this brief historical vignette of one active area in the 1970s, I would like to focus on some implications of quasi-periodic versus chaotic behavior. It plays a key role in unimolecular reaction statistical theory (e.g. in RRKM theory). There can be regions of quasi-periodic behaviour and regions of chaotic behaviour in these molecular nonlinear mechanical systems. The theory of N. B. Slater for unimolecular reactions [36] was based on an assumed quasi-periodicity of the vibrational motion of the molecule, in the form of a harmonic vibrational Hamiltonian. In this model, because of the constraint of having N fixed actions, the molecule spends its time on an N dimensional vibrational subspace, a torus, in a $2N$ dimensional vibrational phase space, and so can be expected to lead to large errors in lifetimes, and even if its classical assumptions would be converted to quantum ones, it would yield a wrong result for typical unimolecular reactions. It was

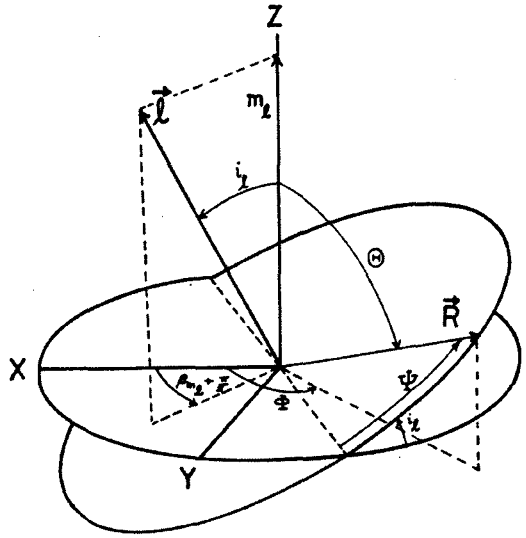

Figure 1. Early example of the use of action-angle variables in molecular collision theory, here for rotational-translational energy transfer [27].

nevertheless admirable in its elegance and introduced novel concepts and terminology.

Recently in some molecular dynamics calculations for ozone dissociation it was estimated that perhaps 10–20% of trajectories at low excess energies either did not dissociate or were slow to do so, and so were quasiperiodic or nearly so [37]. It would be interesting to undertake pump-dump experiments in which a ground electronic state molecule is excited to repulsive electronic state but then with a second laser is dumped into the ground electronic state but with enough energy to dissociate. Do all such isolated molecules dissociate, or are there some residual ones that don't? There is the problem of detecting a small amount of residual O_3^* in the presences of a large excess of O_3 [38]. However, a third laser, this one in the infrared, could dissociate the O_3^* and so permit their detection via the O atoms formed. Because of possible tunneling between tori, whose existence is a consequence of a local quasi-periodicity, and between tori and rest of the phase space the quantum and the classical behaviour may be different.

The 1970s were indeed an exciting time in semiclassical theory as well as in an increased analysis of vibrationally excited molecules, but it is encouraging that the search for improved treatments of collisions and for improved understanding of dissociating molecules continues to this day.

Acknowledgements

It is a pleasure to acknowledge the support of the author's research and of that of his coworkers by NSF, ARO and ONR. I would like to conclude with an acknowledgement taken from my 1971 paper: 'I am indebted to Dr W. H. Miller for sending me copies of his excellent manuscripts[6] in advance of publication. Their clarity and incisiveness helped expedite work on my own present approach.' The papers referred to are [1] and [2].

References

[1] W.H. Miller, J. Chem. Phys. **53**, 1949 (1970).
[2] W.H. Miller, J. Chem. Phys **53**, 3578 (1970).
[3] W.H. Miller, Chem. Phys. Lett. **7**, 431 (1970).
[4] C.C. Rankin and W.H. Miller, J. Chem. Phys. **55**, 3150 (1971).
[5] W.H. Miller and T.F. George, J. Chem. Phys. **57**, 2458 (1972).
[6] J.D. Doll and W.H. Miller, J. Chem. Phys. **57**, 5019 (1972).
[7] A.W. Raczokwski and W.H. Miller, J. Chem. Phys. **61**, 5413 (1974).
[8] W.H. Miller, Adv. Chem. Phys. **25**, 69 (1974).
[9] W.H. Miller, Adv. Chem. Phys. **30**, 77 (1975).
[10] H.D. Meyer and W.H. Miller, J. Chem. Phys. **70**, 3214 (1979).
[11] R.A. Marcus, Chem. Phys. Lett. **7**, 525 (1970).
[12] R.A. Marcus, J. Chem. Phys. **54**, 3965 (1971).
[13] J.N.L. Connor and R.A. Marcus, J. Chem. Phys. **55**, 5637 (1971).
[14] R.A. Marcus, J. Chem. Phys. **56**, 311 (1972).
[15] J. Stine and R.A. Marcus, Chem. Phys. Lett. **15**, 536 (1972).
[16] R.A. Marcus, J. Chem. Phys. **59**, 5135 (1973).
[17] J. Stine and R.A. Marcus, J. Chem. Phys. **59**, 5145 (1973).
[18] J. Stine and R.A. Marcus, Chem. Phys. Lett. **29**, 575 (1974).
[19] H. Kreek, R.L. Ellis and R. Marcus, J. Chem. Phys. **62**, 913 (1975).
[20] D.W. Noid, M.L. Koszykowski and R.A. Marcus, Ann. Rev. Phys. Chem. **32**, 267 (1981).
[21] P. Pechukas, Phys. Rev. **181**, 166 (1969).
[22] K.W. Ford and J.A. Wheeler, Ann. Phys. (NY) **7**, 259, 287 (1959).
[23] R.B. Bernstein, Advan. Chem. Phys. **10**, 75 (1966).
[24] M.V. Berry, J. Phys. **B**, **2**, 381 (1969).
[25] H.C. Corben and P. Stehle, *Classical Mechanics* (Wiley, New York, 1960).
[26] M. Born, *The Mechanics of the Atom* (Ungar, New York, 1960) English translation.
[27] A.O. Cohen and R.A. Marcus, J. Chem. Phys. **49**, 4509 (1968).
[28] A.O. Cohen and R.A. Marcus, J. Chem. Phys. **52**, 3140 (1970).

[29] M. Attermeyer and R.A. Marcus, J. Chem. Phys. **52**, 393 (1970).
[30] R.A. Marcus, J. Chem. Phys. **43**, 1598 (1965).
[31] R.A. Marcus, J. Chem. Phys. **45**, 4493 (1966).
[32] R.A. Marcus, J. Chem. Phys. **45**, 4500 (1966).
[33] M.L. Goldberger and K.M. Watson, *Collision Theory* (Wiley, New York, 1964).
[34] A. Einstein, Verh. Dtsch. Phys. Ges. **19**, 82 (1917).
[35] V.I. Arnold, *Mathematical Methods of Classical Mechanics* (Springer, New York, 1978).
[36] N.B. Slater, *Theory of Unimolecular Reactions* (Cornell University, Ithaca, 1959).
[37] N. Ghaderi and R.A. Marcus, to be submitted.
[38] M. Okumura, private communication.