MELDOLA MEDAL LECTURE*

Molecular Collisions and the Semiclassical Approximation

By J. N. L. Connor
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANCHESTER,
MANCHESTER M13 9PL

1 Introduction

An understanding of atomic and molecular collisions is fundamental for gas-phase chemistry. Only *binary collisions* are important when the gas is not too dense.[1] They involve the collision of one atom or molecule with a second atom or molecule. Three types of collision can occur in a binary collision, as shown in Figure 1.

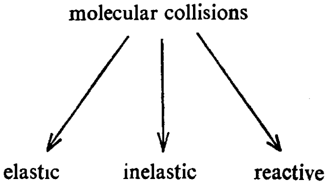

Figure 1 *Elastic, inelastic, and reactive molecular collisions.*

The simplest collision process is *elastic* scattering; it involves a change only in the translational motion of the colliding partners. *Inelastic* scattering changes the internal state of a particle as a result of the collision and *reactive* scattering results in a change in chemical species as well. The experimental observables for binary collisions are elastic, inelastic, and reactive collision *cross-sections*. From them, macroscopic properties of the gas can be calculated such as transport coefficients and reaction rate constants.[1,2]

The theoretical framework underlying gas-phase chemistry is shown in Figure 2. The starting point involves nuclei, electrons, Coulomb's Law, and the fundamental constants. From them intermolecular curves and surfaces can be calculated by

---

*Delivered 24 September, 1974 at the Autumn Meeting of the Chemical Society, University of Leicester.

[1] R. D. Levine and R. B. Bernstein, 'Molecular Reaction Dynamics', Clarendon Press, Oxford, 1974.

[2] R. E. Weston and H. A. Schwarz, 'Chemical Kinetics', Prentice Hall, Englewood Cliffs, 1972.

the techniques of molecular quantum chemistry.[3–6] These intermolecular interactions determine the dynamics of the colliding particles.[1,7] Next, molecular collision theory is used to calculate collision cross-sections. In favourable cases, theory can be compared directly with experiment at this point. This is the case for collisions of Li^+ with H_2 for example.[8] The final step in Figure 2 involves statistical mechanics to calculate macroscopic properties of the gas.

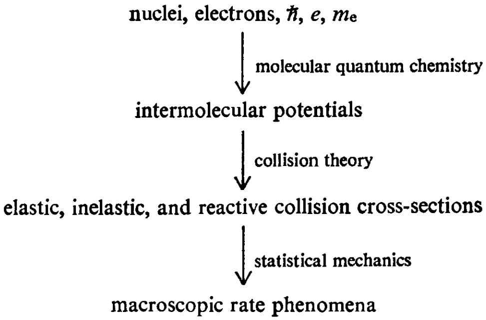

Figure 2 *Theoretical framework of gas-phase chemistry.*

The most direct means for studying the dynamics of molecular collisions are *molecular beam*,[9–15] *laser*,[16,17] and *chemiluminescence*[18] experiments. These experiments have provided a wealth of information and insight that is inaccessible

[3] H. F. Schaefer, tert., 'The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results', Addison–Wesley, Reading, Mass., 1972.

[4] J. Goodisman, 'Diatomic Interaction Potential Theory', Academic Press, New York, 1973 (2 vols.).

[5] C. Thomson, *Ann. Reports*, (*A*), 1974, **71**, 5.

[6] G. C. Maitland and E. B. Smith, *Chem. Soc. Rev.*, 1973, **2**, 181.

[7] M. A. D. Fluendy and K. P. Lawley, *Essays in Chem.*, 1973, **5**, 25.

[8] J. P. Toennies, *Chem. Soc. Rev.*, 1974, **3**, 407. J Schaefer and W. A. Lester, *J. Chem. Phys.*, 1975, **62**, 1913.

[9] R. J. Cross, *Accounts Chem. Res.*, 1975, **8**, 225.

[10] J. L. Kinsey, in 'Chemical Kinetics', ed. J. C. Polanyi, [M.T.P. International Review of Science, Physical Chemistry (Series One), Vol. 9], Butterworths, London, 1972, Ch. 6; J. M. Farrar and Y. T. Lee, *Ann. Rev. Phys. Chem.*, 1974, **25**, 357.

[11] M. A. D. Fluendy and K. P. Lawley, 'Chemical Applications of Molecular Beam Scattering', Chapman and Hall, London, 1973.

[12] 'Molecular Beam Scattering', *Faraday Discuss. Chem. Soc.*, 1973, No. 55.

[13] J. P. Toennies, 'Physical Chemistry, An Advanced Treatise', Vol. VIA, 'Kinetics of Gas Reactions', ed. H. Eyring, W. Jost, and D. Henderson, Academic Press, New York, 1974, Ch. 5. See also Vol. VIB.

[14] M. A. D. Fluendy, *Contemp. Phys.*, 1975, **16**, 147.

[15] *Adv. Chem. Phys.*, 1975, Vol. 30.

[16] 'Chemical and Biochemical Applications of Lasers', ed. C. B. Moore, Academic Press, New York, 1974, Vol. 1.

[17] K. L. Kompa, *Topics Current Chem.*, 1973, **37**, 1; M. J. Berry, *Ann. Rev. Phys. Chem.*, 1975, **26**, 259.

[18] T. Carrington and J. C. Polanyi, in 'Chemical Kinetics', ed. J. C. Polanyi, [M.T.P. International Review of Science, Physical Chemistry (Series One), Vol. 9], Butterworths, London, 1972. Ch. 5.

to the traditional kind of 'test tube' experiment, since the latter necessarily involves some kind of statistical average of molecular properties, an average that obscures the information being sought (see Figure 2 again). It is well known, for example, that reaction rate-constant data provide weak constraints on any model of the collision itself.

Collisions between atoms and molecules are *dynamic* phenomena and are more difficult to treat theoretically than *static* properties.[19] Consequently theoretical collision dynamics has not achieved the same level of accuracy that is now possible for static chemical properties (such as those of spectroscopy). Nevertheless, important advances have been made in recent years, and interpretative and predictive ability is considerable.

Theories of molecular collisions can be classified in many ways. A classification suggested by Marcus[20] is shown in Figure 3. *Dynamical* theories involve a solution of Schrödinger's equation (quantum dynamics) or Hamilton's equations (classical dynamics). In contrast, *statistical* theories avoid the solution of a dynamical problem by statistical assumptions. Transition State Theory as usually formulated is an example of a statistical theory.[21] *Statistical-dynamical* theories treat some degrees of freedom by a statistical approach and the remainder by dynamical models.

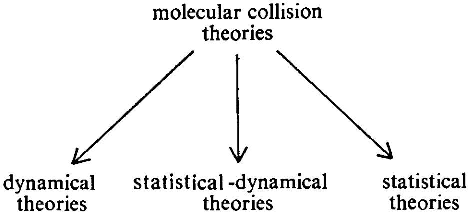

Figure 3 *Molecular collision theories.*

Dynamical models can be further divided into *exact* and *approximate* ones, as shown in Figure 4.

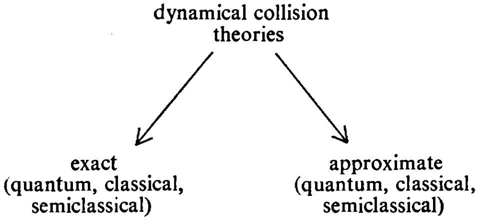

Figure 4 *Dynamical collision theories.*

[19] A. C. Wahl and C. W. Wilson, 'Computers in Chemical Research and Education', Proc. Internat. Conf. Ljubljana/Zagreb, 12—17 July 1973, ed. D. Hadži, Elsevier, Amsterdam, 1973, Vol. 2, p. 4/133.

[20] R. A. Marcus, *Faraday Discuss. Chem. Soc.*, 1973, No. 55, p. 9.

[21] R. A. Marcus, 'Techniques of Chemistry, Investigation of Rates and Mechanisms of Reactions', ed. E. S. Lewis, Wiley, New York, 1974, Vol. 6, Part 1, Ch. 2.

Approximate theories make dynamical approximations, in contrast to exact theories, which do not. *Quantal* and *classical* theories solve Schrödinger's equation and Hamilton's equations, respectively. The solutions can be analytic or numerical. An exact quantal treatment[22–24] is always correct but is not feasible in most cases. A purely classical treatment, on the other hand, is feasible for many collision systems.[25–29]

However, a purely classical calculation can be highly inaccurate with regard to certain features of the scattering. For example, a purely classical treatment cannot account for important tunnelling and interference effects that occur in atom–atom collisions.[30–32] A *semiclassical* treatment[33] constructs an asymptotic or short (de Broglie) wavelength solution to the Schrödinger equation with the help of *real-* and *complex-valued* solutions of Hamilton's equations. Although it uses classical trajectory data as input, semiclassical theories can account for essentially all the 'quantum effects' such as diffraction, interference, quantization, quasi-bound states, resonances, selection rules, and tunnelling that purely classical theories miss. This technique of using real- and complex-valued classical trajectories in such a way that quantum effects are correctly accounted for is aptly described by the phrase 'Sewing quantum flesh on classical bones'.[34–37]

Complex-valued classical trajectories were introduced into short-wavelength theories in a systematic way by Keller in 1958 in his 'Geometrical Theory of Diffraction'.[38] They have subsequently been used in numerous wave-propagation problems.[39] The important role of classical trajectories in semiclassical elastic

[22] *Methods Computer Phys.*, 1971, Vol. 10.

[23] D. J. Kouri, 'The Physics of Electronic and Atomic Collisions.' Invited Lectures and Progress Reports, VIII'th ICPEAC, ed. B. C. Čobić and M. V. Kurepa, Institute of Physics, Beograd, 1973, p. 529.

[24] D. A. Micha, *Adv. Chem. Phys.*, 1975, **30,** 7.

[25] P. J. Kuntz, 'The Physics of Electronic and Atomic Collisions'. Invited Papers and Progress Reports, VII'th ICPEAC, ed. T. R. Govers and F. J. de Heer, North Holland, Amsterdam, 1972, p. 427.

[26] D. L. Bunker, *Methods Computer Phys.*, 1971, **10,** 287.

[27] J. C. Polanyi and J. L. Schreiber, 'Physical Chemistry – An Advanced Treatise', Vol. VIA, 'Kinetics of Gas Reactions', ed. H. Eyring, W. Jost, and D. Henderson, Academic Press, New York, 1974, Ch. 6.

[28] M. Karplus, 'Collision Dynamics of Chemical Reactions', 16 mm Colour Sound Film, Harper and Row, London.

[29] R. N. Porter, *Ann. Rev. Phys. Chem.*, 1974, **25,** 317.

[30] Sir Harrie Massey, *Contemp. Phys.*, 1973, **14,** 497.

[31] E. E. Nikitin and M. Ya. Ovchinnikova, *Uspekhi fiz. Nauk*, 1971, **104,** 379 (*Soviet Phys. Uspekhi*, 1972, **14,** 394).

[32] U. Buck, *Adv. Chem. Phys.*, 1975, **30,** 313.

[33] Some theories treat the internal motion quantum mechanically and the translational motion classically. These 'classical path theories' are included in the quantum category in this review. They are sometimes also called 'semiclassical theories'.

[34] B. E. Kimber, adapted from a quotation in refs. 35—37.

[35] Yu. A. Kravtsov, *Izvest. V.U.Z. Radiofiz.*, 1967, **10,** 1283. (*Radio. Phys. Quant. Electron.*, 1967, **10,** 719).

[36] Yu. A. Kravtsov, *Akust. Zhur.*, 1968, **14,** 1 (*Soviet Phys. Acoust.*, 1968, **14,** 1).

[37] M. V. Berry and K. E. Mount, *Reports Progr. Phys.*, 1972, **35,** 315.

[38] J. B. Keller, *Proc. Symp. Appl. Math.*, 1958, **8,** 27.

[39] See for example 'Special Issue on Rays and Beams', *Proc. I.E.E.E.*, 1974, **62,** No. 11.

scattering was emphasized by Smith[40] and Berry,[41] following on from the pioneering researches of Ford and Wheeler in 1959.[42] Applications to inelastic and reactive molecular collisions started in 1970 due to the efforts of Miller[43] and Marcus.[44]

This review will describe some recent applications of semiclassical mechanics to elastic, inelastic, and reactive molecular collisions. One example of each type of collision will be described, believing that this is more valuable than a discussion of many examples in a more cursory manner. No derivations of equations will be presented; instead, some important features will be pointed out. Of particular note will be the way the theory depends on the topological structure of families of real- and complex-valued classical trajectories.[45]

For further information on semiclassical mechanics the book by Child[46] and the reviews referred to below are recommended. A large number of references on semiclassical collision theory can be found in some recent literature surveys.[47-49]

Asymptotic approximations are commonly used in physical calculations (often without realizing it). They are usually very accurate, frequently more so than one would expect.

As an example, consider Stirling's asymptotic approximation for the Gamma (factorial) function:[50]

$$\Gamma(x) \sim (2\pi)^{\frac{1}{2}}\, x^{x-\frac{1}{2}}\, \mathrm{e}^{-x}$$

widely used in statistical mechanics. Table 1 shows that this approximation is valid for $x \gg 1$, but even for $x = 1$ or 2 (which are not usually thought of as large numbers) it compares favourably with the exact result.

A similar situation holds in semiclassical theories of molecular collisions.[51] A general condition for the validity of short-wavelength theories is $S \gg \hbar$, where S is a classical action variable, but in practice good results are often obtained when $S \approx \hbar$, and in some cases the exact answer is produced.[52] Action variables were used in the Old Quantum Theory,[53-55] for example the Bohr–

---

[40] F. T. Smith, *J. Chem. Phys.*, 1965, **42**, 2419.

[41] M. V. Berry, *Proc. Phys. Soc.*, 1966, **89**, 479.

[42] K. W. Ford and J. A. Wheeler, *Ann. Phys.*, 1959, **7**, 259, 287.

[43] W. H. Miller, *J. Chem. Phys.*, 1970, **53**, 1949.

[44] R. A. Marcus, *Chem. Phys. Letters*, 1970, **7**, 525.

[45] M. V. Berry, *Sci. Progr.*, 1969, **57**, 43.

[46] M. S. Child, 'Molecular Collision Theory', Academic Press, London, 1974.

[47] T. F. George and J. Ross, *Ann. Rev. Phys. Chem.*, 1973, **24**, 263.

[48] D. Secrest, *Ann. Rev. Phys. Chem.*, 1973, **24**, 379.

[49] J. N. L. Connor, *Ann. Reports* (*A*), 1973, **70**, 5.

[50] F. W. J. Olver, 'Asymptotics and Special Functions', Academic Press, New York, 1974, p. 88.

[51] I. C. Percival, 'Atomic Physics', Vol. 2, ed. P. G. H. Sandars, Plenum Press, New York, 1971, p. 345.

[52] A. Norcliffe, *Case Studies Atom. Phys.*, 1973, **4**, No. 1.

[53] M. Born, 'The Mechanics of the Atom', translated from the German by J. W. Fisher and revised by D. R. Hartree, Ungar Publishing, New York, 1960.

[54] M. Jammer, 'The Conceptual Development of Quantum Mechanics', McGraw-Hill, New York, 1966.

[55] F. Hund, 'The History of Quantum Theory', Harrap, London, 1974.

Table 1 *Stirling's approximation for the Gamma function as an example of an asymptotic approximation*

x	$\Gamma(x)$	$(2\pi)^{\frac{1}{2}}\, x^{x-\frac{1}{2}}\, e^{-x}$
1	1.00000×10^{0}	0.92214×10^{0}
2	1.00000×10^{0}	0.95950×10^{0}
3	2.00000×10^{0}	1.94540×10^{0}
4	6.00000×10^{0}	5.87654×10^{0}
5	2.40000×10^{1}	2.36038×10^{1}
6	1.20000×10^{2}	1.18346×10^{2}
7	7.20000×10^{2}	7.11485×10^{2}
8	5.04000×10^{3}	4.98780×10^{3}
9	4.03200×10^{4}	3.99485×10^{4}
10	3.62880×10^{5}	3.59870×10^{5}
20	1.21645×10^{17}	1.21139×10^{17}
30	8.84176×10^{30}	8.81724×10^{30}
40	2.03979×10^{46}	2.03554×10^{46}
50	6.08282×10^{62}	6.07269×10^{62}

Sommerfeld quantization condition which is the basis of the very accurate Rydberg–Klein–Rees method of molecular spectroscopy,[56] and other examples of action variables are described in the following sections.

In the development of molecular collision theory, an important role has been played by certain *canonical models* of the collision process.[49] These replace the actual (complicated and possibly unknown) intermolecular potential by a simpler one. In addition, the three-dimensional space in which the collision occurs is often reduced to two dimensions (planar) or one dimension (linear). This removes some degrees of freedom from the problem and simplifies the theoretical treatment. Table 2 lists a few of these canonical models for collisions involving a single potential energy surface (electronically adiabatic approximation).

The three examples of semiclassical mechanics considered in the following Sections make use of the canonical models in Table 2. This is so that some important features of the collision are established as clearly as possible.

Section 2 considers quasi-bound states in the elastic scattering of two atoms and the topic of complex eigenvalues. In Section 3, the interaction of a Morse oscillator with an atom is considered as an example of an inelastic collision, whilst Section 4 is devoted to reactive scattering and the definition of tunnelling. In every case the semiclassical results are compared with exact quantum ones to illustrate the good agreement that can be obtained (typically within a few per cent). It should be noted that exact quantum results are, in general, only available for simple systems of the kind in Table 2. Conclusions are in Section 5.

2 Elastic Collisions: Quasi-bound States and Complex Eigenvalues

Quasi-bound states arise in the elastic scattering of two atoms in the following way. Consider the radial Schrödinger equation for the collision:[37,46]

[56] E. A. Mason and L. Monchick, *Adv. Chem. Phys.*, 1967, **12**, 329.

Table 2 *Canonical models for molecular collisions*

Collision process	*Canonical model*
Elastic scattering	Lennard-Jones (12, 6) potential
Vibrationally inelastic collision	Collinear collision of atom and a harmonic oscillator with exponential repulsion
Rotationally inelastic collision	Atom–rigid rotator collision with a Lennard-Jones (12, 6) and $P_2(\cos\theta)$ interaction
Reactive collision	Collinear atom–molecule collision on the Porter–Karplus potential-energy surface

$$\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\psi(r)}{\mathrm{d}r^2} + \left[E - V(r) - \frac{\hbar^2 l(l+1)}{2\mu r^2}\right]\psi(r) = 0 \tag{1}$$

where l is the orbital angular momentum quantum number, μ is the reduced mass of the system, and E is the collision energy. Typically, the potential-energy curve $V(r)$ has a long-range attraction and a short-range repulsion; a well known example is the Lennard-Jones (12, 6) potential (see Table 2):

$$V(r) = \epsilon\left[\left(\frac{r_\mathrm{m}}{r}\right)^{12} - 2\left(\frac{r_\mathrm{m}}{r}\right)^{6}\right] \tag{2}$$

where r_m is the distance at which the well depth is ϵ.

Now for a certain range of l values, the effective potential $V_l(r)$ defined by:

$$V_l(r) = V(r) + \hbar^2 l(l+1)/2\mu r^2 \tag{3}$$

can have a *barrier* in addition to a *well*. This is illustrated in Figure 5. The barrier may support quasi-bound states; these states have a finite lifetime because they can decay by tunnelling through the barrier, unlike true bound states which have an infinite lifetime. Other names for quasi-bound states are 'shape resonances' (from the shape of the effective potential) and 'orbiting states' because classically the particles orbit around each other when the collision energy is close to the barrier maximum.

Quasi-bound states play an important role in a number of phenomena. These include:

(*a*) rotational predissociation of diatomic molecules[57,58]

(*b*) long-range interatomic forces[59]

---

[57] M. S. Child, 'Molecular Spectroscopy', ed. R. F. Barrow, D. A. Long, and D. J. Millen (Specialist Periodical Reports), The Chemical Society, London, 1974, Vol. 2, Ch. 7.

[58] W. C. Stwalley, *J. Chem. Phys.*, 1975, **63**, 3062

[59] R. J. Le Roy, 'Molecular Spectroscopy' ed. R. F. Barrow, D. A. Long, and D. J. Millen, (Specialist Periodical Reports) The Chemical Society, London, 1973, Vol. 1, Ch. 3.

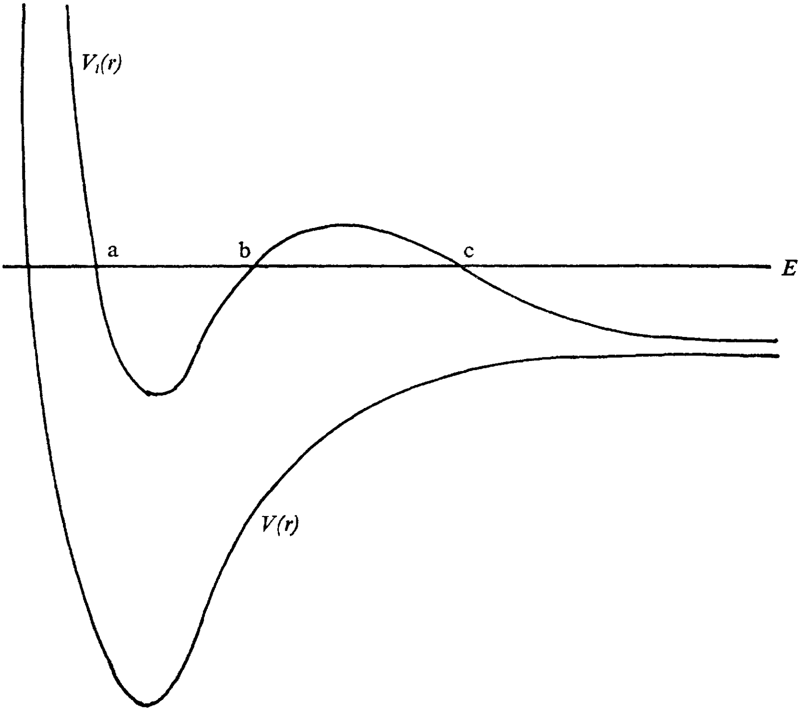

Figure 5 *Origin of quasi-bound states in the elastic scattering of two atoms.* a, b, *and* c *are classical turning points.*

(*c*) elastic and inelastic scattering experiments[60-63]

(*d*) three-body recombination reactions[64,65]

(*e*) low-temperature transport property of gases[66]

(*f*) Penning ionization[67]

(*g*) pressure-induced absorption spectra of gases[68]

A quasi-bound state can be characterized by the boundary conditions:[69]

$$\left.\begin{aligned} &\psi_l(0) = 0 \\ &\psi_l(r) \underset{r\to\infty}{\sim} \text{outgoing wave only} \end{aligned}\right\} \tag{4}$$

---

[60] J. P. Toennies, W. Welz, and G. Wolf, *J. Chem. Phys.*, 1974, **61**, 2461.
[61] A. Schutte, D. Bassi, F. Tommasini, and G. Scoles, *J. Chem. Phys.*, 1975, **62**, 600.
[62] J. G. Maas, N. P. F. B. Van Asselt, and J. Los, *Chem. Phys.*, 1975, **8**, 37.
[63] P. D. Gait, *Chem. Phys. Letters*, 1975, **35**, 72.
[64] R. T. Pack, R. L. Snow, and W. D. Smith, *J. Chem. Phys.*, 1972, **56**, 926.
[65] P. A. Whitlock, J. T. Muckerman, and R. E. Roberts, *J. Chem. Phys.*, 1974, **60**, 3658.
[66] R. A. Buckingham and E. Gal, *Adv. Atom. Mol. Phys.*, 1968, **4**, 37.
[67] R. J. Bieniek, *J Phys.* (*B*), 1974, **7**, L266.
[68] G. E. Ewing, *Accounts Chem. Res.*, 1975, **8**, 185.
[69] V. de Alfaro and T. Regge, 'Potential Scattering', North Holland, Amsterdam, 1965.

The outgoing wave at infinity, with no incoming wave, is in accord with the idea of a quasi-bound state decaying by tunnelling through the barrier.

The boundary conditions (4) have the important mathematical consequence that they give rise to a *complex eigenvalue* problem.[69]

When l is restricted to (physical) integer values, the energy becomes complex-valued, and its eigenvalues can be written:

$$E_n = \mathscr{E}_n - \mathrm{i}\tfrac{1}{2}\Gamma_n, \quad \mathscr{E}_n > 0, \Gamma_n > 0; n = 0, 1, 2, \ldots \qquad (5)$$

where $\mathscr{E}_n$ is the resonance energy and Γ_n the resonance width. The physical interpretation of Γ_n follows from the time evolution factor for the wavefunction:

$$|\exp(-\,\mathrm{i}E_n t/\hbar)|^2 = \exp(-\,\Gamma_n t/\hbar) \qquad (6)$$

Equation (6) shows that the system decays exponentially in time, with a 'lifetime' $\tau_n = \hbar/\Gamma_n$. A long-lived state corresponds to a small Γ_n and a short-lived one to a large Γ_n.

Equation (5) gives the complex eigenvalues for the Schrödinger equation (1) that satisfy boundary conditions (4). An alternative possibility consistent with these boundary conditions is to keep E real and allow the angular momentum to become complex-valued. Its eigenvalues can be written:

$$l_n = l_n^{(r)} + \mathrm{i}l_n^{(i)}, \quad l_n^{(r)} > 0, l_n^{(i)} > 0; n = 0, 1, 2, \ldots \qquad (7)$$

The complex eigenvalues (7) are called 'Regge Poles' (so called because the Scattering matrix takes the form:

$$S = r_n/(l - l_n)$$

close to a pole l_n, where r_n is its residue).[69] The physical interpretation of $l_n^{(i)}$ follows from the fact that the system decays exponentially with scattering angle θ according to $\exp(-\,l_n^{(i)}\,\theta)$. The quantity $1/l_n^{(i)}$ can be defined as the 'angular life' of the system.[69] For a long-lived state which orbits many times before decaying $l_n^{(i)}$ is small whereas for a short-lived one $l_n^{(i)}$ is large.

It can be seen that complex angular momentum and scattering angle are conjugate variables analogous to complex energy and time.

When the Schrödinger equation (1) is solved semiclassically, the solution is of the form:[37,46]

$$\psi(r) \sim \frac{1}{\sqrt{p(r)}} \exp\left[\pm \frac{\mathrm{i}}{\hbar}\int p(r)\,\mathrm{d}r\right] \qquad (8)$$

where

$$p(r) = \left\{2\mu\left[E - V(r) - \frac{\hbar^2 (l + \frac{1}{2})^2}{2\mu r^2}\right]\right\}^{\frac{1}{2}} \qquad (9)$$

The appearance of $(l + \frac{1}{2})^2$ instead of $l(l + 1)$ in equation (9) is the Langer substitution.[37,70] Provided $\hbar(l + \frac{1}{2})$ is identified with the classical angular

---

[70] R. E. Langer, *Phys. Rev.*, 1937, **51**, 669.

momentum, $p(r)$ is the classical radial momentum, except that it can take on complex values instead of being restricted to being purely real. It can be seen that the semiclassical wavefunction (8) possesses the important property that it is composed of (*real-* or *complex-valued*) classical dynamical quantities.

The semiclassical approximation (8) is clearly not valid close to real or complex points where

$$p(r) = 0 \tag{10}$$

because there the solution 'blows up'. Points satisfying equation (10) are usually called 'turning points' or 'transition points' (see Figure 5). A major problem in semiclassical mechanics is to connect the solution valid on one side of a turning point with the solution valid on the other side.

Figure 5 is an example showing three turning points. To overcome the *connection problem* mentioned above, the semiclassical wavefunction in the neighbourhood of turning point 'a' can be mapped onto the solution of the Schrödinger equation for a linear potential (the solution involves the Airy function).[37,46,71] The turning points 'b' and 'c' can come close together or coalesce, and a *uniformly* valid treatment requires that the semiclassical wavefunction be mapped onto the solution of the Schrödinger equation for a parabolic barrier (the solution involves Weber parabolic cylinder functions this time).[37,46,71] In this way, the semiclassical wavefunction for equation (1) that satisfies boundary conditions (4) can be constructed. The semiclassical eigenvalue equation is found to be:[72–77]

$$\alpha(E, l_n) = (n + \tfrac{1}{2})\,\pi + \tfrac{1}{2}[\epsilon - \epsilon \ln(-\epsilon)] - \frac{\mathrm{i}}{2} \ln \left[\frac{(2\pi)^{\frac{1}{2}} \exp(\pi\epsilon/2)}{\Gamma(\frac{1}{2} - \mathrm{i}\epsilon)}\right] \tag{11}$$

where

$$\hbar\alpha(E, l_n) = \int_{\mathrm{a}}^{\mathrm{b}} p(E, l_n; r)\, \mathrm{d}r \tag{12}$$

is the classical action integral associated with the well and

$$-\hbar\pi\epsilon(E, l_n) = \mathrm{i}\int_{\mathrm{b}}^{\mathrm{c}} p(E, l_n; r)\, \mathrm{d}r \tag{13}$$

is the one for the barrier. Equation (11) is also valid for the complex energy eigenvalues provided the replacements $E \rightarrow E_n$ and $l_n \rightarrow l$ are made.

The quantization formula (11) again involves only classical dynamical quanti-

---

[71] S. C. Miller and R. H. Good, *Phys. Rev.*, 1953, **91**, 174.

[72] J. N. L. Connor, *Mol. Phys.*, 1968, **15**, 621; *ibid.*, 1969, **16**, 525.

[73] J. N. L. Connor, *Mol. Phys.*, 1972, **23**, 717.

[74] J. N. L. Connor, *Mol. Phys.*, 1973, **25**, 1469.

[75] J. B. Delos and C. E. Carlson, *Phys. Rev.* (*A*), 1975, **11**, 210.

[76] C. V. Sukumar and J. N. Bardsley, *J. Phys* (*B*), 1975, **8**, 568.

[77] C. V. Sukumar, S. L. Lin, and J. N. Bardsley, *J. Phys.* (*B*), 1975, **8**, 577.

ties, namely the two complex-valued action integrals $\hbar\alpha$ and $\hbar\pi\epsilon$. The form of equation (11) is characteristic of two turning points (which may be nearly coincident), both of them being well separated from the third one.

Limiting cases of equation (11), when all three turning points are well separated from each other, are of interest. When $\pi\epsilon$ is large in magnitude (in terms of Figure 5 this corresponds to the energy being well above the barrier), equation (11) simplifies to:

$$\frac{1}{\hbar}\int_{a}^{c} p(E, l_n; r)\,\mathrm{d}r = (n + \tfrac{1}{2})\,\pi \tag{14}$$

This is a Bohr–Sommerfeld quantization condition for the positions of the Regge Poles l_n. The simpler form of equation (14) compared with the more general equation (11) reflects the simpler turning-point distribution in this case. Table 3 compares equation (14) with exact quantum results for the Lennard-Jones potential (2).[78] The parameters approximate elastic scattering of K by HBr.[79] The agreement is seen to be excellent.

Table 3 *Exact quantum and semiclassical Regge Pole positions for a Lennard-Jones* (12, 6) *potential*[a]

	Quantum[b]		*Semiclassical*[b]	
n	Re l_n	Im l_n	Re l_n	Im l_n
0	180.012	21.219	180.015	21.218
1	179.239	24.035	179.242	24.034
2	178.522	26.890	178.526	26.889
3	177.866	29.780	177.869	29.779
4	177.272	32.700	177.275	32.699
5	176.742	35.645	176.745	35.644
6	176.277	38.609	176.279	38.608
7	175.877	41.588	175.880	41.587
8	175.544	44.576	175.547	44.575
9	175.276	47.568	175.279	47.567

[a] Parameters in equations (1) and (2) are $E = 2.0 \times 10^{-20}$ J, $\mu = 4.377 \times 10^{-23}$ g, $\epsilon = 4.0 \times 10^{-21}$ J, $r_m = 4.0 \times 10^{-10}$ m. These values correspond approximately to K + HBr elastic scattering. See R. B. Bernstein and R. D. Levine, *J. Chem. Phys.*, 1968, **49**, 3872; [b] J. N. L. Connor, W. Jakubetz, and C. V. Sukumar (unpublished results). The semiclassical results are calculated from equation (14).

Another interesting limiting case arises when the energy in Figure 5 is well below the barrier maximum. The quantization formula (11) simplifies to (for the complex energy eigenvalues this time):[72–74]

---

[78] J. N. L. Connor, W. Jakubetz, and C. V. Sukumar (unpublished results).

[79] R. B. Bernstein and R. D. Levine, *J. Chem. Phys.*, 1968, **49**, 3872.

$$\alpha(\mathscr{E}_n, l) = (n + \tfrac{1}{2})\,\pi + \tfrac{1}{2}\phi[-\,|\epsilon(\mathscr{E}_n, l)|] \tag{15}$$

and

$$\Gamma_n = \frac{\hbar\omega(\mathscr{E}_n, l)}{2\pi} \ln\{1 + \exp[-\,2\pi|\epsilon(\mathscr{E}_n, l)|]\} \tag{16}$$

Equation (15) is a Bohr–Sommerfeld quantization formula for the resonance energy $\mathscr{E}_n$ in which ϕ is a small term giving rise to a level shift

$$\phi(-\,|\epsilon|) = |\epsilon| \ln |\epsilon| - |\epsilon| - \arg \Gamma(\tfrac{1}{2} + \mathrm{i}\,|\epsilon|)$$

In equation (16) for the resonance width, ω is the classical angular frequency of oscillation in the well. In deriving equations (15) and (16), advantage has been taken of the fact that Γ_n is small (corresponding to a long-lived quasi-bound state), with the consequence that the action integrals become real-valued.

Table 4 shows some resonance energies and widths calculated from equations (15) and (16) for the Lennard-Jones (12, 6) potential (2) compared with exact quantum results.[57,80] The agreement is again seen to be excellent.

Table 4 *Some exact quantum and semiclassical resonance energies and widths for a Lennard-Jones* (12, 6) *potential*[a]

	Quantum[b]		*Semiclassical*[c]	
l	$\mathscr{E}_n{}^d$	$\Gamma_n{}^d$	$\mathscr{E}_n{}^d$	$\Gamma_n{}^{d,e}$
118	0.31004	1.2×10^{-17}	0.31003	1.21×10^{-17}
197	0.31008	9.6×10^{-28}	0.31007	9.36×10^{-28}
25	0.34862	6.0×10^{-4}	0.34846	6.00×10^{-4}
77	0.34935	6.9×10^{-8}	0.34938	6.89×10^{-8}
128	0.35007	2.0×10^{-11}	0.35007	2.02×10^{-11}
123	0.38961	8.4×10^{-5}	0.38962	8.64×10^{-5}
87	0.39009	4.2×10^{-4}	0.39008	4.22×10^{-4}
137	0.40233	3.4×10^{-3}	0.4025	3.20×10^{-3}

[a] The potential parameters are given by R. B. Bernstein, C. F. Curtiss, S. Imam-Rahajoe, and W. T. Wood, *J. Chem. Phys.*, 1966, **44**, 4072; [b] R. A. Bain and J. N. Bardsley, *J. Chem. Phys.*, 1971, **55**, 4535; [c] A. S. Dickinson, *Mol. Phys.*, 1970, **18**, 441. The semiclassical results are calculated from equations (15) and (16); [d] Resonance energies and widths are expressed as a fraction of the well depth; [e] These values are more accurate than in the original paper of A. S. Dickinson, *Mol. Phys.*, 1970, **18**, 441 and are reported by M. S. Child 'Molecular Spectroscopy', ed. R. F. Barrow, D. A. Long, and D. J. Millen (Specialist Periodical Reports), The Chemical Society, London, 1974, Vol. 2, Ch. 7.

Equation (16) for the widths is based on the approximation that Γ_n is small. Table 5 compares equation (16) with exact quantum results[57,81] for the broad quasi-bound states of ground-state H_2. (These calculations use the very accurate

---

[80] A. S. Dickinson, *Mol. Phys.*, 1970, **18**, 441.

[81] R. J. Le Roy and R. B. Bernstein, *J. Chem. Phys.*, 1971, **54**, 5114.

Table 5 *Exact quantum and semiclassical resonance widths for the* H_2 *ground state*[a]

n	l	*Quantum* Γ_n [b]/cm^{-1}	*Semiclassical*[d] Γ_n [c]/cm^{-1}
11	14	17.9	19.2
8	21	39.4	38.2
7	23	30.4	31.6
6	25	26.5	27.8
5	27	25.1	26.4
4	29	24.7	25.8
3	31	23.6	24.5
2	33	20.4	21.0
1	35	14.1	14.3
0	38	80.0	64.4

[a] Adapted from M. S. Child 'Molecular Spectroscopy', ed. R. F. Barrow, D. A. Long, and D. J. Millen (Specialist Periodical Reports), The Chemical Society, London, 1974, Vol. 2, Ch. 7; [b] R. J. Le Roy and R. B. Bernstein, *J. Chem. Phys.*, 1971, **54**, 5114; [c] Calculated from equation (16); [d] Less accurate values were reported in Table 2 of ref. 49.

potential-energy curve of Kolos and Wolniewicz[82]). There is good agreement even though the widths are relatively large, and equation (16) might be thought to be invalid.

To summarize this section: it has been shown how quasi-bound states can be characterized by complex energy or complex angular-momentum eigenvalues. The semiclassical eigenvalue equations involve only real- or complex-valued classical dynamical quantities. The agreement with exact quantum results is very good.

3 Inelastic Collisions: Collinear Collision of an Atom with a Morse Oscillator

An inelastic collision is the next example of semiclassical mechanics to be considered. The model is that of a collinear collision of an atom with a Morse oscillator[83–86] (*cf.* Table 2). An exponential repulsion between the atom and the end of the molecule is assumed. The oscillator is initially in quantum state n and the problem is to calculate the probability that the oscillator is in a quantum state m after the collision.

In the quasi-bound system discussed in Section 2, the distribution of classical turning points played an important role in the semiclassical analysis. It is instructive to consider the turning-point distribution in the present case. An inelastic collision is more complicated than the previous example because,

---

[82] W. Kolos and L. Wolniewicz, *J. Chem. Phys.*, 1964, **41**, 3663; *ibid.*, 1965, **43**, 2429; *ibid.*, 1968, **49**, 404.

[83] A. P. Clark and A. S. Dickinson, *J. Phys. (B)*, 1973, **6**, 164.

[84] J. N. L. Connor, *Mol. Phys.*, 1974, **28**, 1569.

[85] R. Schinke and J. P. Toennies, *J. Chem. Phys.*, 1975, **62**, 4871.

[86] J. W. Duff and D. G. Truhlar, *Chem. Phys.*, 1975, **9**, 243.

in addition to the radial co-ordinate R, the oscillator co-ordinate q must also be considered.

The classical Hamiltonian for the collision (in reduced units) is:[84]

$$\begin{aligned} H &= (2\mu)^{-1} p_R^2 + \tfrac{1}{2} p_q^2 + V_M(q) + V(R, q) \\ &= E \end{aligned} \tag{17}$$

where p_R and p_q are the classical momenta conjugate to R and q, respectively, and E is the total energy. $V_M(q)$ is the Morse oscillator potential:

$$V_M(q) = D\{\exp[-q/(2D)^{\frac{1}{2}}] - 1\}^2 \tag{18}$$

and $V(R, q)$ is the exponential interaction between the atom and the oscillator:

$$V(R, q) = \exp[-\alpha(R - q)] \ . \tag{19}$$

Figure 6 shows some classical trajectories in (R, q) space for the Hamiltonian (17) calculated by numerical integration of Hamilton's equations on a computer.[84] The collision starts and finishes at a value of R sufficiently large that the interaction $V(R, q)$ is negligible. The parameters for the collision correspond approximately to a collision between He and H_2.[83–86]

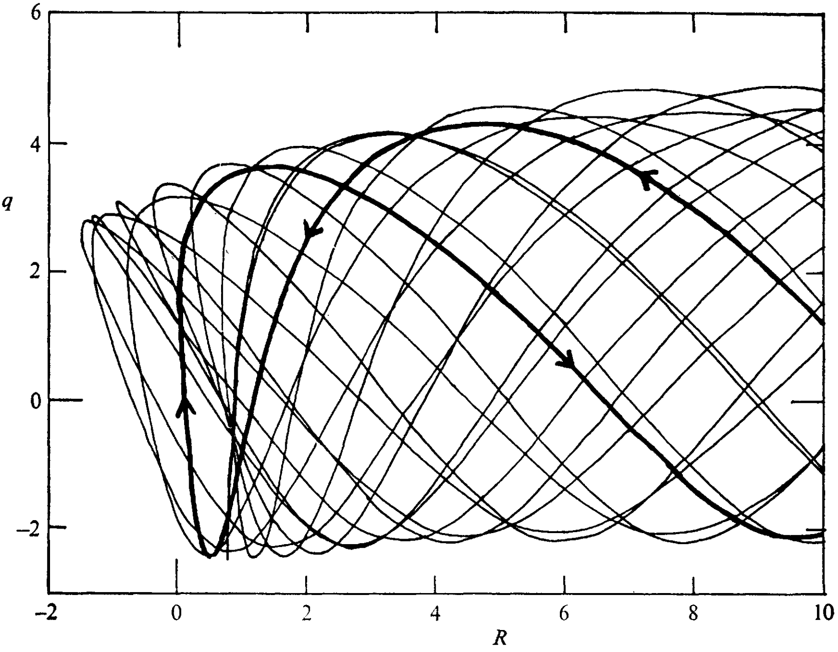

Figure 6 *Collinear collision of an atom and Morse oscillator defined by equations* (17)—(19), *plotted in* (R, q) *space. The collision parameters are* $\alpha = 0.314$, $\mu = 0.667$, *and* $D = 9.3$. *The collision energy* $E = 6$ *and the initial state of the oscillator is* $n = 4$ [*see equation* (22)]. *One trajectory has been drawn thicker than the others to show its structure more clearly.*

The turning points of the oscillator (q motion) and that of the incoming atom (R motion) can be seen clearly. Figure 6 implies that, in a semiclassical analysis, using (p_q, q) as variables for the oscillator will cause difficulties because of the singular behaviour of semiclassical wavefunctions at turning points [see equation (8)]. Another important problem that arises in a semiclassical calculation of a transition probability $P_{m\leftarrow n}$ is 'What is the classical equivalent of a quantum number?'.

These problems can be overcome by using *action-angle* variables[87] (J, w) for the oscillator instead of (p_q, q). Figure 7 shows the same collision as in Figure 6 but plotted in (R, w) space.[84] It is immediately clear that the turning points in the oscillator motion have been eliminated, and only one in the R motion remains.

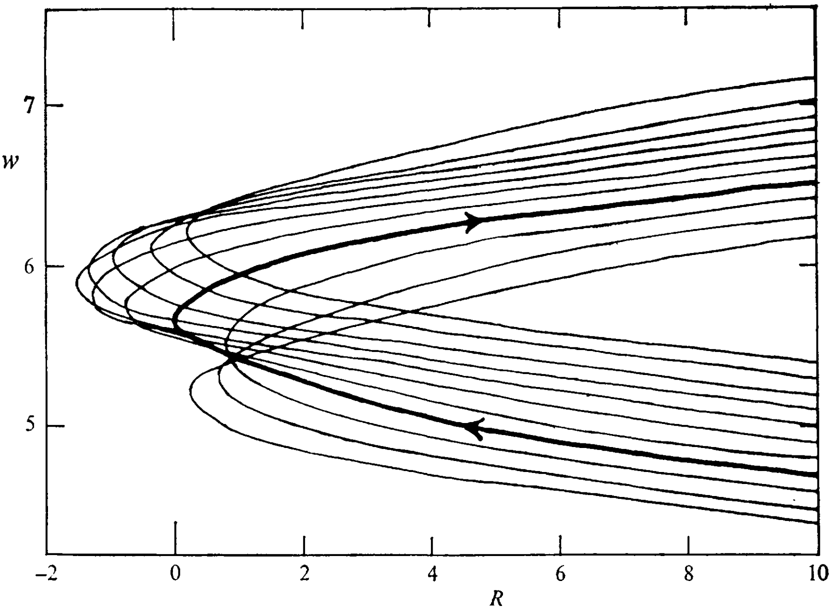

Figure 7 *Same collision as in Figure 6, but plotted in* (R, w) *space. The Hamiltonian for the collision is defined by equations* (21)—(23).

The connection between action variables and quantum numbers is found by applying the Bohr–Sommerfeld quantization relation to the oscillator [*cf.* equations (14) and (15)]. Because of this relation, it is convenient to replace J by a (continuous) classical variable $\bar{n}$ (the 'quantum number variable') defined by:[44,88]

$$J = \oint p_q \, \mathrm{d}q = 2\pi(\bar{n} + \tfrac{1}{2})\hbar \tag{20}$$

---

[87] H. Goldstein, 'Classical Mechanics', Addison-Wesley, Reading, Mass., 1950, p. 288.
[88] R. A. Marcus, *J. Chem. Phys.*, 1971, **54**, 3965.

In terms of $(\bar{n}, w)$, the classical Hamiltonian for the collision becomes:[84]

$$H = (2\mu)^{-1} p_R^2 + \epsilon(\bar{n}) + V(R, q) \qquad (21)$$
$$= E$$

where the Morse oscillator energies are:

$$\epsilon(\bar{n}) = (\bar{n} + \tfrac{1}{2}) - (4D)^{-1}(\bar{n} + \tfrac{1}{2})^2 \qquad (22)$$

and q is related to w by:

$$q = (2D)^{\frac{1}{2}} \{\ln[1 + (\epsilon/D)^{\frac{1}{2}} \cos(2\pi w)] - \ln[1 - (\epsilon/D)]\} \qquad (23)$$

It is interesting to note that in the Old Quantum Theory action-angle variables were called 'uniformizing variables'.[89] Table 6 summarizes the main properties of action-angle variables that are useful in semiclassical calculations.[43,44,49]

Table 6 *Properties of action-angle variables useful in semiclassical calculations*

1. Use of action-angle variables removes singularities in the unperturbed semiclassical wavefunction for the internal states.
2. The action variables bear a simple (Bohr–Sommerfeld) relation to quantum numbers.
3. Initial angle variables occur in [0, 1].

A transition probability $P_{m \leftarrow n}$ involves the oscillator initially in a state n and finally in a state m. Now the final value of the quantum number variable $\bar{n}$ depends on the initial value of the angle variable (phase) of the oscillator w^0. This is illustrated[84] in Figure 8 for the collision already shown in Figures 6 and 7. The final $\bar{n}$ *versus* initial w^0 plot is seen to have a simple sinusoidal shape.

Consider now the elastic transition 4 → 4. It is clear from Figure 8 there are two values of w^0 (called $w_1{}^0$ and $w_2{}^0$) such that the final value of $\bar{n}$ is $m = 4$. The two values of w^0 occur where the horizontal line $m = 4$ intersects the $\bar{n}(w^0)$ curve.

The simplest semiclassical approximation for the transition probability is:[43,44,84,88]

$$P^{\text{Classical}}_{m \leftarrow n} = p_1 + p_2 \qquad (24)$$

where

$$p_i = \left| \frac{\mathrm{d}\bar{n}}{\mathrm{d}w^0} \right|^{-1}_{w^0 = w_i{}^0} \qquad ; i = 1, 2 \qquad (25)$$

is the classical probability associated with each individual trajectory contributing to the transition $n \rightarrow m$ and is found from the slope of the curve in Figure 8.

The primitive semiclassical approximation is an asymptotic one that assumes that the two contributing trajectories are well separated from one another:[43,44,88]

---

[89] N. Bohr, 'On the Application of the Quantum Theory to Atomic Structure', Supplement to *Proc. Cambridge Phil. Soc.*, 1924, p. 4.

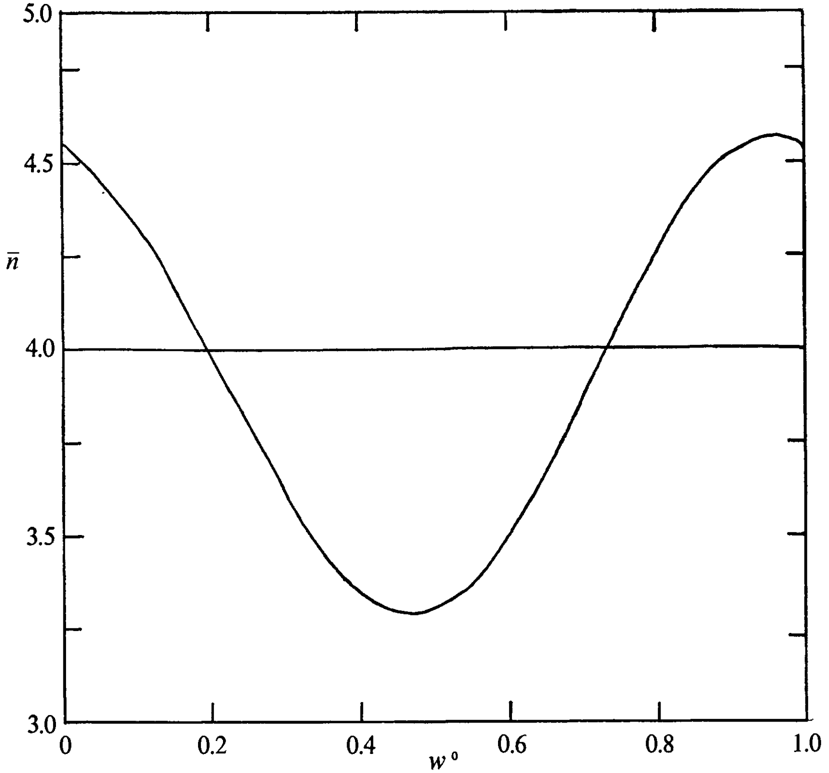

Figure 8 *Final value of the quantum-number variable $\bar{n}$ plotted against initial angle variable w^0 for the same collision shown in Figures 6 and 7. The horizontal line at $m = 4$ indicates the two trajectories that contribute to the transition 4 → 4.*

$$P^{\text{Primitive}}_{m\leftarrow n} = p_1 + p_2 + 2(p_1 p_2)^{\frac{1}{2}} \sin(\Delta_2 - \Delta_1) \qquad (26)$$

where the classical phase:

$$\Delta = -\,2\pi \int_{t_0}^{t} w(t)\,\dot{\bar{n}}(t)\,\mathrm{d}t - \int_{t_0}^{t} R(t)\,\dot{p}_R(t)\,\mathrm{d}t + \tfrac{1}{2}\pi \qquad (27)$$

is evaluated along each contributing trajectory from initial time t_0 to a final time t.

The last term in equation (26) gives rise to an interference effect. Since the average of this term is zero, the primitive approximation (26) oscillates about the classical result (24). This interpretation of equations (24) and (26) is the same as that for the famous 'two slit' experiment often discussed in books on quantum mechanics.[90]

---

[90] R. P. Feynman and A. R. Hibbs, 'Quantum Mechanics and Path Integrals', McGraw-Hill, New York, 1965, Ch. 1.

The primitive approximation (26) breaks down when the two contributing trajectories come close together because $p_i \to \infty$. This catastrophic behaviour[91] can be removed by using a uniform Airy approximation that is valid regardless of whether the trajectories are close together or far apart:[92,93]

$$P^{\text{Airy}}_{m\leftarrow n} = \pi(p_1{}^{\frac{1}{2}} + p_2{}^{\frac{1}{2}})^2\, \chi^{\frac{1}{2}}\, \text{Ai}(-\chi) + \pi(p_1{}^{\frac{1}{2}} - p_2{}^{\frac{1}{2}})^2\, \chi^{-\frac{1}{2}}\, \text{Ai}'^2(-\chi) \qquad (28)$$

where

$$\chi = (\tfrac{3}{4}[\varDelta_2 - \varDelta_1])^{\frac{2}{3}} \qquad (29)$$

and Ai is the regular Airy function (already mentioned in Section 2). When the trajectories are well separated, equation (28) reduces to the primitive approximation (26).[92,93]

Finally, equation (28) requires for its validity that the amplitude of the $\bar{n}$ *versus* w^0 plot be large. When the amplitude is small, a uniform Bessel approximation can be derived for this case:[94]

$$P^{\text{Bessel}}_{m\leftarrow n} = \tfrac{1}{2}\pi(p_1{}^{\frac{1}{2}} + p_2{}^{\frac{1}{2}})^2\, J_k{}^2(\zeta)\, \zeta\cos\theta + \tfrac{1}{2}\pi(p_1{}^{\frac{1}{2}} - p_2{}^{\frac{1}{2}})^2\, J_k{}'^2(\zeta)\, \zeta/\cos\theta \qquad (30)$$

where

$$(\zeta^2 - k^2)^{\frac{1}{2}} - k\cos^{-1}(k/\zeta) = \tfrac{1}{2}(\varDelta_2 - \varDelta_1)$$

and

$$\cos\theta = [1 - (k/\zeta)^2]^{\frac{1}{2}}\ , \quad k = |m - n| \qquad (31)$$

Equation (30) reduces to the Airy approximation (28) when the amplitude in the $\bar{n}$ *versus* w^0 plot becomes large.[94,95]

The structure of equations (24)—(31) is interesting. Their validity increases in the order classical → primitive → Airy → Bessel for the results discussed below, but so does the complexity of the equations. In each case, however, they involve only (real-valued) classical dynamical quantities, namely the p_i and $\varDelta_i$.

Consider next the transition 4 → 3 in Figure 8. It is clear there are no real values of w^0 such that the equation:

$$\bar{n}(w^0) = 3 \qquad (32)$$

is satisfied. Thus the transition is dynamically forbidden in classical mechanics even though it is energetically allowed. The 4 → 3 transition is an example of a 'classically forbidden' transition, in contrast to the 4 → 4 one which is 'classically allowed'.[43,44] The classical approximation for this transition would be simply zero:

---

[91] The use of the word 'catastrophic' is deliberate. Application of 'Catastrophe Theory' to the classical and semiclassical mechanics of molecular collisions leads to a deep understanding of their inter-relationship (J. N. L. Connor, 'Catastrophes and Molecular Collisions', *Mol. Phys.*, in the press).

[92] J. N. L. Connor and R. A. Marcus, *J. Chem. Phys.*, 1971, **55**, 5636.

[93] J. N. L. Connor, *Mol. Phys.*, 1973, **25**, 181.

[94] J. R. Stine and R. A. Marcus, *J. Chem. Phys.*, 1973, **59**, 5145.

[95] J. N. L. Connor, *Chem. Phys. Letters*, 1974, **25**, 611.

$$P_{3\leftarrow 4}^{\text{Classical}} = 0$$

In semiclassical mechanics, however, complex values of w^0 satisfying equation (32) must also be considered. Such complex solutions of equation (32) do indeed exist, and can be used to integrate Hamilton's equations, in which the coordinates, momenta, and time become complex-valued during the collision. Figure 9 shows a plot of Re $\bar{n}$ against Im $\bar{n}$ for the transition 4 → 1 of Figure 8.[84]

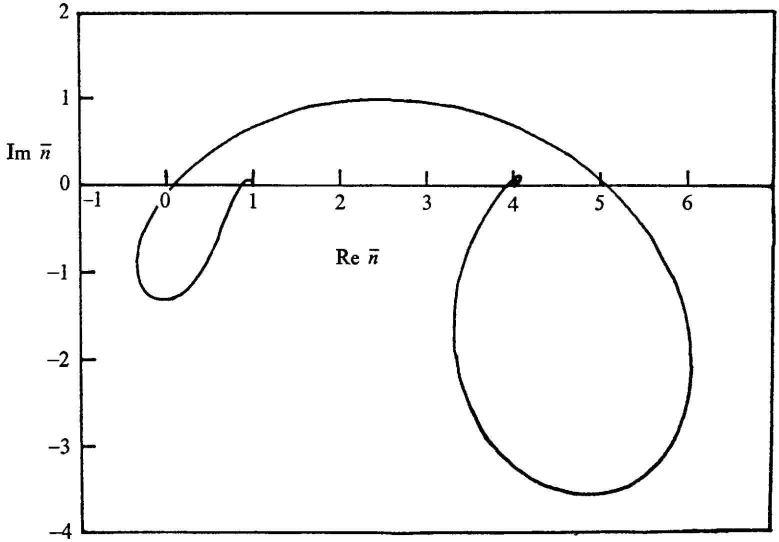

Figure 9 *Plot of* Re $\bar{n}$ *against* Im $\bar{n}$ *for the transition* 4 → 1 *of Figure* 8. *The collision parameters are the same as in Figures* 6—8.

The expressions for the transition probabilities for classically forbidden transitions are the appropriate extensions of equations (25)—(31) in which the p_i's and Δ_i's become complex-valued[84] [*cf.* equations (11)—(14) of Section 2].

Table 7 compares a few exact quantum results[83] with the various semiclassical approximations.[84] The uniform Bessel approximation (30) is generally in very good agreement with the quantum results, although the Airy approximation (28) is of comparable accuracy for inelastic transitions. The primitive approximation is generally less accurate than either the Airy or Bessel approximations.

More advanced reviews of the semiclassical mechanics of inelastic (and reactive) collisions have been written by Miller[96-98] and Child,[99] where further

[96] W. H. Miller, *Adv. Chem. Phys.*, 1974, **25**, 69.

[97] W. H. Miller, 'The Physics of Electronic and Atomic Collisions.' Invited Lectures and Progress Reports, VIII'th ICPEAC, ed. B. C. Čobič and M. V. Kurepa, Institute of Physics, Beograd, 1973, p. 503.

[98] W. H. Miller, *Adv. Chem. Phys.*, 1975, **30**, 77.

[99] M. S. Child, 'Modern Theoretical Chemistry', Vol. 3, 'Dynamics of Molecular Collisions', ed. W. H. Miller, Plenum Press, New York, 1976.

Table 7 *Some exact quantum and semiclassical transition probabilities for collinear* He–H$_2$ *collisions when* $E = 6$[a]

Transition $n \rightarrow m$	*Classical*[b,c]	*Primitive*[b]	*Airy*[b]	*Bessel*[b]	*Quantum*[d]
$4 \rightarrow 4$	0.504×10^{0}	0.985×10^{0}	0.892×10^{0}	0.818×10^{0}	0.818×10^{0}
$4 \rightarrow 3$	0	0.173×10^{0}	0.122×10^{0}	0.117×10^{0}	0.117×10^{0}
$4 \rightarrow 2$	0	0.634×10^{-2}	0.584×10^{-2}	0.566×10^{-2}	0.564×10^{-2}
$4 \rightarrow 1$	0	0.141×10^{-3}	0.135×10^{-3}	0.132×10^{-3}	0.138×10^{-3}
$5 \rightarrow 5$	0.828×10^{0}	1.402×10^{0}	1.124×10^{0}	0.925×10^{0}	0.925×10^{0}
$5 \rightarrow 6$	0	0.155×10^{-1}	0.142×10^{-1}	0.130×10^{-1}	0.130×10^{-1}
$5 \rightarrow 4$	0	0.762×10^{-1}	0.634×10^{-1}	0.597×10^{-1}	0.597×10^{-1}
$5 \rightarrow 3$	0	0.220×10^{-2}	0.207×10^{-2}	0.199×10^{-2}	0.198×10^{-2}
$5 \rightarrow 2$	0	0.461×10^{-4}	0.445×10^{-4}	0.433×10^{-4}	0.456×10^{-4}

[a] J. N. L. Connor, *Mol. Phys.*, 1974, **28**, 1569; [b] Semiclassical results are calculated from equations (24)—(31) when the transition is classically allowed. For equations in the classically forbidden case see the reference in footnote (*a*); [c] Classical transition probabilities that are identically zero are classically forbidden transitions; [d] A. P. Clark and A. S. Dickinson, *J. Phys.* (*B*), 1973, **6**, 164.

references can be found together with those in the literature surveys of refs. 47—49.

To summarize this section: it has been shown how action-angle variables play an important role in applying semiclassical mechanics to inelastic collisions. Classically forbidden transitions can be treated with the help of complex-valued solutions of Hamilton's equations. Very good agreement with exact quantum results can be obtained.

4 Reactive Collisions: Collinear H + H_2 Reaction

The final example of semiclassical mechanics to be considered is the collinear exchange reaction:

$$H + H_2\ (n = 0) \rightarrow H_2\ (m = 0) + H \qquad (33)$$

in which the reactant and product molecules are in their ground vibrational states. The potential-energy surface used for the reaction is the one of Porter and Karplus[100] (*cf.* Table 2). This has a barrier height of $\approx$ 38 kJ mol^{-1}, and since the zero-point energy of H_2 is $\approx$ 26 kJ mol^{-1} there is a barrier of $\approx$ 12 kJ mol^{-1} to reaction.

The system can tunnel through the barrier to form reaction products in a way similar to the decay of a quasi-bound state discussed in Section 2. This tunnelling region is an interesting one because it dominates the thermal energy kinetics. In a semiclassical framework, tunnelling is a classically forbidden process that can be treated by complex-valued classical trajectories. Since the semiclassical theory is similar to that for the non-reactive inelastic collision of Section 3, only the results will be described. The calculations discussed below were carried out by Miller and co-workers.[101–103]

Figure 10 shows the semiclassical reaction transition probability $P^{R}{}_{0\leftarrow 0}$ together with the exact quantum results.[104] The agreement between the two over ten orders of magnitude is impressive.

Figure 11 shows the same results on a linear scale, together with the transition probability obtained in a classical Monte-Carlo (real-valued) trajectory calculation.[105]

Figure 11 is useful for discussing the concept of tunnelling in systems with many degrees of freedom.[101,102] It is necessary to have a procedure that defines tunnelling, since in an exact quantum-mechanical calculation no distinction is made between it and non-tunnelling processes.

From the examples discussed in Sections 2 and 3, it should be clear that, in semiclassical mechanics, tunnelling is a classically forbidden process that uses complex-valued classical trajectories in its description.

[100] R. N. Porter and M. Karplus, *J. Chem. Phys.*, 1964, **40**, 1105.

[101] T. F. George and W. H. Miller, *J. Chem. Phys.*, 1972, **56**, 5722.

[102] T. F. George and W. H. Miller, *J. Chem. Phys.*, 1972, **57**, 2458.

[103] S. M. Hornstein and W. H. Miller, *J. Chem. Phys.*, 1974, **61**, 745.

[104] See J. W. Duff and D. G. Truhlar, *Chem. Phys. Letters*, 1973, **23**, 327, and references therein.

[105] D. J Diestler and M. Karplus, *J. Chem. Phys.*, 1971, **55**, 5832.

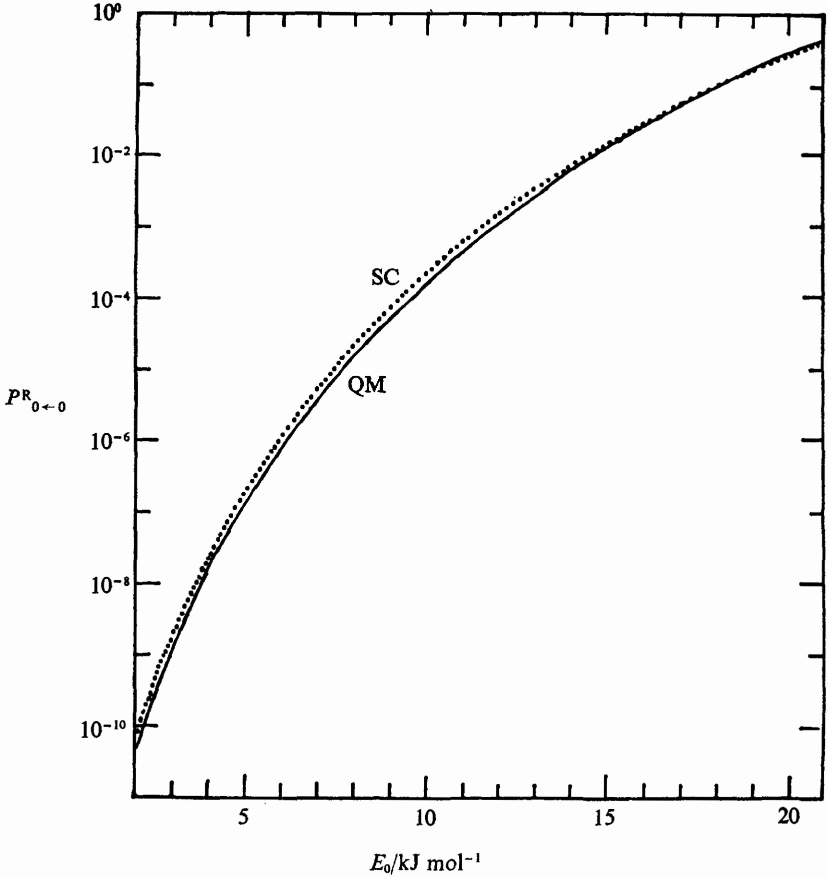

Figure 10 *Reaction probability* $P^R_{0\leftarrow 0}$ *for the ground-state to ground-state* $H + H_2 \rightarrow H_2 + H$ *collinear reaction on the Porter–Karplus surface as a function of the relative collision energy* E_0. *The solid line (QM) is the exact quantum mechanical result (see J. W. Duff and D. G. Truhlar,* Chem. Phys. Letters, 1973, **23**, 327) *and the dotted line (SC) is the semiclassical result (S. M. Hornstein and W. H. Miller,* J. Chem. Phys., 1974, **61**, 745).

For the transition probability curves in Figure 11, complex-valued trajectories occur up to an energy of ≈ 22 kJ mol^{-1}. There is thus a considerable amount of tunnelling in this system.

Another definition of tunnelling compares the results of a classical Monte-Carlo calculation with the exact quantum ones. From Figure 11, the Monte-Carlo threshold is ≈ 21 kJ mol^{-1}, so again there is a considerable amount of tunnelling, though less than in the semiclassical definition.

There is a difficulty with the Monte-Carlo definition, however. The usual

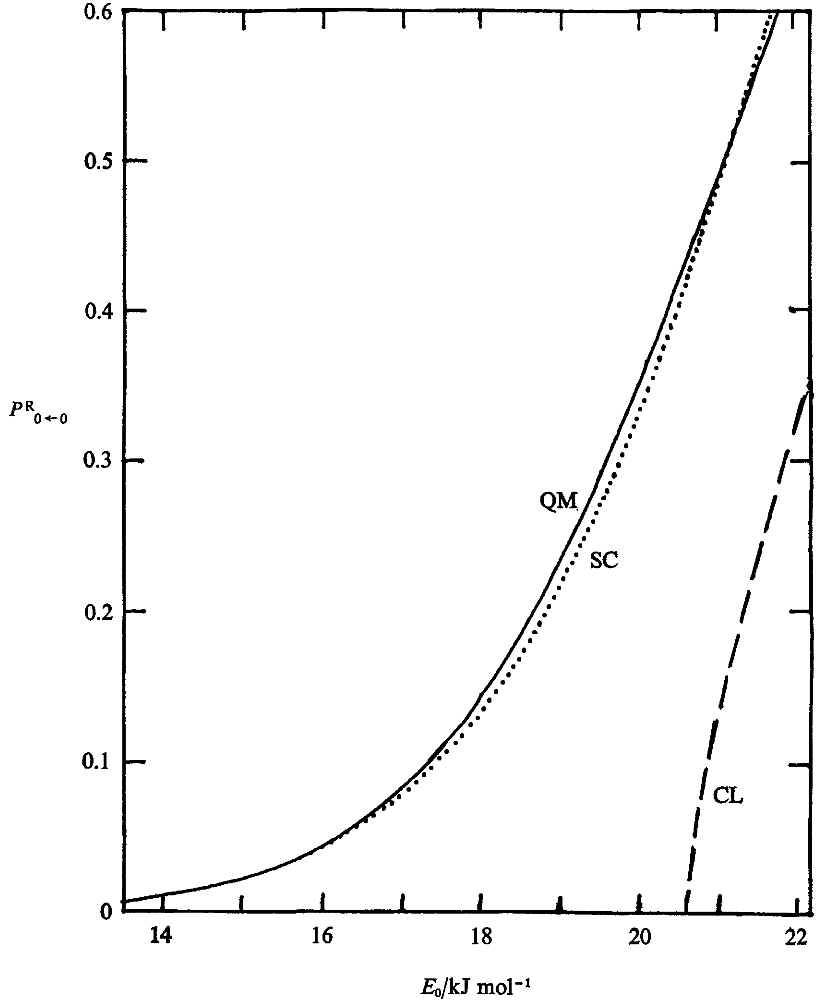

Figure 11 *Same as Figure* 10 *except that the ordinate is shown on a linear scale. The dashed line (CL) is the classical Monte-Carlo result (D. J. Diestler and M. Karplus,* J. Chem. Phys., 1971, **55**, 5832).

Monte-Carlo method assigns an initial quantum number to the oscillator and averages over its initial phase. This results in a continuous range of $\bar{n}$ values for the products (*cf.* Figure 8). To quantize these classical trajectories, they are assigned to 'boxes' labelled by the closest integer value of $\bar{n}$. Although reasonable, this method of 'quantizing' classical trajectories is nevertheless an arbitrary one, and other 'quantization' methods[106-108] produce different thresholds for the reaction and hence different amounts of tunnelling. These difficulties do not arise in the semiclassical theory, where quantization is unambiguous and tunnelling is associated with complex-valued classical trajectories.

The definitions discussed above are *dynamic* ones, *i.e.* tunnelling is defined as something that does not occur according to (real-valued) classical dynamics. In contrast, an *energetic* definition can be used. According to this, tunnelling occurs if the collision energy is less than the barrier height. As already mentioned, the barrier to reaction on the Porter–Karplus surface is $\approx$ 12 kJ mol^{-1}, so from Figures 10 and 11 there is a very small amount of tunnelling if this definition is used.

The dynamic and energetic definitions are identical for systems with one degree of freedom: if the system has sufficient energy to go over a barrier, then classical dynamics will also take the system over that barrier. However, this need no longer be the case in systems with more than one degree of freedom because certain processes may be energetically allowed but dynamically forbidden (*cf.* Figure 8).

To summarize this section: it has been shown how semiclassical mechanics can be applied to reactive molecular collisions, and that good agreement with exact quantum results can be obtained. The definition of tunnelling has also been discussed.

5 Conclusions

This review has discussed the application of semiclassical mechanics to elastic, inelastic, and reactive molecular collisions. Simple examples were considered to illustrate some important features of each type of collision as clearly as possible. In addition, comparison with exact quantum results showed the semiclassical approximations to be numerically very accurate. However, the semiclassical approach can be applied to more complicated (yet realistic) systems where the standard quantum mechanical techniques are not applicable or converge very slowly.

The difficulty of solving a problem by semiclassical methods is related to the complexity of the structure of classical trajectories. In all cases, however, the semiclassical formalism involves $\hbar$ and real- or complex-valued classical quantities. The semiclassical approach allows a clear distinction between quantum effects, which a purely classical theory cannot describe, and dynamical effects, which are common to both classical and quantum descriptions. The semiclassical approach thus allows a broad understanding and physical insight that is frequently lacking in the usual quantum theories, as well as often being numerically very accurate.

I am grateful to the Society of Maccabaeans and the Royal Institute of Chemistry for the award of the Meldola Medal. I would also like to thank my teachers of theoretical chemistry: A. D. Buckingham, P. W. Atkins, M. S. Child, and R. A. Marcus.

---

[106] R. A. La Budde and R. B. Bernstein, *J. Chem. Phys.*, 1975, **59**, 3687.
[107] W. H. Miller, *J. Chem. Phys.*, 1974, **61**, 1823.
[108] J. M. Bowman, G. C. Schatz, and A. Kuppermann, *Chem. Phys. Letters*, 1974, **24**, 378.