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William H. Miller

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THE SEMICLASSICAL NATURE OF ATOMIC AND MOLECULAR COLLISIONS*

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ABSTRACT

The dynamical features of atomic and molecular collisions (including quantum effects) can be accurately described by classical mechanics provided one retains the quantum mechanical principle of superposition. This means that one uses the solution of the classical equations of motion (i.e., numerically computed classical trajectories) to construct the classical limit of the transition amplitude for the process of interest, and then combines these amplitudes according to the laws of quantum mechanics-- i.e., one adds probability amplitudes corresponding to indistinguishable processes rather than the probabilities themselves. In this way interference features absent in a purely classical approach are included; tunneling can be taken into account by analytic continuation of this interference structure into classically forbidden regions. Quantization of bound degrees of freedom, the only quantum effect other than interference and tunneling, is achieved via the well-established semiclassical procedure: the classical action associated with each of these internal degrees of freedom is required to be an integer (or perhaps a half-integer). Application of these ideas to some simple collision systems indicate this to be an accurate description of molecular collision dynamics.

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) has been 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 backwards 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, and experiments pertained 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 eV, say) 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 question of immense importance is, 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 this question 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.⁶

Although quantum effects in the case of elastic atom-atom scattering can be quite striking and pronounced, an important fact is that they can all be accounted for (even quantitatively) by the appropriate use of classical mechanics. 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

The 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 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, Equation (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 Equation (2), and ϕ_{I} and ϕ_{II} are the classical actions associated with the two classical paths. Forming the square modulus of Equation (3) gives the semiclassical expression

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

it is the interference terms 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 S-matrix (or, for short, the classical S-matrix) and then uses it quantum mechanically. The only other type of quantum dynamical effect (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.

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

The Feynman Propagator.

R. P. Feynman⁸ has developed a formulation of quantum mechanics that is particularly well-suited to a semiclassical 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

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

Another way of interpreting the propagator is that its matrix elements in any representation are the transition amplitudes between the basis states; for example, in the coordinate representation,

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

is 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:

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

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

This formulation of quantum mechanics (which is completely equivalent to the conventional Schroedinger approach) has actually not proved 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 the contribution to the path integral from all functions $r(t)$ cancel one another, except for that particular function (or there may be

more than one such function) which is a solution of the classical equations of motion. In the classical limit, therefore, Equation (8) becomes

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

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 Equation (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 Equation (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 .

The Classical S-Matrix.

With the classical limit of the propagator established, it is a short step to the S-matrix itself. If H is the total Hamiltonian governing the collision system and H_0 is the Hamiltonian for the non-interacting 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.⁹ S is not a function of time,

for the scattering boundary conditions imply the limit $(t_2 - t_1) \rightarrow \infty$ in Equation (10); it is to insure the existence of this infinite time limit that the unperturbed time dependence must be subtracted out in the definition of S.

The physical 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;¹⁰ 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 S-matrix is the matrix of S in the momentum representation of these variables. If (p, q) 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 Equations (10) and (11), therefore, the S-matrix is related to the propagator by

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

or with the classical approximation to the propagator one finds the classical S-matrix to be given by

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

where the sum is over all classical paths for which the action is p_1 before collision and p_2 after collision; the phase ϕ in Equation (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 Equation (13); to see its physical meaning, consider the square modulus of a single term in Equation (13):

$$\left| \frac{\partial q_1}{\partial p_2} \right|_{p_1} / 2\pi$$

This is the probability of the $p_1 \rightarrow p_2$ transition associated with a particular trajectory; i.e., the relation is

$$\text{prob}(p_2 \leftarrow p_1) \times dp_2 = dq_1 / 2\pi ;$$

the probability that p has a final value in the interval $(p_2, p_2 + dp_2)$ is equal to the probability that q had an initial value in the interval $(q_1, q_1 + dq_1)$. Since the initial value of q is random, this later probability is just dq_1 divided by 2π (the width of the total q_1 interval). Thus the classical probability, the square root of which is the magnitude of each term in Equation (13), is simply the Jacobian relating the final momentum to the initial coordinate.¹¹

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 approach

is applicable to systems of any number of degrees of freedom; the formulae are generalized in a fairly straight-forward 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.

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 S-matrix element in the usual manner:

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

and we wish to construct the classical approximation 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 the action n and phase angle q ; for an isolated oscillator only integer values of the action are allowed, and in this way quantitation is achieved. (This is the standard semiclassical quantum condition.¹²)

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 them numerically. To evaluate the general

expression for the classical S-matrix [Equation (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 specified¹³ and the classical equations of motion integrated numerically; this determines some definite final value for 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 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

$$n_2(q_1, 1) = 2 \quad ;$$

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,

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

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,

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

where the semiclassical approach provides the interference term¹⁴

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

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 mechanics values¹⁵ of the transition probability; on the scale of this drawing these values are essentially indistinguishable from the semiclassical results.¹⁶ 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 judgement 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 were 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 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 semi-classical 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.¹⁷ For example, if $n_2(q_1)$ in Figure 3 is expanded in a Taylor series about its maximum,

$$n_2(q_1) = n_2^x + 1/2 n_2'' (q_1^x) (q_1 - q_1^x)^2 + \dots,$$

then one can solve

$$n_2(q_1) = 5 \tag{18}$$

to obtain

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

i.e., there are two complex roots, complex conjugates of one another. In general one can show that the exact complex roots of Equation (18) are complex conjugates of one another.

Furthermore, the phase difference between these two roots is pure imaginary; consequently one can show that the oscillatory expression of Equation (17) becomes

$$P_{n_2, n_1} = p e^{-|\Delta\phi|} ; \quad (19)$$

i.e., the complex exponential functions are replaced by real exponential functions. The factor p in Equation (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 tunneling¹⁸)

Tunneling transitions, therefore, have smaller probability than non-tunneling, 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 states¹⁹ 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 out¹⁹ 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 dynamical 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.

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 interaction, 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 de-excited 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 has been examined to some detail in classical trajectory studies.²⁰

Summary.

There are essentially only two types of quantum dynamical effects: interference and tunneling. It has been shown how both of these 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, 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 features obscured in a completely quantum mechanical calculation--such as the degree to which tunneling participates in the transition under study.

Quantum effects (i.e., interference and tunneling) in macroscopic rate properties should ordinarily be negligible, a possibly common exception being the case that all transitions under observation are classically forbidden; all contributions to the observed rate are then via classically forbidden (tunneling) processes. Quantum effects are expected to be important, however, if one's goal is to deduce precise quantitative information about the intermolecular potential from single-collision scattering data--the reason being that data sufficiently accurate for this purpose will almost certainly detect these effects; in fact, they may be quite prominent in such high resolution data (individually selected and detected quantum states). As such they may prove to be a powerful tool for "inverting" scattering measurements to obtain the intermolecular potential.

FOOTNOTES

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- † Alfred P. Sloan Fellow.
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11. This is exactly analogous to the Jacobian relation for simple elastic scattering whereby the classical differential cross section is derived:

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

implies that

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

see reference 9, p. 126 for more details.

12. See, for example, E. Merzbacher, Quantum Mechanics, John Wiley and Sons, Inc., N.Y., pp. 119-121.
13. 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 non-interacting.
14. The interference term is $\sin(\Delta\phi)$, rather than $\cos(\Delta\phi)$, due to the $\frac{\pi}{2}$ phase difference arising because $n_2'(q_1)$ has a different sign for the two terms in Equation (15).
15. D. Secrest and B. R. Johnson, J. Chem. Phys., 45, 4556 (1966).
16. To obtain such good numerical results one must actually employ a uniform semiclassical formula which is obtained from Equation (17); see reference 7b for details of this procedure.
17. The situation is exactly analogous to the rainbow effect in simple elastic scattering; see reference 6. A classically forbidden transition is analogous to being on the "dark side" of the rainbow angle.
18. Consider, for example, the probability of a particle tunneling through a 1-dimensional barrier; the probability is $\exp(-2\theta)$, where θ is the barrier penetration integral (the classical action for this

process); see reference 12, pp. 121-122.

19. R. D. Levine, Acct. Chem. Res., 3, 273 (1970).
20. P. Brumer, private communication.

FIGURE CAPTIONS

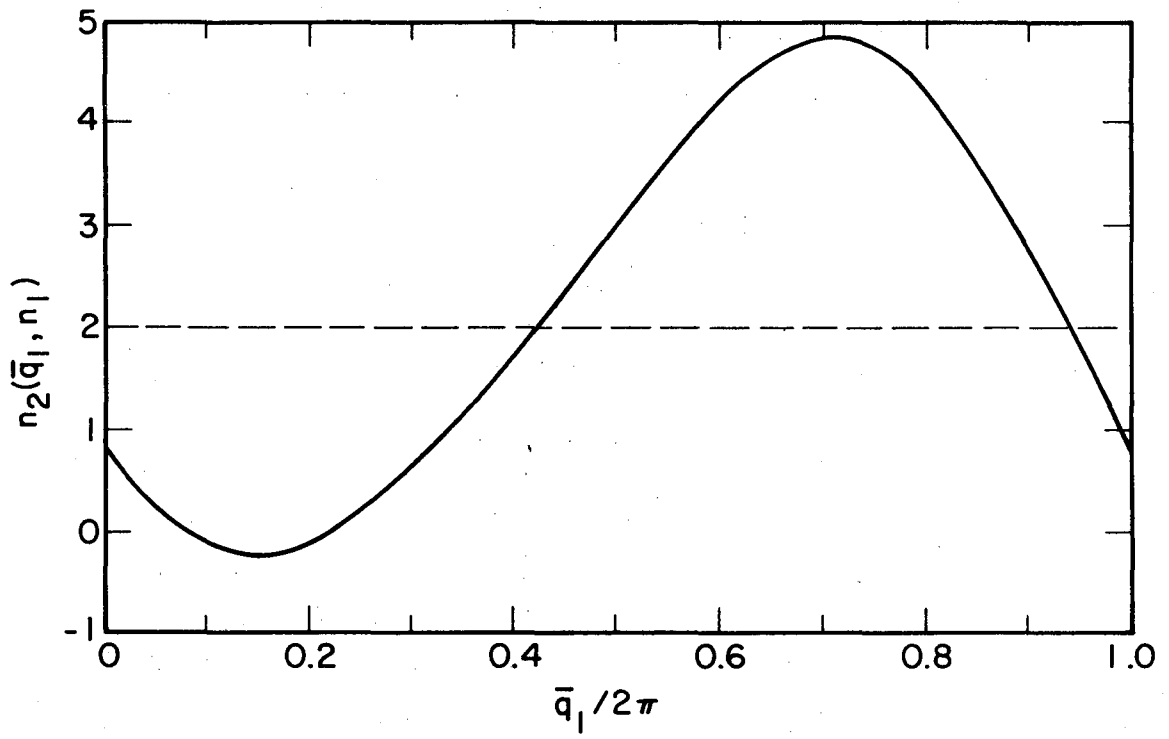
1. An outline of the stages necessary to determine macroscopic chemical properties beginning only with electrons, nuclei, Coulomb's law, and the physical constants. The double arrow between stages 2 and 3 indicate the possibility of going in either direction: one can solve the collision problem to predict 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.
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 reference 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 , 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 $n_2 = 2$, $n_1 = 1$.
3. Transition probabilities for linear $H_2 + He$ collisions (see reference 7b for more details) with initial vibrational quantum number $n_1 = 0$ (top), 1, and 2 (bottom). The dotted lines connect results of the completely classical approximation [Equation (10)], and the solid

lines connect the exact quantum mechanical results of reference 15; on the scale of this drawing there is essentially no difference between the exact quantum results and the uniform semiclassical results of references 7b and 7c.

Theoretical Structure of Gas Phase Chemistry

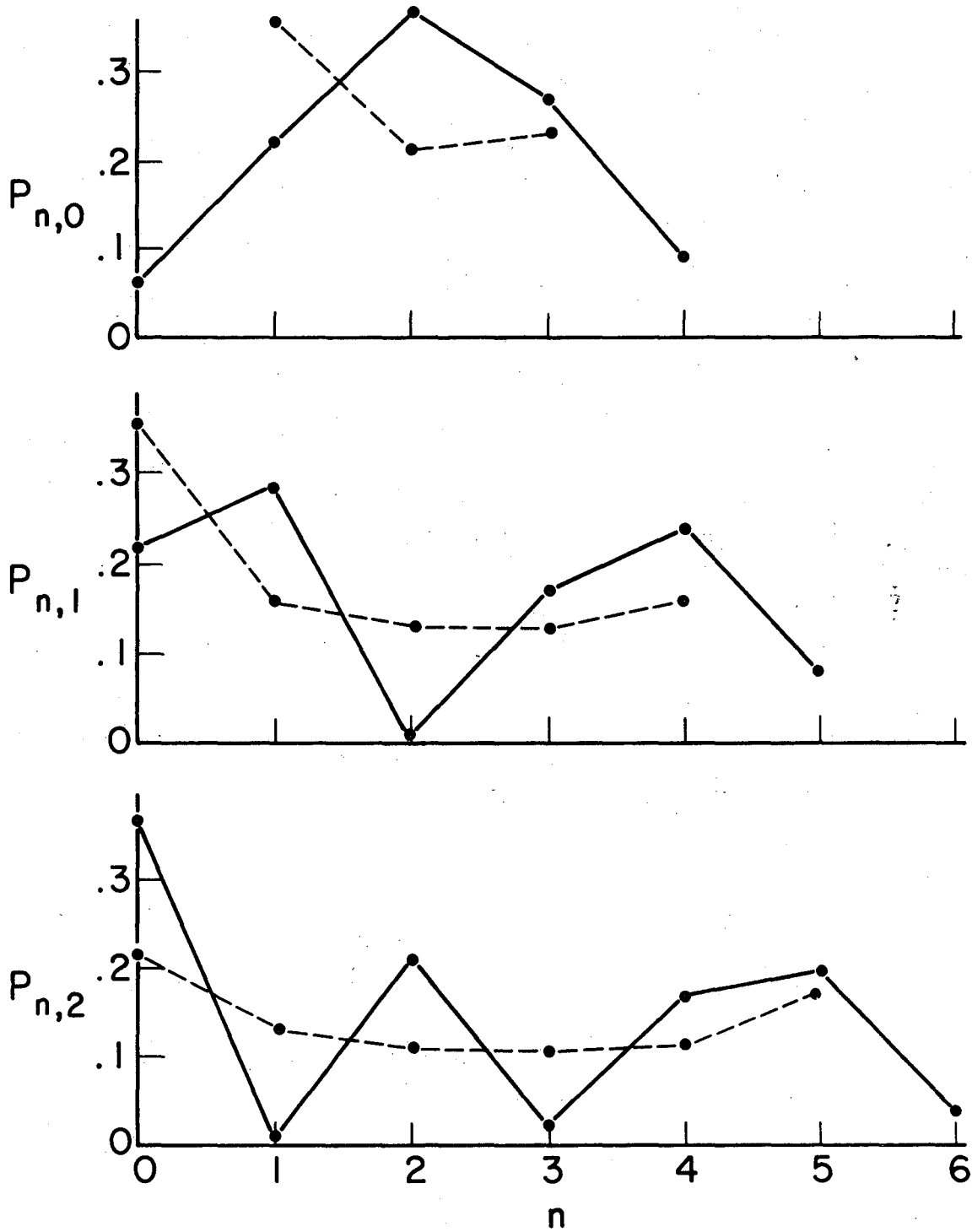
1. Electrons, nuclei, \hbar , e , c , m_e
↓ (Electronic Schrodinger Equation)
2. Intermolecular potentials
↕ (Collision Theory)
3. Dynamics of individual, binary collisions: cross sections
↓ (Statistical Mechanics)
4. Macroscopic rate phenomena: reaction rate coefficients,
relaxation times, transport coefficients

Figure 1



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Figure 2



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Figure 3

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