

The Semiclassical Nature of Atomic and Molecular Collisions

WILLIAM H. MILLER

*Inorganic Materials Research Division of the Lawrence Radiation Laboratory,
and the Department of Chemistry, University of California, Berkeley, California*

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Chemistry of the gas phase is essentially a study of what happens when atoms and molecules collide with one another. If the gas is not too dense, then one only needs to consider the collision of an individual atom or molecule with another individual atom or molecule. From a detailed understanding of this relatively simple binary encounter one can, in principle (and to some extent in practice), deduce the macroscopic kinetic properties of the gas, such as rate constants for chemical reaction, relaxation times for decay of molecular excitation (electronic, vibrational, or rotational), and transport coefficients.¹

From another point of view, the accurate measurement of atomic and molecular scattering properties under single-collision conditions can lead to rather direct, quantitative information about the intermolecular forces between the collision partners. For the simplest collision system, the elastic scattering of two atoms, this "inversion problem" (the construction of that unique intermolecular potential which produces a given set of scattering data) is essentially solved,²⁻⁴ and Buck and Pauly⁵ have recently carried out the procedure in constructing the Na-Hg interatomic potential directly from molecular beam scattering data. For a more complicated collision system the inversion problem has not yet been rigorously solved, but it is nevertheless possible to obtain some quantitative information about the intermolecular potential.

Study of the dynamics of elemental atomic and molecular collisions, therefore, has two-pronged implications: one can use the collision results, obtained experimentally or theoretically, to deduce (*via* the machinery of statistical mechanics) macroscopic observables, or one can start with experimentally obtained scattering data and work backward to construct the intermolecular potential giving rise to the observed scattering. Figure 1 illustrates the relation between

these various stages of chemical theory from the "elementary particles" of chemistry to macroscopic observables; theory of, an experiments pertaining to, atomic and molecular collisions thus stand midway in our understanding of gas-phase chemistry.

There is another sense, too, in which molecular dynamics is an intermediate case. Although quantum mechanics governs the dynamics of all particles, from electrons to baseballs, it obviously makes sense to use classical mechanics to treat the dynamics of macroscopic bodies, at no loss of meaningful accuracy. Electrons, on the other hand, at energies of chemical interest (less than a few electron volts, *e.g.*) are highly quantum-like, and serious error would result by use of classical mechanics to describe their dynamics. Atoms and molecules obviously fall somewhere between these extremes, but the questions of immense importance are: to what extent are the dynamics of these collisions adequately described by classical mechanics, and in precisely what manner, if at all, does quantum mechanics manifest itself?

The answer to these questions depends a great deal on "which direction" in Figure 1 one wishes to go—*i.e.*, the purpose for which the collision theory is to be used. Since one expects at least the gross dynamical features of the collision to be adequately described by classical mechanics, the averagings over internal states, relative velocity, etc., necessary in deriving macroscopic observables will likely obliterate any quantum effects in these quantities. It requires more refined, higher resolution scattering data, however, to extract much quantitative information about the intermolecular potential; correspondingly greater detail is thus required in the theoretical treatment of the collision, so that it is much more likely that "quantum effects" will come into play when one attempts to go in this direction (from stage 3 to stage 2 in Figure 1). It may even turn out that the observed quantum effects themselves will be a rather direct handle on certain quantitative features of the intermolecular potential; this is indeed the case for elastic atom-atom scattering.

Although quantum effects in the case of elastic atom-atom scattering can be quite striking and pro-

(1) See, for example, J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, N. Y., 1954.

(2) O. B. Firsov, *Zh. Eksp. Teor. Fiz.*, **24**, 279 (1953).

(3) W. H. Miller, *J. Chem. Phys.*, **51**, 3631 (1969).

(4) T. J. P. O'Brien and R. B. Bernstein, *ibid.*, **51**, 5112 (1969).

(5) U. Buck and H. Pauly, *ibid.*, **51**, 1662 (1969).

Theoretical Structure of Gas-Phase Chemistry

- (1) electrons, nuclei, h , e , c , m_e
 ↓ (electronic Schroedinger equation)
- (2) Intermolecular potentials
 ↓ (collision theory)
- (3) dynamics of individual, binary collisions: cross sections
 ↓ (statistical mechanics)
- (4) macroscopic rate phenomena: reaction rate coefficients, relaxation times, transport coefficients

Figure 1. An outline of the stages necessary to determine macroscopic chemical properties beginning only with electrons, nuclei, Coulomb's law, and the physical constants. The double arrow between stages 2 and 3 indicates the possibility of going in either direction: one can solve the collision problem to predict the scattering features expected for the system on the basis of a given intermolecular potential, or one may begin with experimental measurements at stage 3 and attempt to solve the "inverse scattering problem"—that is, to construct the intermolecular potential from the observed scattering data.

nounced, an important fact is that they can all be accounted for (even quantitatively) by the appropriate use of classical mechanics.⁶ In fact, it is the principal contention of this Account that essentially all quantum dynamical effects in atomic and molecular collisions can be adequately treated by the appropriate use of classical mechanics. The remainder of the article will outline just what is this "appropriate use" of classical mechanics and discuss the way in which various quantum effects are contained in the semiclassical theory. In short, one employs the classical limit of quantum mechanics rather than using classical mechanics directly.⁷

Classical Limit of Quantum Mechanics

To clarify the difference between the classical limit of quantum mechanics and classical mechanics itself, consider some process involving a transition from an initial state 1 to some final state 2. The observed quantity, classically or quantum mechanically, is the transition probability $P_{1,2}$. To compute $P_{1,2}$ quantum mechanically one must solve the Schroedinger equation and obtain first a transition amplitude (or \mathbf{S} -matrix element) $S_{1,2}$, the square modulus of which gives the transition probability

$$P_{1,2} = |S_{1,2}|^2 \quad (1)$$

Proceeding classically, on the other hand, one uses the

classical equations of motion to obtain a transition probability directly, never making reference to a transition amplitude. The classical limit of quantum mechanics means use of the classical equations of motion to generate the classical approximation to $S_{1,2}$ from which the transition probability is then obtained by the quantum mechanical prescription (eq 1).

The difference between these two ways of using classical mechanics becomes apparent if one supposes that there are two (or more) classical paths, or trajectories, which give rise to the $1 \rightarrow 2$ transition. The completely classical approximation gives

$$P_{1,2}^{\text{CL}} = p_{\text{I}} + p_{\text{II}} \quad (2)$$

where p_{I} and p_{II} are the probabilities (obtained by solving the classical equations of motion) associated with trajectories I and II, respectively. The classical approximation to $S_{1,2}$ is

$$S_{1,2}^{\text{CL}} = p_{\text{I}}^{1/2} e^{i\phi_{\text{I}}} + p_{\text{II}}^{1/2} e^{i\phi_{\text{II}}} \quad (3)$$

where p_{I} and p_{II} are the same quantities as in eq 2, and ϕ_{I} and ϕ_{II} are the classical actions associated with the two classical paths. Forming the square modulus of eq 3 gives the semiclassical expression

$$P_{1,2}^{\text{SC}} = p_{\text{I}} + p_{\text{II}} + 2(p_{\text{I}}p_{\text{II}})^{1/2} \cos(\phi_{\text{I}} - \phi_{\text{II}}) = p_{1,2}^{\text{CL}} + \text{interference} \quad (4)$$

It is the interference term that the purely classical approach misses and which is the quantum effect.

The only extent to which quantum mechanics is retained, therefore, is through the quantum principle of superposition—that one adds probability amplitudes for indistinguishable processes and squares, rather than *vice versa*. A concise statement of the overall approach is that one employs classical dynamics, but quantum mechanical superposition. From another point of view, one may say that a quantum mechanical formulation of the collision problem is employed but with all dynamical parameters appearing in the quantum mechanical expressions evaluated by the appropriate use of classical mechanics.

The above discussion has indicated how interference features appear when one constructs the classical limit of the \mathbf{S} matrix (or, for short, the classical \mathbf{S} matrix) and then uses it quantum mechanically. The only other type of quantum dynamical effect⁸ (apart from quantization of bound degrees of freedom) is tunneling. It will be seen below how this is also contained in this semiclassical approach. Tunneling is actually a different type of "interference"; rather than there being oscillatory structure due to the interference, however, there is a damping effect.

(8) We are assuming throughout that only one electronic state of the system is involved; there are obviously other quantum effects which arise when more than one such state participates in the collision. There are, too, nondynamical quantum effects arising due to the indistinguishability of identical particles; these effects, however, are easily incorporated in the semiclassical framework: one solves the dynamical problem classically, treating all particles as distinguishable, and then adds the probability amplitudes which correspond to interchange of identical particles. See Smith⁸ for this idea applied to collisions involving symmetric charge transfer.

(6) The first giant step in the semiclassical theory of elastic scattering was by K. W. Ford and J. A. Wheeler [*Ann. Phys. (New York)*, **7**, 259, 287 (1959)], and the basic semiclassical idea (classical mechanics plus quantum superposition) has been advanced in relation to elastic scattering by a number of workers, notably F. T. Smith [*J. Chem. Phys.*, **42**, 2419 (1965)] and R. J. Munn, E. A. Mason, and F. J. Smith [*ibid.*, **41**, 3978 (1964)]. A fairly recent comprehensive survey which summarizes these semiclassical treatments of elastic scattering in a unified way is R. B. Bernstein, *Advan. Chem. Phys.*, **10**, 75 (1966).

(7) The semiclassical theory to be discussed has been developed and applied in a series of papers: (a) W. H. Miller, *J. Chem. Phys.*, **53**, 1949 (1970); (b) *ibid.*, **53**, 3578 (1970); (c) *Chem. Phys. Lett.*, **7**, 431 (1970). Some other important work along this same line is: (d) P. Pechukas, *Phys. Rev.*, **181**, 166, 174 (1969); (e) R. A. Marcus, *J. Chem. Phys.*, in press. A different semiclassical approach, still with many ideas in common with ours, has been formulated in a series of papers by (f) R. J. Cross, Jr., *ibid.*, **52**, 5703 (1970), and earlier work cited therein.

We now outline the approach by which the classical limit of quantum mechanics is actually carried out.

The Feynman Propagator

Feynman⁹ has developed a formulation of quantum mechanics that is particularly well suited to a semi-classical analysis. The approach focuses on the quantum mechanical time evolution operator (also known as the propagator)

$$U(t_2, t_1) \equiv \exp[-iH(t_2 - t_1)/\hbar] \quad (5)$$

where H is the (time-independent) Hamiltonian governing the system. The propagator determines the time evolution of the system in that the wave function at any time t_2 is related to that at an earlier time t_1 by eq 6. Another way of interpreting the propagator is

$$\Psi(t_2) = U(t_2, t_1)\Psi(t_1) \quad (6)$$

that its matrix elements in any representation are the transition amplitudes between the basis states; for example, in the coordinate representation eq 7 is

$$\langle r_2 | U(t_2, t_1) | r_1 \rangle = \langle r_2 | \exp[-iH(t_2 - t_1)/\hbar] | r_1 \rangle \quad (7)$$

the probability amplitude that the particle is at position r_2 at time t_2 if it was at position r_1 at time t_1 ; the square modulus of this matrix element is the probability of this "event."

The basic tenet of Feynman's quantum mechanics is that the propagator can be expressed as eq 8, where

$$\langle r_2 | \exp[-iH(t_2 - t_1)/\hbar] | r_1 \rangle \sim \sum_{\text{all paths}} \exp\{i\phi[r(t)]/\hbar\} \quad (8)$$

the "sum over all paths" is actually a special kind of integral (a path integral) over all functions $r(t)$, restricted only so that $r(t_1) = r_1$ and $r(t_2) = r_2$; the symbol \sim in eq 8 means that there is an overall normalization which is unspecified. The function ϕ in eq 8 is the classical action associated with the function $r(t)$.

This formulation of quantum mechanics (which is completely equivalent to the conventional Schrodinger approach) has actually not proven useful in many cases for quantum mechanical calculations, for it is only possible to evaluate path integrals in a few special cases. Equation 8 is extremely useful, however, in obtaining the classical limit of the propagator; in this limit ($\hbar \rightarrow 0$) the oscillatory character of the integrand means that only those paths contribute about which the action functional $\phi[r(t)]$ is stationary—*i.e.*, the classical paths¹⁰ (or path) which connect r_1 and r_2 . In the classical limit, therefore, eq 8 becomes eq 9,

$$\langle r_2 | \exp[-iH(t_2 - t_1)/\hbar] | r_1 \rangle \sim \sum_{\substack{\text{all} \\ \text{classical} \\ \text{paths}}} \exp[i\phi(r_2, r_1)/\hbar] \quad (9)$$

where the sum is now an ordinary finite sum over the classical paths for which $r(t_2) = r_2$ and $r(t_1) = r_1$.

To see that there can be more than just one term in eq 9, consider the nature of classical mechanics. If the position r_1 and momentum p_1 are specified at time t_1 , then $r(t)$ and $p(t)$ are determined for all later times; in particular $r_2 \equiv r(t_2)$ is uniquely determined, so that one may write $r_2(r_1, p_1)$, meaning that r_2 is indeed a single-valued function of r_1 and p_1 . In eq 9, however, r_1 and r_2 are the independent variables which specify the classical trajectory, and it is not necessarily true that r_1 and r_2 determine a unique trajectory (as do r_1 and p_1); in other words, with r_1 fixed, there may be more than one value of p_1 (and therefore several classical paths) which lead to the same value of r_2 .

It cannot be overemphasized that the "double-ended" boundary conditions discussed in the preceding paragraph are the appropriate ones to use for making the correspondence between classical and quantum mechanics; failure to realize this has led in the past to the belief that the deterministic nature of classical mechanics was incompatible with quantum mechanics.¹¹ It is the specification of r_1 and p_1 as boundary conditions for the trajectories which is incompatible with quantum mechanics (*i.e.*, the uncertainty principle), and not classical mechanics itself; as has been seen above, there is a direct correspondence between probability amplitudes in quantum mechanics and classical trajectories with "double-ended" boundary conditions.

The Classical S Matrix

With the classical limit of the propagator established, it is a short step to the \mathbf{S} matrix itself. If H is the total Hamiltonian governing the collision system and H_0 is the Hamiltonian for the noninteracting collision partners, then

$$S = e^{iH_0 t_2/\hbar} e^{-iH(t_2-t_1)/\hbar} e^{-iH_0 t_1/\hbar} \quad (10)$$

i.e., S is the propagator with the unperturbed time dependence (that due to H_0) subtracted out in the correct manner.¹² S is *not* a function of time, for the scattering boundary conditions imply the limit $(t_2 - t_1) \rightarrow \infty$ in eq 10; it is to ensure the existence of this infinite time limit that the unperturbed time dependence must be subtracted out in the definition of S .

The physical \mathbf{S} matrix, the transition amplitude from some initial state of H_0 to a final state of H_0 , is the matrix of the above S operator in the following particular representation. One transforms from the ordinary coordinates and momenta to that particular set of generalized coordinates and momenta known as action-angle variables;¹³ the momenta (the action variables) are the constants of the motion of H_0 and are the precise classical equivalent of the quantum mechanical quantum numbers; the conjugate coordinates are phase angles. The desired \mathbf{S} -matrix is the matrix of S in the momentum representation of these variables. If (p, q)

(11) (a) A. Burgess and I. C. Percival, *Advan. At. Mol. Phys.*, **4**, 109 (1968); (b) D. Rapp and T. Kassal, *Chem. Rev.*, **69**, 61 (1969).

(12) R. G. Newton, "Scattering Theory of Waves and Particles," McGraw-Hill, New York, N. Y., 1966, pp 160-162.

(13) H. Goldstein, "Classical Mechanics," Addison-Wesley, Reading, Mass., 1950, pp 288-307.

(9) R. P. Feynman and A. R. Hibbs, "Quantum Mechanics and Path Integrals," McGraw-Hill, New York, N. Y., 1965.

(10) It is well known that the requirement on the path $r(t)$ expressed by $\delta\phi[r(t)] = 0$, Hamilton's principle, is equivalent to the classical equations of motion for the path.

denote the set of action-angle variables, then

$$e^{\pm iH_0 t/\hbar}|p\rangle = e^{\pm iEt/\hbar}|p\rangle \quad (11)$$

since the states $|p\rangle$ are eigenstates of H_0 . From eq 10 and 11, therefore, the \mathbf{S} matrix is related to the propagator by eq 12, or with the classical approximation to

$$\langle p_2 | \mathcal{S} | p_1 \rangle = e^{iE(t_2-t_1)/\hbar} \langle p_2 | e^{-iH(t_2-t_1)/\hbar} | p_1 \rangle \quad (12)$$

the propagator one finds the *classical S matrix*¹⁴ to be given by eq 13, where the sum is over all classical paths

$$\langle p_2 | \mathcal{S} | p_1 \rangle = \sum \left[2\pi \left(\frac{\partial p_2}{\partial q_1} \right)_{p_1} \right]^{-1/2} e^{i\phi(p_2, p_1)} \quad (13)$$

for which the action is p_1 before collision and p_2 after collision; the phase ϕ in eq 13 is

$$\phi(p_2, p_1) = - \int_{-\infty}^{\infty} dt q(t) \frac{d}{dt} p(t)$$

with $q(t)$ and $p(t)$ being determined by the classical equations of motions

$$\frac{dq}{dt} = \frac{\partial H(p, q)}{\partial p}$$

$$\frac{dp}{dt} = - \frac{\partial H(p, q)}{\partial q}$$

The appropriate classical-limit normalization has also been supplied in eq 13; it has a simple physical interpretation which can be seen by the following argument. Considering p_1 to be fixed throughout, the classical equations of motion determine a unique relation between q_1 and p_2 ; *i.e.*, given q_1 , p_2 is determined, or given p_2 , q_1 is determined. Thus the probability distributions of q_1 and p_2 are related by

$$\text{Prob}(p_2) dp_2 = \text{Prob}(q_1) dq_1$$

i.e., for fixed p_1 , the probability that p_2 has a specific value in the interval $(p_2, p_2 + dp_2)$ times the increment dp_2 is equal to the probability that q_1 has a specific value in the interval $(q_1, q_1 + dq_1)$ times the increment dq_1 . However, the uncertainty principle implies that, with p_1 fixed, q_1 can have *any* value (*i.e.*, it is random), or that the distribution in q_1 is constant. The above relation, therefore, states that

$$\text{Prob}(p_2) \equiv P_{p_2 \leftarrow p_1} = \text{constant} \times \left| \frac{\partial q_1}{\partial p_2} \right|_{p_1}$$

and by invoking unitarity of the propagator one can show^{7a} that the "constant" is $1/(2\pi)$; the square modulus of each term in eq 13, therefore, is the probability of the $p_1 \rightarrow p_2$ transition associated with that particular trajectory and is simply the Jacobian relating the final momentum to the initial coordinate.¹⁵

The expressions above have all been written as though there were just one degree of freedom and one pair of coordinates and momenta. This has been done only for simplicity of presentation, however, and the

(14) More details of the steps involved in proceeding from eq 12 to eq 13 are given in ref 7a.

approach is applicable to systems of any number of degrees of freedom; the formulas are generalized in a fairly straightforward manner.

Example: Vibrational Excitation

The general ideas presented above become much clearer by discussion of a simple example.^{7b} The system consists of a diatomic molecule with a vibrational degree of freedom and an atom, constrained so that all three atoms lie on a line.¹⁶

Initially the atom is moving toward the diatom with some definite velocity and with the diatom in some definite vibrational state with quantum number n_1 . After colliding, the atom departs, leaving the diatom in some final vibrational state, n_2 ; the dynamical observable is the probability matrix P_{n_2, n_1} , giving the probability that the final vibrational quantum number is n_2 provided the initial one is n_1 . The probability is given in terms of an \mathbf{S} -matrix element in the usual manner, and we wish to construct the classical approxi-

$$P_{n_2, n_1} = |S_{n_2, n_1}|^2 \quad (14)$$

mation to S_{n_2, n_1} according to the general prescription of the preceding section.

This system possesses two degrees of freedom: translation, characterized by ordinary coordinate R and momentum P ; and vibration, characterized by its action variable n (the classical counterpart of the vibrational quantum number) and phase angle q ; for an isolated oscillator only integral values of n are allowed, and in this way quantization is achieved. (This is the standard semiclassical quantum condition.¹⁷)

Even for this fairly simple system, however, it is not possible to solve the quantum mechanical or classical equations of motion in closed form; one is forced to solve then numerically. To evaluate the general expression for the classical \mathbf{S} matrix (eq 13), one must find the classical trajectories for which n has the value n_1 before collision and the value n_2 after collision; this is done in the following manner. The initial coordinate and momentum q_1 and n_1 are specified¹⁸ and the classical equations of motion integrated numerically; this determines some definite final value of n_2 , and we write $n_2(q_1, n_1)$ with the meaning that n_2 is a function of q_1 and n_1 (the functional value of which is determined by integrating the classical equations of motion with these initial conditions). The desired initial value n_1 can

(15) This is exactly analogous to the Jacobian relation for simple elastic scattering whereby the classical differential cross section is derived

$$\sigma(\theta) \sin \theta d\theta = b db$$

which implies that

$$\sigma(\theta) = b |db/d\theta| / \sin \theta$$

See ref 12, p 126, for more details.

(16) For a recent review of various classical and quantum mechanical treatments of this collision system, see ref 11b.

(17) See, for example, E. Merzbacher, "Quantum Mechanics," Wiley, New York, N. Y., pp 119-121.

(18) The initial translational momentum P is determined by specifying the total energy, and the scattering boundary conditions require only that R be so large initially that the two collision partners are noninteracting.

therefore be chosen directly, but one does not know what value to choose for q_1 so that $n_2(q_1, n_1)$ takes on the specified integer value n_2 ; this value of q_1 must therefore be determined iteratively.

Figure 2 shows the function $n_2(q_1, n_1)$ as a function of q_1 , with $n_1 = 1$. The dotted line at $n_2 = 2$ indicates the graphical solution of the equation $n_2(q_1, 1) = 2$; *i.e.*, it is clear that there are *two* values of q_1 for which $n_2(q_1, n_1)$ takes on the value 2, or that there are two classical trajectories for which n is 1 before collision and 2 after collision. There are two terms, therefore, in the classical S matrix

$$S_{n_2, n_1} = p_I^{1/2} e^{i\phi_I} + p_{II}^{1/2} e^{i\phi_{II}} \quad (15)$$

where $p = [2\pi |n_2'(q_1)|]^{-1}$, with $q_1 = q_I$ for p_I and q_{II} for p_{II} . The situation is just like that discussed earlier; the completely classical approximation for P_{n_2, n_1} is the sum of the probabilities associated with the two trajectories (eq 16), whereas the semiclassical

$$P_{n_2, n_1}^{CL} = p_I + p_{II} \quad (16)$$

approach provides the interference term¹⁹

$$P_{n_2, n_1}^{SC} = p_I + p_{II} + 2(p_I p_{II})^{1/2} \sin(\Delta\phi) \quad (17)$$

Figure 3 shows typical results of this approach for the case that the mass of the atoms and potential parameters are chosen to correspond to a $H_2 + He$ collision; for light atoms such as these the quantum effects should be prominent and thus provide a severe test for the semiclassical theory. The solid line connects points which are essentially the exact quantum mechanical values²⁰ of the transition probability; on the scale of this drawing these values are essentially indistinguishable from the semiclassical results.²¹ The dashed line connects points of the completely classical approximation in which the interference term is omitted.

It is clear in these results just how important are the interference effects; a judgment of classical mechanics based on the purely classical approximation, omitting the interference term, would indicate it to be completely unreliable as to the magnitude of individual transition probabilities. One might conclude that the dynamics of these collisions was highly quantum-like. The fact is, though, that classical mechanics describes the dynamics extremely accurately, and the quantum effects all arise through the quantum principle of superposition.

Figure 3 also illustrates the fact that the completely classical approach is correct on the *average*. If one were to look at the *net* transition probability resulting from a sum over several final vibrational states, or an average over several initial ones, then it is clear that the completely classical approximation would be more

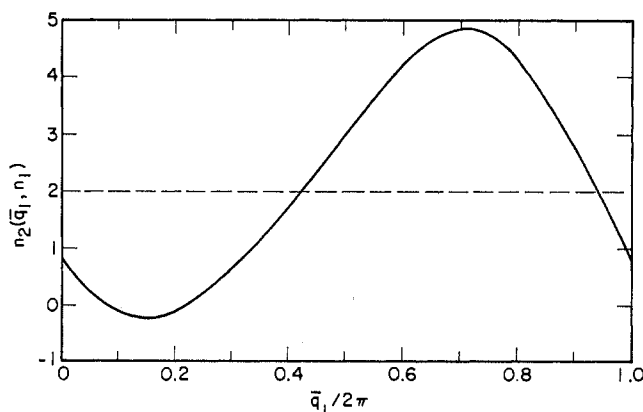


Figure 2. An example of the trajectory function $n_2(q_1, n_1)$ as discussed in the text; this example has $n_1 = 1$ and corresponds to a linear $H_2 + He$ collision (see ref 7b for more details). This function is the final value of the classical action variable n (the classical counterpart to the quantum mechanical quantum number) as a function of the initial value of the action, n_1 , and the initial value of the phase of the oscillator, q_1 ; *i.e.*, one specifies n_1 and q_1 and integrates the classical equations of motion, and n_2 is thus determined. The dotted line at $n_2 = 2$ indicates the graphical solution for the two values of q_1 which satisfy the equation $n_2(q_1, n_1) = n_2$, here with $n_2 = 2$, $n_1 = 1$.

satisfactory. As discussed earlier, this is the expected nature of things. If one is interested primarily in deriving macroscopic kinetic properties, this situation is viewed as fortunate—one can disregard quantum interference effects. If one is interested in gaining precise information about the intermolecular potential, however, this is discouraging, for it means that macroscopic kinetic measurements will be of little use for this purpose, experiments detecting the results of single-collision processes being required.

Classically Forbidden Transitions (Tunneling)

In Figure 2 one sees another feature that can arise in this semiclassical theory. Suppose one is interested in the $1 \rightarrow 5$ transition; since there is no value of q_1 for which $n_2(q_1) = 5$, there is no classical trajectory for which $n_1 = 1$ and $n_2 = 5$; the transition probability is therefore zero. Such a transition is referred to as *classically forbidden*.

Although there are no *real* values of q_1 for which $n_2(q_1) = 5$, one can easily show that there are *complex* values.²² For example, if $n_2(q_1)$ in Figure 3 is expanded in a Taylor series about its maximum

$$n_2(q_1) = n_2^x + \frac{1}{2} n_2''(q_1^x) (q_1 - q_1^x)^2 + \dots$$

then one can solve

$$n_2(q_1) = 5 \quad (18)$$

to obtain

$$q_1 = q_1^x \pm i \{2[5 - n_2^x]/|n_2''|\}^{1/2}$$

i.e., there are two complex roots, complex conjugates of one another. In general one can show that the *exact*

(19) The interference term is $\sin(\Delta\phi)$, rather than $\cos(\Delta\phi)$, due to the $\pi/2$ phase difference arising because $n_2'(q_1)$ has a different sign for the two terms in eq 15.

(20) D. Secrest and B. R. Johnson, *J. Chem. Phys.*, **45**, 4556 (1966).

(21) To obtain such good numerical results one must actually employ a *uniform* semiclassical formula which is obtained from eq 17; see ref 7b for details of this procedure.

(22) The situation is exactly analogous to the rainbow effect in simple elastic scattering; see Bernstein.⁹ A classically forbidden transition is analogous to being on the "dark side" of the rainbow angle.

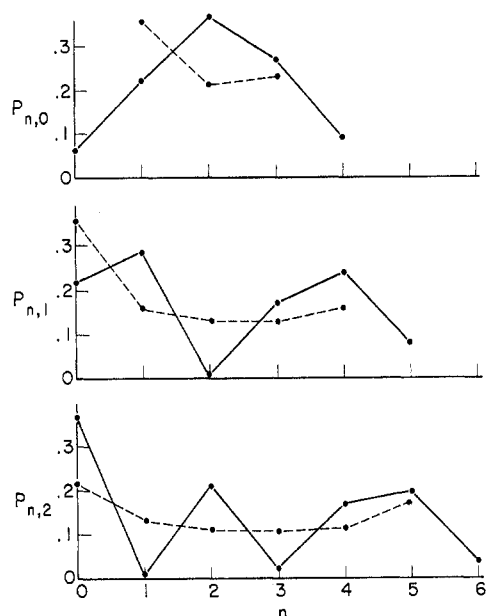


Figure 3. Transition probabilities for linear $H_2 + He$ collisions (see ref 7b for more details) with initial vibrational quantum number $n_i = 0$ (top), 1, and 2 (bottom). The dotted lines connect results of the completely classical approximation (eq 10), and the solid lines connect the exact quantum mechanical results of ref 15; on the scale of this drawing there is essentially no difference between the exact quantum results and the uniform semiclassical results of ref 7b and 7c.

complex roots of eq 18 are complex conjugates of one another.

Furthermore, the phase difference between these two roots is purely imaginary; consequently one can show that the oscillatory expression of eq 17 becomes

$$P_{n_i, n_f} = p e^{-|\Delta\phi|} \quad (19)$$

i.e., the complex exponential functions are replaced by real exponential functions. The factor p in eq 19 is a Jacobian, as earlier, and the negative exponential factor expresses the fact that the transition is classically forbidden, *i.e.*, that it takes place by tunneling (the exponential damping is characteristic of tunneling²³).

Tunneling transitions, therefore, have smaller probabilities than nontunneling, or classically allowed ones. If one is again interested in a *net* transition probability involving a number of transitions, some of which are classically allowed and others of which are classically forbidden, the classically forbidden transitions will make a negligible contribution in comparison to the allowed ones. Tunneling, therefore, will be a significant effect only if *all* of the transitions are classically forbidden, or if one explicitly selects individual quantum states initially and detects individual quantum states finally.

In Figure 3 the transitions $0 \rightarrow 0$, $0 \rightarrow 4$, $1 \rightarrow 5$, $2 \rightarrow 6$ are all classically forbidden; the semiclassical theory accounts for these, however, as accurately as it

does the classically allowed transitions. Although the above discussion has been specifically related to the linear atom-diatom model problem, the features are general and expected to be typical of any system.

One other interesting advantage of this semiclassical approach to tunneling is that one sees exactly what role tunneling plays in the process of interest. If one performs a strictly quantum mechanical calculation for the transition probability, there is actually no way to tell what tunneling is; quantum mechanics does not distinguish between classically forbidden and classically allowed processes. To assess the importance of tunneling, therefore, it is necessary to have a well-defined procedure that actually distinguishes tunneling processes. Since the semiclassical theory does this, it could provide a useful way to study precisely, for example, the part tunneling plays in the dynamics of chemical reactions.

Resonances

It is not our intention to discuss here in detail the phenomenon of resonances, or quasi-bound states²⁴ in molecular collisions, but to indicate briefly how this quantum effect appears in the present semiclassical framework.

One generally refers to two types of resonances, distinguished on physical grounds by the nature of interaction giving rise to the short-lived collision complex; it has been pointed out²⁴ that in quantum mechanics there is actually not a precise distinction between these two types. In the semiclassical theory, however, the two types of resonances are definitely different, and this again points to a usefulness of the semiclassical approach in studying a dynamic system.

Potential, or single particle, resonances come about by tunneling of the translational degree of freedom; they are therefore classically forbidden processes. This is the only type of resonance that can occur in purely elastic scattering.²⁵

Internal excitation, or Feshbach-type resonances, on the other hand, are classically allowed processes in the semiclassical theory. They can arise, however, only when at least one of the collision partners has internal degrees of freedom, and may be thought of in the following manner. Considering the linear atom-diatom example discussed above, suppose the long-range atom-diatom interaction is attractive; upon colliding, the diatom may be excited to a vibrational state which would be energetically forbidden if the colliding atom were not present and, by virtue of the attractive inter-

(24) R. D. Levine, *Accounts Chem. Res.*, **3**, 273 (1970).

(23) Consider, for example, the probability of a particle tunneling through a one-dimensional barrier; the probability is $\exp(-2\theta)$, where θ is the barrier penetration integral (the classical action for this process); see ref 17, pp 121-122.

(25) The semiclassical treatment of potential resonances is one of the principal topics regarding elastic scattering which is not discussed in Bernstein's review article (ref 6). The first work on this was that of K. W. Ford, D. L. Hill, M. Wakano, and J. A. Wheeler, *Ann. Phys. (New York)*, **7**, 239 (1959), and more recent contributions have been made by M. V. Berry, *Proc. Phys. Soc.*, **88**, 285 (1966); R. B. Bernstein, C. F. Curtiss, S. Iman-Rahajoe, and H. T. Wood, *J. Chem. Phys.*, **44**, 4072 (1966); P. M. Livingston, *ibid.*, **45**, 601 (1966); R. R. Herm, *ibid.*, **47**, 4290 (1967); W. H. Miller, *ibid.*, **48**, 1651 (1968); J. N. L. Connor, *Mol. Phys.*, **15**, 621 (1968).

action, lowering the energy so that this vibrational state is temporarily accessible. When the atom and diatom begin to separate, however, energy conservation prevents the atom from escaping; it stops and returns toward the diatom. These multiple collisions can take place any number of times, until the diatom is finally deexcited to a state for which the relative translational energy makes it possible for the atom and diatom to separate. This type of resonance or collision complex is being examined to some detail in classical trajectory studies.²⁶

Conclusions and Outlook

It has been shown how the effect of interference and tunneling in molecular collisions can be described completely within the framework of classical mechanics, provided one uses classical mechanics to construct the classical limit of the quantum mechanical transition amplitude, or *S*-matrix element, for the process of interest, and then manipulates it quantum mechanically. The quantum effects arise solely as a consequence of the quantum principle of superposition—that one adds the probability amplitudes corresponding to indistinguishable processes rather than the probabilities themselves.

Although quantum effects are accounted for qualitatively by this semiclassical theory, there remains the question of the quantitative accuracy of this approach. Preliminary studies with some simple examples (the linear atom-diatom) indicate classical mechanics to be quite accurate when used in this manner, but more thorough studies, particularly with more realistic dynamical systems, are required before definitive conclusions can be made about the typical accuracy one expects. Even in cases for which the semiclassical treatment may not be accurate enough quantitatively, it may still be valuable in elucidating dynamical fea-

tures obscured in a completely quantum mechanical calculation, such as the degree to which tunneling participates in the transition under study.

Due to the averaging over internal and translational degrees of freedom, interference effects in macroscopic rate quantities should ordinarily be negligible. In fact, the conclusion seems to be developing²⁷ that “a little averaging goes a long way” in washing out quantum interference structure; *i.e.*, it may be that these effects will only be observable in completely state-selected, single-collision experiments. For this reason, too, it is doubtful that anything beyond a strictly classical treatment is warranted for collisions involving large molecules (*i.e.*, larger than diatomic), since complete state selection for such systems is out of the question.²⁸

Quantum effects are expected to be important, however, when one attempts to deduce precise quantitative information about the intermolecular potential for simple systems (atoms, and diatomic molecules) from single-collision scattering data, the reason being that data sufficiently accurate for this purpose will almost certainly detect them; in fact, they may be quite prominent in such high resolution data. Furthermore, it may be that the quantum effects themselves, coupled with a semiclassical analysis, will provide a direct handle on certain quantitative features of the intermolecular potential without a complete solution of the inversion problem.

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(27) On the basis of work in progress of applying this semiclassical treatment to the rotational excitation of a diatomic molecule by collision with an atom.

(28) This is also a natural limit for the practicality of the present semiclassical theory: to quantize the internal degrees of freedom correctly it is necessary that the noninteracting problem be exactly solvable so that the transformation to action-angle variables can be carried out; this is only possible for two body systems (*i.e.*, diatomic molecules).

(26) P. Brumer and M. Karplus, private communication.