Articles

Semiclassical Methods in Chemical Physics

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Semiclassical theory finds use in chemical physics both as a computational method and as a conceptual framework for interpreting quantum features in experiments and in numerical quantum calculations. The semiclassical description of one-dimensional dynamical systems is essentially a solved problem for eigenvalue and scattering situations and for general topologies of potential functions (simple potential wells, multiple wells, multiple barriers, and so forth). Considerable progress has also been made in generalizing semiclassical theory to multidimensional dynamical systems (such as inelastic and reactive scattering of atoms and molecules and vibrational energy levels of polyatomic molecules), and here, too, it provides a useful picture of quantum features (interference in product state distribution, generalized tunneling phenomena, and others) in these more complex systems.

SEMICLASSICAL APPROXIMATIONS TO QUANTUM MECHANICS have become widespread in chemical and molecular physics over the last two decades and have even found significant use in nuclear and elementary particle physics (*1–6*). As this is the 100th year since the birth of Niels Bohr, the father of the Old Quantum Theory, it is timely to survey some of these more modern developments. A recent conference (*1*) honoring Bohr's centenary has been devoted entirely to semiclassical methods.

The reason classical and semiclassical descriptions of chemical phenomena are so useful is that atoms and molecules are relatively heavy particles; this means that typically many quantum states are strongly coupled, so that Bohr's Correspondence Principle becomes relevant. (Simply stated, the principle is that classical mechanics emerges from quantum mechanics in the limit of large quantum numbers.) The usefulness of semiclassical methods is twofold.

1) Semiclassical theory plays an interpretive role; that is, it provides an understanding of the nature of quantum effects in chemical phenomena, such as interference effects in product state distributions and tunneling corrections to rate constants for chemical reactions. This interpretive role is important whether one observes quantum effects in actual experiments or in numerical quantum mechanical calculations. The glory effect (an interference feature in the energy-dependence of total cross sections), for example, was first seen (*7, 8*) in completely quantum mechanical scattering calculations, but was not understood until its semiclassical origin was realized.

2) Semiclassical approaches are often useful for carrying out practical calculations, also because of the Correspondence Principle. If many quantum states are strongly coupled, then purely quantum mechanical calculations (basis set expansions, matrix diagonalizations, and so forth) may be impractical, while classical and semiclassical methods become more accurate. The effort in solving the Schrödinger equation increases with the number of strongly coupled quantum states, while the effort in solving the classical equation of motion, on which semiclassical theories are built, grows only with the number of strongly coupled degrees of freedom.

Semiclassical methods are actually now so widespread in chemical physics that it is not possible to cover all such approaches in this short presentation. For example, I will not discuss older semiclassical approaches, now often called classical path models, in which classical motion is assumed for the translational degrees of freedom, and then a time-dependent Schrödinger equation is used to describe the internal degrees of freedom. Such approaches have been particularly useful in nuclear physics (*9*) (coulomb excitation) and have found some use in molecular collisions (*10, 11*) and scattering of atoms and molecules from surfaces (*12*). Also not discussed explicitly are methods that attach a Gaussian wave packet (coherent state) to classical trajectories (*6, 13*), although some of the examples discussed below can be treated in a parallel fashion by such methods.

Eigenvalues

One-dimensional systems. The most startling quantum effect is that the energy of bound systems can be only certain discrete values; the crowning achievement of the Old Quantum Theory (*14*) was the Bohr-Sommerfeld quantization rule

$$(n + 1/2)\pi = \int_{x_1}^{x_2} dx \sqrt{2\mu[E - V(x)]/\hbar^2} \qquad (1)$$

$$n = 0, 1, 2, \ldots$$

which applies to simple potential wells (Fig. 1). (In Eq. 1, μ is the reduced mass for the one-dimensional motion and n is the vibrational quantum number.) With proper inclusion for rotation, this now-called Wentzel-Kramers-Brillouin (WKB) quantum condition accurately describes the vibrational and rotational energy levels of diatomic molecules. Furthermore, it can be inverted to determine the potential energy function V in terms of experimentally determined energy levels; it is by this Rydberg-Klein-Rees method (*15*) that accurate potential energy functions for diatomic molecules are determined.

In semiclassical theory each new topology presents a new problem to be solved. Thus Eq. 1 applies to simple potential wells but not to a potential with several wells separated by potential barriers (Fig. 2). For one-dimensional systems, though, the semiclassical quantum condition has been derived for essentially all cases, that is, an arbitrary number of wells and barriers. For a system with M identical wells and barriers (an M-fold hindered rotor), for example, the quantum condition (*16*) is

$$\phi = (n + 1/2)\pi + (-1)^{n+1}\sin^{-1}\left[\cos\left(\frac{2\pi k}{M}\right)/\sqrt{1 + e^{2\theta}}\right] \qquad (2)$$

$$k = 1, \ldots, M \text{ for each } n = 0, 1, 2, \ldots$$

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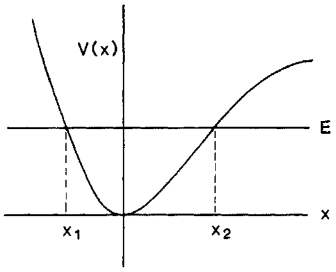


Fig. 1. Typical one-dimensional potential well; x_1 and x_2 denote the classical turning points for energy E.

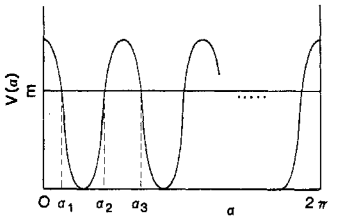


Fig. 2. Potential energy for a hindered rotor as a function of the rotation angle α; α_1, α_2, and α_3 denote classical turning points for E.

where ϕ and θ are phase integrals across the well and through the barrier, respectively (Fig. 2):

$$\phi = \int_{\alpha_1}^{\alpha_2} d\alpha \sqrt{2I[E - V(\alpha)]/\hbar^2} \tag{3}$$

$$\theta = \int_{\alpha_2}^{\alpha_3} d\alpha \sqrt{2I[V(\alpha) - E]/\hbar^2} \tag{4}$$

where I is the moment of inertia of the rotor. [A small phase shift correction (*17*) to ϕ and to θ has been neglected here.] Equation 2 takes into account tunneling through the barriers and is uniformly valid for energy below ($\theta > 0$) or above ($\theta < 0$) the top of the barrier. For weak tunneling, that is, $e^{2\theta} >> 1$, Eq. 2 leads to the following well-known splitting pattern for the nth M-fold multiplet

$$E_{n,k} = E_n^{(0)} + e^{-\theta}(-1)^{n+1}\frac{\hbar\omega_n}{\pi}\cos\left(\frac{2\pi k}{M}\right)$$
$$k = 1, \ldots, M$$

where the vibrational frequency $\hbar\omega_n$ is given by

$$\hbar\omega_n = \partial E_n^{(0)}/\partial n \tag{5}$$

and where $E_n^{(0)}$ is the center of the nth multiplet, which is determined by the single-well quantum condition

$$\phi(E^{(0)}) = (n + 1/2)\pi \tag{6}$$

Equations 2 to 5 apply also in the continuum limit, $M \rightarrow 0$, $k/M \equiv \kappa$, and give rise to energy bands $E_n(\kappa)$ as κ varies from 0 to 1.

Multidimensional systems. Since semiclassical eigenvalues work so well for essentially all one-dimensional systems, it would be useful to generalize them to nonseparable systems of more than 1 degree of freedom, for example, vibrational states of polyatomic molecules. This is relevant because of the many new experimental techniques being developed for investigating highly excited vibrational states (*18*) for which the traditional normal mode analysis is inadequate.

For simple multidimensional systems, that is, those that are topologically a simple potential well in all dimensions, the Old Quantum Theory (*14*) provided the ready generalization of Eq. 1: one expresses the classical Hamiltonian in terms of the good action variables $\{I_k\}$ of the system and then requires that they be equal to half-integer (for vibrational motion) multiples of $\hbar$

$$I_k = (n_k + 1/2)\hbar \tag{7}$$
$$n_k = 0, 1, 2, \ldots$$

Equation 1 is this condition for the one-dimensional case. The difficult step in this procedure is not Eq. 7, but rather the task of expressing the classical Hamiltonian in terms of the good action variables. To do so requires one to solve the Hamilton-Jacobi equation for the multidimensional, nonseparable system, which is not possible in general without resorting to numerical methods. In the days of the Old Quantum Theory (*14*) perturbative methods were used to carry out the calculation approximately (*14*), and the results obtained are actually quite accurate in comparison with the analogous quantum perturbative values (*19–21*). Although the failure of the Old Quantum Theory to deal with multidimensional systems has been cited as a clue that some more complete theory was necessary, this failure is less that of the Old Quantum Theory itself than of our inability to solve the classical equations of motion for multidimensional systems (without resorting to numerical calculations).

More recently, methods have been developed for expressing the Hamiltonian in terms of its good action variables by integrating the classical equations of motion numerically. Marcus and co-workers (*2, 22*) did this by using Poincaré surfaces of section, and subsequently a number of other methods have been developed (*23–34*), some of which seem practical for systems with more than 3 degrees of freedom. This is an active area of research.

Less well settled is semiclassical quantization for multidimensional systems with more complicated topologies, for example, a two-dimensional double-well potential (Fig. 3). The problem is that good action variables do not exist globally, although they may exist locally. In this case, for example, one expects three sets of locally good action variables, one in each of the two potential wells and one in the barrier region. For a one-dimensional double well, the three locally good actions are the phase integrals across each of the wells, ϕ_1 and ϕ_2, and the phase integral through the barrier, θ, in terms of which the quantization condition is (*35, 36*)

$$\tan\phi_1 \tan\phi_2 = (e^{\theta} + \sqrt{1 + e^{2\theta}})^2 \tag{8}$$

Intuition suggests that there should exist an analogous uniform quantization formula for the multidimensional case, one that makes use of the locally good actions. This idea has been implemented (*37*) even though it is not on solid theoretical ground.

Even less well understood is how to effect semiclassical quantization if good action variables do not exist at all, that is, if the classical motion is chaotic (*25*). This question has received considerable attention, and although there is not universal agreement, in such cases semiclassical quantization may not exist in the sense of providing individual energy levels. Statistical characteristics of the energy levels, however, which are perhaps the quantities of actual physical interest in such situations, can be described semiclassically (*38–41*).

Scattering

Scattering experiments had not become common in physics and chemistry before the Old Quantum Theory was laid to rest, so the theory was not developed extensively for such applications. (Rutherford—that is, coulomb—scattering is well described by classical mechanics.) With the advent of crossed molecular beam methods (*42*) by chemists in the late 1950's it became possible to study chemical reactions and energy transfer collisions at the microscopic single-collision level, which stimulated enormous activity among physical chemists in developing scattering theory for such applications. Because semiclassical approximations are so natural for atomic and molecular systems, such methods have developed rapidly.

Elastic scattering. Because of conservation of angular momentum, the elastic scattering of two structureless particles—for example, two rare gas atoms within the Born-Oppenheimer approximation—reduces to a one-dimensional dynamical problem for the radial motion. The WKB approximation can thus be applied; Ford and Wheeler (*43*) showed how interference and tunneling effects in

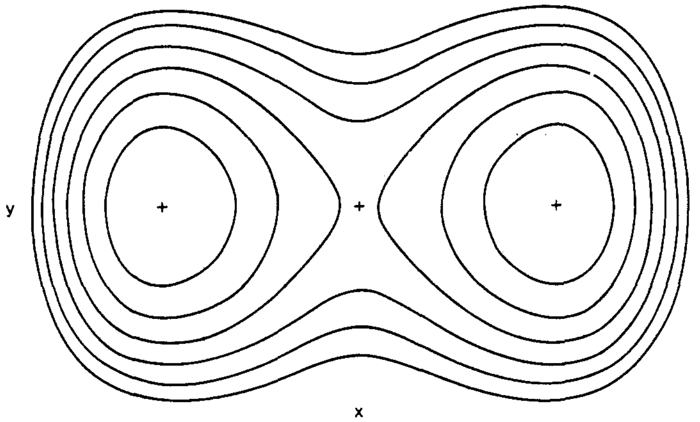


Fig. 3. Contour plot of a two-dimensional double-well potential energy surface.

elastic scattering are described semiclassically. Essentially, one computes the scattering amplitude for scattering at angle θ semiclassically, from the classical trajectory that actually scatters at θ; if more than one classical trajectory scatters at θ, one adds the semiclassical contribution for each such trajectory. Thus the scattering amplitude is given by

$$f(\theta) = \Sigma\left[\frac{b}{\sin\theta\,\Theta'(b)}\right]^{1/2} e^{i\Phi/\hbar} \qquad (9)$$

where $\Theta(b)$ is the classical scattering angle for impact parameter b. The sum in Eq. 9 is over all roots of the equation

$$\Theta(b) = \pm\theta \qquad (10)$$

that is, over all classical trajectories that arrive at angles $+\theta$ or $-\theta$; Φ is an action integral along the trajectory. Typically there are three terms in Eq. 10.

This description and its extensions allow one to understand rainbows (and supernumerary rainbows) in angular distributions, glories in the energy dependence of total cross sections, and tunneling resonances in the scattering (*44, 45*). Later extensions show how diffraction oscillations from repulsive potentials arise within this picture (*46*) and how the picture can be applied to complex potentials (*47*) (particularly in nuclear scattering) that account for loss of flux to inelastic channels. Essentially all features of elastic scattering can be described within this semiclassical framework, usually quantitatively. The theory can do such a complete job because the dynamical problem is a one-dimensional one, and, as noted for the eigenvalue problem, it is possible to deal with essentially all topologies of one-dimensional systems.

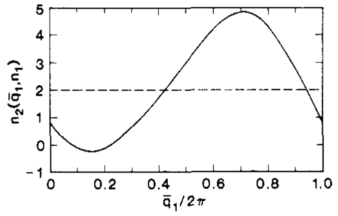
Inelastic and reactive scattering. The semiclassical picture of elastic scattering can be generalized to deal with inelastic and reactive scattering, that is, multidimensional dynamical systems (*48–50*), where classical trajectories must be computed numerically. The basic semiclassical results can be obtained from the stationary phase approximation to a Feynman path integral representation of the propagator (*51, 52*)

$$\langle \mathbf{x}_2|e^{-iH(t_2-t_1)/\hbar}|\mathbf{x}_1\rangle = \Sigma\left[(2\pi i\hbar)^F\,\frac{\partial \mathbf{x}_2}{\partial \mathbf{p}_1}\right]^{-1/2} e^{i\phi(\mathbf{x}_2,\mathbf{x}_1)/\hbar} \qquad (11)$$

where H is the Hamiltonian of the system, F is the number of degrees of freedom, and the sum is over all classical trajectories connecting position $\mathbf{x}_1$ at time t_1 and $\mathbf{x}_2$ at t_2; $\mathbf{p}$ are the momentum variables conjugate to $\mathbf{x}$ and ϕ is the action integral along the classical trajectory

$$\phi = \int_{t_1}^{t_2} dt[\mathbf{p}\cdot\dot{\mathbf{x}} - H(\mathbf{p}, \mathbf{x})] \qquad (12)$$

Fig. 4. The final vibrational quantum number (more precisely, the vibrational action variable) that results from a classical trajectory for an He + H_2 collision with a given total energy E, as a function of the initial vibrational angle variable $\bar{q}_1$. The intersection of the curve with the dashed line indicates the graphical solution of Eq. 15 for $n_2 = 2$.



The pre-exponential factor is the square root of the classical probability of the $\mathbf{x}_1 \rightarrow \mathbf{x}_2$ transition associated with the specific classical trajectory. Within this primitive semiclassical model, all quantum effects arise because the two-time boundary conditions ($\mathbf{x}_1$, $\mathbf{x}_2$) do not in general determine a single classical trajectory [in contrast to initial conditions ($\mathbf{x}_1$, $\mathbf{p}_1$), which do].

The above semiclassical expressions actually apply for any classical coordinates and momenta, and to describe inelastic scattering one chooses the initial and final variables to be the good action variables $\mathbf{n}$ (that is, the classical counterpart of the quantum numbers) for the internal degrees of freedom of the colliding molecules. Since the *S*-matrix of quantum scattering theory is directly related to the infinite time limit of the propagator, one is able to write a corresponding semiclassical approximation for it.

For a generic inelastic scattering problem, vibrational excitation, or de-excitation of a diatomic molecule by collision with an atom (*53*),

$$A + BC(n_1) \rightarrow A + BC(n_2) \qquad (13)$$

The semiclassical approximation for the *S*-matrix (the transition amplitude) has the same structure as the amplitude for elastic scattering in Eq. 9

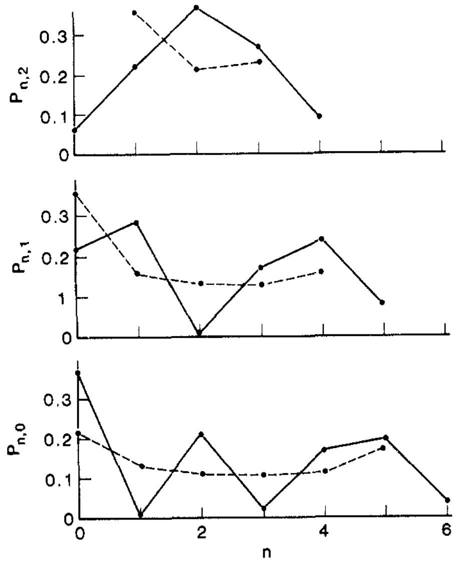
$$S_{n_2,n_1} = \Sigma[-2\pi i n_2'(q_1)]^{-1/2} e^{i\phi/\hbar} \qquad (14)$$

Here $n_2(q_1)$ is the final value of the vibrational action variable that results from a classical trajectory with the initial angle variable q_1 (and initial action variable n_1, an integer). The sum in Eq. 14 is over all roots of the equation

$$n_2(q_1) = n_2 \text{ (an integer)} \qquad (15)$$

that is, over all trajectories for which the action variable is the integer n_1 before collision and the integer n_2 after collision. The pre-exponential factor in Eq. 14 is the square root of the classical

Fig. 5. Vibrational transition probabilities for He + $H_2(n_1) \rightarrow$ He + $H_2(n_2)$ as a function of the final vibrational quantum number n_2. The points connected by the solid lines are the results of the semiclassical (and quantum mechanical) theory, whereas the dashed lines connect those of the completely classical theory, which omits interference and tunneling.



probability of the $n_1 \rightarrow n_2$ transition, and Φ is a classical action integral.

Figure 4 shows the quantum number from $n_2(q_1)$ for a simple model of a He + H_2 collision (*48*). Since it is periodic, $n_2(q_1 + 2\pi) = n_2(q_1)$, there must be an even number of roots to Eq. 15. For the simplest topology seen in Fig. 4 there are two roots, so that the transition probability has a simple interference structure

$$P_{n_2\leftarrow n_1} \equiv |S_{n_2,n_1}|^2 = P_1 + P_2 + 2\sqrt{P_1P_2}\cos\left(\frac{\Phi_2 - \Phi_1}{\hbar}\right) \qquad (16)$$

where P_k ($k = 1, 2$) are the classical transition probabilities associated with the two trajectories which contributed to the $n_1 \rightarrow n_2$ transition. Figure 5 shows typical semiclassical results compared to the classical transition probabilities.

The situation is precisely analogous to the Ford and Wheeler picture of elastic scattering (*43*): for fixed n_1, $P_{n_2\leftarrow n_1}$ of Fig. 5 is the discretized distribution of final vibrational quantum numbers, analogous to the differential cross section $\sigma(\theta)$, which is the distribution of final scattering angles. The quantum number function $n_2(q_1)$ is the analog of the classical deflection function $\Theta(b)$ of elastic scattering. The interference structure, rainbow effects, and other quantum effects seen in the differential cross sections of elastic scattering thus also exist in the distribution of final quantum states after an inelastic collision. Such effects are prominent in rotationally inelastic scattering (*54*), and their semiclassical analysis (*55*) has been important for determining the anisotropic interaction potentials that cause the inelasticity.

This classical S-matrix model has been applied to a wide variety of dynamical phenomena: vibrational and rotational inelastic scattering (*48, 56–59*), reactive scattering (*60–65*), diffraction of He atoms from crystal surfaces (*66, 67*), collisional broadening of molecular spectral lines (*68*), collision-induced dissociation (*69*), Senftleben-Beenakker effects (*70*), photodissociation (*71*), collisional depolarization and rotational relaxation in open-shell diatomic molecules (*72*), and coulomb excitation of rotational states of nuclei (*73, 74*). One can also show that discrete symmetries of a dynamical system lead to symmetries in the quantum number functions, and the resulting interference effects give the quantum selection rules (for example, even Δj transitions for rotational excitation of homonuclear diatomic molecules) (*49*). This makes the approach useful for describing weak selection rules that result when these symmetries are slightly broken (*75*).

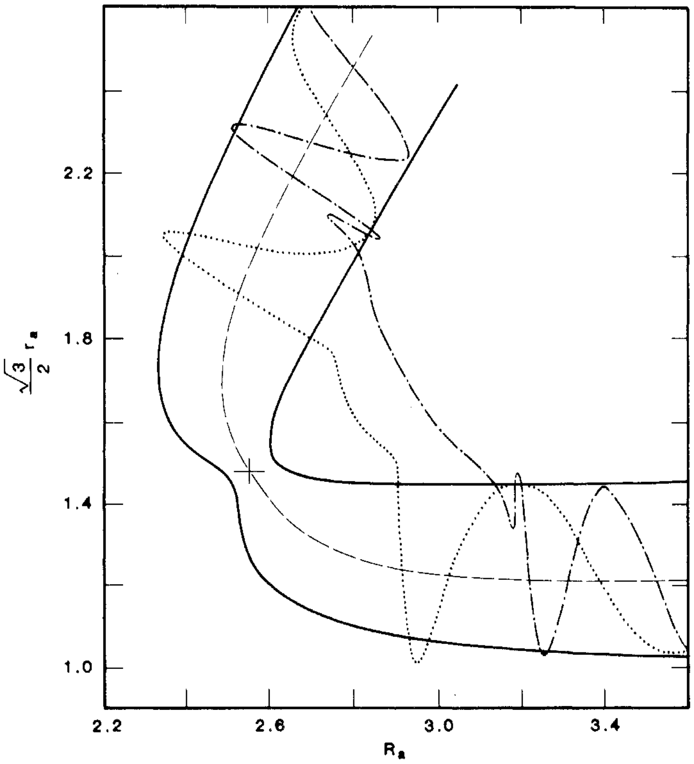


Fig. 6. Example of the tunneling trajectory for the collinear reaction H + $H_2(n_1 = 0) \rightarrow H_2(n_2 = 0)$ + H at energies below the classical threshold for reaction. Two potential energy contours are indicated as boldface lines, and the minimum energy reaction path by a dashed line. The dotted curve is the trajectory for an initial translational energy of 0.20 eV (very close to threshold), and the dash-dot curve for an initial translational energy of 0.02 eV (far below threshold). R_a and r_a are the translational and vibrational coordinates, respectively, for the H + H_2 system.

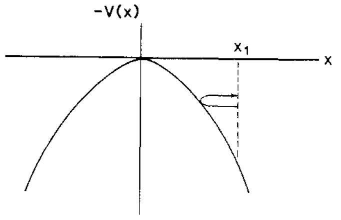


Fig. 7. Sketch of the upside-down potential function for a potential well and the classical trajectory in pure imaginary time τ that satisfies the boundary conditions $x(0) = x(\hbar\beta) = x_1$.

One can also extend the theory to describe classically forbidden processes, a kind of generalized tunneling. In Fig. 4, for example, one sees that no trajectories (at the given energy) lead to final vibrational states $n_2 = 5$ or greater, whereas in this case final states up to $n_2 = 9$ are energetically open channels. The semiclassical resolution of the situation is that there are complex roots to Eq. 15 for $n_2 > 5$, and thus complex-valued classical trajectories that satisfy the correct initial and final boundary conditions. (The classical trajectory for ordinary one-dimensional barrier tunneling has complex values; it has imaginary momentum in the classically forbidden region.) Appropriate analytic continuation gives the transition probability for such transitions as

$$P_{n_2\leftarrow n_1} = [2\pi|n_2(q_1)|]^{-1}\, e^{-2 Im\Phi/\hbar} \qquad (17)$$

where Φ is the complex-valued classical action integral along the tunneling trajectory. The structure of Eq. 17, namely, the exponential of an imaginary action in units of $\hbar$, also shows the tunneling character of these classically forbidden processes.

Tunneling is particularly important near the threshold for chemical reactions, and this analytically continued version of the classical S-matrix model is able to describe it (*60*). One significant feature seen in such calculations is how tunneling trajectories "cut the corner" from reactant to product valleys (Fig. 6). Approximate, simple-to-use analytic models based on this feature have been useful in describing tunneling corrections for a variety of chemical reactions (*76, 77*).

The classical S-matrix description is relatively simple to apply and accurate, even for several degrees of freedom, as long as the topology of the quantum number functions is simple. It is more difficult to apply and less accurate when the quantum number functions become more structured. [This is also true in elastic scattering if the deflection function $\Theta(b)$ becomes too structured, that is, has multiple maximums and minimums.] The situation is analogous to the multidimensional eigenvalue problem described above, where the essential difficulty arises when the potential energy surface is not a simple well in all dimensions. The advances made in the development of higher order, multidimensional uniform semiclassical formulas (*78–80*) to deal with these more complex topologies have been difficult undertakings since each new topology requires a new uniformization formula. The extreme limit, which is analogous to chaotic dynamics for the eigenvalue problem, occurs when the collision partners form a long-lived collision complex. Here the

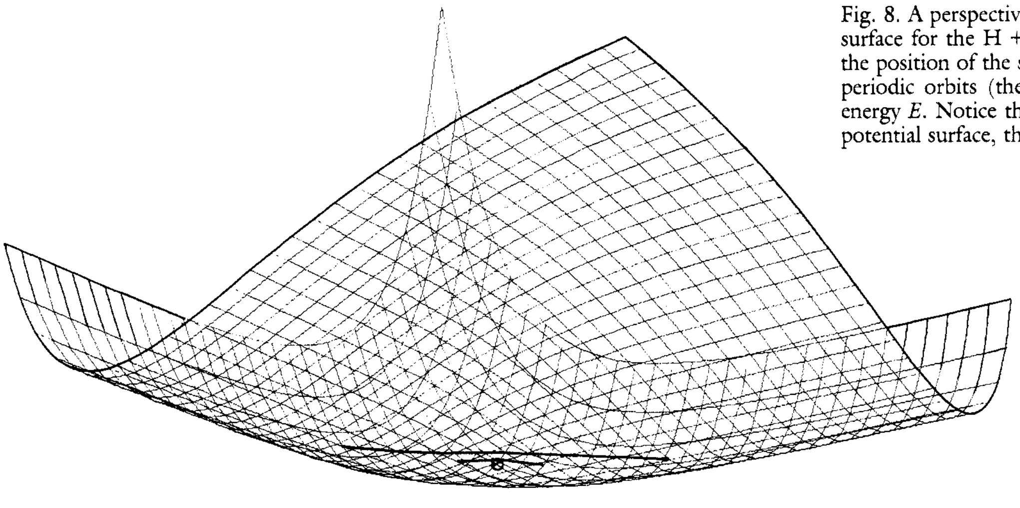


Fig. 8. A perspective view of the upside-down potential energy surface for the $H + H_2 \rightarrow H_2 + H$ reaction. The circle shows the position of the saddle point, and the two solid lines are the periodic orbits (the "instantons") for two values of the total energy E. Notice that the periodic orbit cuts the corner of the potential surface, that is, falls inside the saddle point.

quantum number function becomes an almost random function of its initial conditions (*60*), and one expects no uniformization to be able to deal with it. In such situations one usually resorts to statistical descriptions of the collision complex, which are also analogous to the use of statistical measures of spectra with chaotic dynamics.

Statistical Mechanics and Thermal Rate Constants

The semiclassical approximation to the propagator, Eq. 11, can be easily converted into one for the Boltzmann operator $e^{-\beta H}$ by the usual replacement $t \rightarrow -i\hbar\beta$. The situation is simple because the time t is pure imaginary (not complex, as for the classically forbidden processes of the previous section), and in terms of the real variable $\tau \equiv i \times t$, the classical equations of motion become (specializing to Cartesian coordinates)

$$m\frac{d^2x_k(\tau)}{d\tau^2} = +\frac{\partial V(\mathbf{x})}{\partial x_k} \tag{18}$$

They look the same as in real time with the sign of the potential changed. One thus considers classical trajectories on the upside-down potential surface.

For the equilibrium density in a one-dimensional potential well, for example, the semiclassical expression is (*81*)

$$\rho(x_1) \equiv <x_1|e^{-\beta H}|x_1> = \left[(2\pi\hbar)\left|\frac{\partial x_2}{\partial p_1}\right|\right]^{-1/2} e^{-\phi(x_1,x_1)/\hbar} \tag{19}$$

$$\phi = \int_0^{\hbar\beta} d\tau \left\{\frac{\bar{p}(\tau)^2}{2m} + V[x(\tau)]\right\} \tag{20}$$

where $\bar{p}(\tau) = -ip(\tau) = mx'(\tau)$ is a real momentum-like variable. The trajectory $x(\tau)$ along which the quantities in Eq. 19 are evaluated is one that evolves in real time in the potential $-V(x)$, such that $x(0) = x_1$ and $x(\hbar\beta) = x_1$ (Fig. 7). For any value of $\hbar\beta$ from 0 to ∞ one can find such a trajectory.

Partition functions can be computed by integrating Eq. 19 over x_1, and the results often describe the quantum effects (*82*) better than the usual Wigner-Kirkwood quantum-correction expression (*83*). The latter also implicitly makes a short imaginary time ($\hbar\beta$) expansion, whereas the semiclassical approximation, Eqs. 18 and 19, is explicitly infinite order in $\hbar\beta$.

A result that can be obtained from the semiclassical approximation to the Boltzmann operator is an expression for the thermally averaged rate constant for reaction through the saddle point of a potential energy surface (*84*). The rate is given by the Boltzmann average of the cumulative reaction probability $N(E)$ (qualitatively, the number of quantum states that react)

$$k \propto \frac{1}{2\pi\hbar}\int^{\infty} dE\, e^{-\beta E}N(E) \tag{21}$$

where the semiclassical approximation for $N(E)$ is

$$N(E) = \sum_{n_1=0}^{\infty} \dots \sum_{n_{F-1}=0}^{\infty} \{1 + \exp[\Phi_{\mathbf{n}}(E)/\hbar]\}^{-1} \tag{22}$$

with

$$\begin{aligned}\Phi_{\mathbf{n}}(E) &= \Phi(E) - \Phi'(E)\sum_{k=1}^{F-1}(n_k + 1/2)\hbar\omega_k(E)\\ &\simeq \Phi[E - \sum_{k=1}^{F-1}(n_k + 1/2)\hbar\omega_k]\end{aligned} \tag{23}$$

Here $\Phi(E)$ is the action integral along the periodic orbit that rocks back and forth through the saddle-point region on the upside-down potential energy surface (Fig. 8), and ω_k are stability frequencies characterizing this unstable periodic orbit.

This periodic orbit on the upside-down potential is essentially the "instanton" that has received much attention in elementary particle physics (*85*). This same kind of periodic orbit analysis in real time also leads to an approximation for semiclassical eigenvalues of multidimensional systems (*86–88*).

Electronically Nonadiabatic Processes

Preceding discussions have ignored dynamical aspects of the electronic degrees of freedom of the molecular system; the electrons have determined, by the Born-Oppenheimer approximation, only the potential energy function for the nuclear dynamics. In many situations, though, transitions between different Born-Oppenheimer potential energy surfaces is facile, so that a realistic classical or semiclassical simulation requires that these features be dealt with. Nonadiabatic processes are particularly relevant to collisions of open-shell atoms and molecular radicals, species that play important roles in atmospheric chemistry and in combustion.

Localized nonadiabaticity due to isolated crossings (or intersections) of Born-Oppenheimer potential curves (or surfaces) is well described by the Landau-Zener-Stuckelberg model (*89*). Here the nuclear degrees of freedom follow classical motion on the adiabatic potential curves with the probability of localized transitions (hops) from one curve to another when they cross (or come close to each

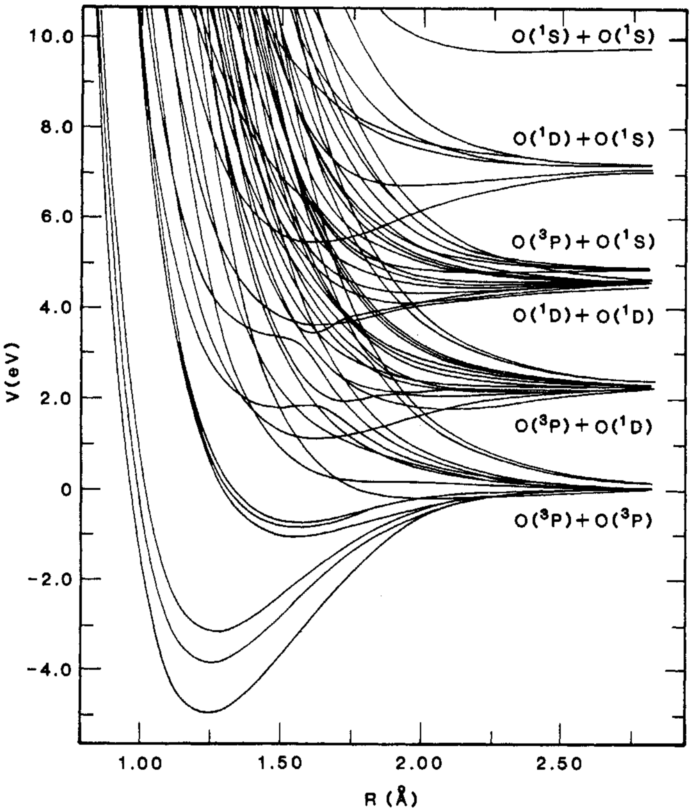


Fig. 9. All the potential energy curves that arise for the valence states (^3P, ^1D, ^1S) of two oxygen atoms, from the calculations in (*94*).

other). For atom-atom collisions, this description can be made fully semiclassical in the Ford and Wheeler sense (*52, 90*) to describe the many kinds of quantum interference features that are seen. The Tully-Preston surface-hopping model (*91*) is the classical version of the theory extended to molecular collisions, the essential feature here being that the classical mechanics must be determined numerically. A semiclassical version, in the sense discussed above, has also been developed (*92, 93*).

If many Born-Oppenheimer potential energy surfaces are strongly coupled, that is, undergo many crossings or avoided crossing with each other, the surface-hopping models begin to lose their validity. To show that this can occur, even with only two relatively light atoms, Fig. 9 shows all the diatomic potential curves that arise from the three valence states (^3P, ^1D, ^1S) of two oxygen atoms (*94*). The lowest few potential curves are well isolated, so that the adiabatic description of the dynamics in these states is appropriate, but for collisions of an $O(^3P)$ atom with an $O(^1D)$ atom, for example, one sees almost a continuum of curve crossings. For more than a two-atom system, the picture worsens and few symmetries would restrict transitions among the various potential energy surfaces.

When many states are strongly coupled, however, the spirit of Bohr's Correspondence Principle suggests the usefulness of classical mechanics. Such considerations have led to the development of models in which the many electronic states are replaced by one (or a few) classical degrees of freedom, the classical Hamiltonian for which is constructed to correspond to the manifold electronic states (*95–97*). Specifically, an electronic Hamiltonian matrix $H_{n,n'}(\mathbf{x})$ that depends on the nuclear coordinates $\mathbf{x}$ (in the Born-Oppenheimer sense) can be replaced by a classical electronic Hamiltonian function (H_{el})

$$H_{n,n'}(\mathbf{x}) \rightarrow H_{el}(\mathbf{n}, \mathbf{q}; \mathbf{x}) \tag{24}$$

where ($\mathbf{n}$, $\mathbf{q}$) are classical action-angle variables describing the collective electronic degrees of freedom. Adding in nuclear kinetic energy gives the complete classical Hamiltonian,

$$H(\mathbf{p}, \mathbf{x}, \mathbf{n}, \mathbf{q}) = \frac{\mathbf{p}^2}{2m} + H_{el}(\mathbf{n}, \mathbf{q}; \mathbf{x}) \tag{25}$$

for the electronic and nuclear degrees of freedom. Classical trajectories for the complete system can then be computed to describe the electronically nonadiabatic dynamics exactly (within this model). Semiclassical versions of the approach, which incorporate interference and tunneling, can be constructed by the methods described above (*96*).

Applications of these approaches have been made to a number of processes: collisional quenching of $F^*(^2P_{1/2})$ by H^+ and Xe (*98*), to electronic-rotational energy transfer in $F^* - H_2$ collisions (*99*), to electronic-vibrational energy transfer in $Br^* - H_2$ collisions (*100*), to electronically nonadiabatic reactive scattering ($H + LiF \rightarrow HF + Li, Li^*$) (*101*), to charge transfer in collisions ($Na + I \rightarrow Na^+ + I^-$) (*102*), to geminate recombination of I atoms (involving ten electronic potential curves) in solution (*103*), to vibronic effects in electronic spectra (*104*), to the effects of electron hole-pair excitations of surface electronic states on the dynamics of adsorbates (*105*), and to Jahn-Teller interactions near a conical intersection (*106*). Most of these have involved only a few electronic states, yet this classical model has worked reasonably well. Its greatest potential usefulness, though, is for systems that involve dynamics in a vibronic soup, for example, for clusters of metal atoms.

Concluding Remarks

In this overview I have attempted to show the pervasiveness of the semiclassical point of view in chemical and molecular physics. Semiclassical methods are an essential element in the tool kit of theorists trying to interpret, model, and simulate chemical and molecular phenomena.

One expects semiclassical theory to grow in importance as experimental methods improve to provide an even more detailed, state-resolved description of chemical dynamics. It is at the most state-specific level that quantum interference and tunneling features become most apparent. Semiclassical theory will also play an increasingly important role in interpreting the results of large, completely quantum mechanical calculations that are becoming increasingly feasible as a result of enhanced computer power. We are reaching the stage that is common in statistical mechanics, where theory is needed to understand the results of large numerical calculations. Semiclassical theory will be useful in this role.

REFERENCES AND NOTES

1. J. Bang and J. deBoer, Eds., *Semiclassical Descriptions of Atoms and Nuclear Collisions* (Elsevier, New York, 1985).
2. D. W. Noid, M. L. Koszykowski, R. A. Marcus, *Annu. Rev. Phys. Chem.* **32**, 267 (1981).
3. I. C. Percival and D. Richards, *Rev. Mod. Phys.*, in press.
4. M. S. Child, in *Theory of Chemical Reaction Dynamics*, M. Baer, Ed. (CRC Press, Boca Raton, FL, 1985), p. 247.
5. W. H. Miller, in (*1*), pp. 9–26.
6. E. J. Heller, *Acc. Chem. Res.* **14**, 368 (1981).
7. R. B. Bernstein, *J. Chem. Phys.* **34**, 361 (1961); *ibid.* **37**, 1880 (1962); *ibid.* **38**, 2599 (1963).
8. R. Düren and H. Pauly, *Z. Phys.* **175**, 227 (1963); *ibid.* **177**, 146 (1964).
9. A. Winther and J. deBoer, in *Coulomb Excitation, Perspectives in Physics*, K. Alder and A. Winter, Eds. (Academic Press, New York, 1966), p. 303.
10. G. D. Billing, *Chem. Phys.* **30**, 387 (1978); *Chem. Phys. Lett.* **75**, 254 (1980); L. L. Poulsen and G. D. Billing, *ibid.* **73**, 313 (1982); *J. Chem. Phys.* **81**, 3866 (1984).
11. R. T. Skodje, W. R. Gentry, C. F. Giese, *Chem. Phys.* **74**, 347 (1983).
12. A. E. Depristo, *J. Chem. Phys.* **78**, 1237 (1983); *ibid.* **83**, 100 (1985).

13. E. J. Heller, *ibid.* **62**, 1544 (1975); *ibid.* **65**, 4979 (1976); *ibid.* **66**, 5777 (1977); *ibid.* **67**, 3339 (1977); *ibid.* **75**, 2923 (1981).
14. N. Bohr, *Z. Phys.* **13**, 177 (1923); M. Born, *The Mechanics of the Atom* (Ungar, New York, 1960); A. Messiah, *Quantum Mechanics* (Wiley, New York, 1961), pp. 27–41.
15. E. A. Mason and L. Monchick, *Adv. Chem. Phys.* **12**, 351 (1967); W. H. Miller, *J. Chem. Phys.* **54**, 4174 (1971).
16. W. H. Miller, *J. Chem. Phys.* **48**, 1651 (1968).
17. J. N. L. Connor, *Mol. Phys.* **25**, 1469 (1973); ———, T. Uzer, R. A. Marcus, A. D. Smith, *J. Chem. Phys.* **80**, 5095 (1984).
18. Symposium on "spectroscopy and dynamics of highly vibrationally and rotationally excited polyatomic molecules" given at the annual meeting of the American Chemical Society, Chicago, 9 to 11 September 1985.
19. J. D. Doll and W. H. Miller, *J. Chem. Phys.* **57**, 4428 (1972).
20. J. G. Leopold, I. C. Percival, A. S. Tworkowski, *J. Phys. B* **13**, 1025 (1980); J. G. Leopold and I. C. Percival, *ibid.*, p. 1037.
21. P. V. Coveney and M. S. Child, *ibid.* **17**, 319 (1984).
22. W. Eastes and R. A. Marcus, *J. Chem. Phys.* **61**, 4301 (1974); D. W. Noid and R. A. Marcus, *ibid.* **62**, 2119 (1975).
23. S. Chapman, B. C. Garrett, W. H. Miller, *ibid.* **64**, 502 (1976).
24. I. C. Percival and N. Pomphrey, *J. Phys. B* **9**, 3131 (1976).
25. I. C. Percival, *Adv. Chem. Phys.* **36**, 1 (1977).
26. K. S. Sorbie and N. C. Handy, *Mol. Phys.* **32**, 1327 (1976); *ibid.* **33**, 1319 (1977).
27. R. T. Swimm and J. B. Delos, *J. Chem. Phys.* **71**, 1706 (1979).
28. C. Jaffe and W. P. Reinhardt, *ibid.* **74**, 1862 (1979).
29. C. W. Eaker and G. C. Schatz, *ibid.* **81**, 2394 (1984).
30. N. DeLeon and E. J. Heller, *ibid.* **78**, 4005 (1983).
31. W. H. Miller, *ibid.* **81**, 3573 (1984).
32. E. A. Solov'ev, *Sov. Phys. JETP* **48**, 635 (1978).
33. B. R. Johnson, *J. Chem. Phys.* **83**, 1204 (1985).
34. C. C. Martens and G. S. Ezra, *ibid.*, p. 2990.
35. N. Froman, *Ark. Fys.* **32**, 79 (1966).
36. J. N. L. Connor, *Chem. Phys. Lett.* **4**, 419 (1969).
37. B. C. Garrett, thesis, University of California (1977); W. H. Miller, *Faraday Discuss. Chem. Soc.* **62**, 40 (1977).
38. M. V. Berry and M. Tabor, *Proc. R. Soc. London Ser. A* **356**, 375 (1977).
39. P. Pechukas, *Phys. Rev. Lett.* **51**, 943 (1983); *J. Chem. Phys.* **88**, 4823 (1984).
40. G. Casati, B. V. Chirikov, I. Guarneri, *Phys. Rev. Lett.* **54**, 1350 (1985).
41. T. Yukawa, *ibid.*, p. 1883.
42. S. Datz and E. H. Taylor, in *Recent Research in Molecular Beams*, I. Estermann, Ed. (Academic Press, New York, 1959), p. 157; J. Ross, Ed., *Adv. Chem. Phys.* **10** (1966) (special issue on molecular beams).
43. K. W. Ford and J. A. Wheeler, *Ann. Phys. (N.Y.)* 7, 259 (1959); *ibid.*, p. 287.
44. R. B. Bernstein, *Adv. Chem. Phys.* **10**, 75 (1966).
45. M. V. Berry and K. E. Mount, *Rep. Prog. Phys.* **35**, 315 (1972).
46. G. E. Zahr and W. H. Miller, *Mol. Phys.* **30**, 951 (1975).
47. J. Knoll and R. Schaeffer, *Phys. Lett. B* **52**, 131 (1974).
48. W. H. Miller, *J. Chem. Phys.* **53**, 1949 (1970); *ibid.*, p. 3578.
49. R. A. Marcus, *Chem. Phys. Lett.* 7, 525 (1970); *J. Chem. Phys.* **54**, 3965 (1971).
50. W. H. Miller, *Adv. Chem. Phys.* **25**, 69 (1974); *ibid.* **30**, 77 (1975).
51. R. P. Feynman and A. R. Hibbs, *Quantum Mechanicals and Path Integrals* (McGraw-Hill, New York, 1965).
52. For an early use of path integrals in atomic and molecular collisions, see P. Pechukas [*Phys. Rev.* **181**, 166 (1969); *ibid.*, p. 174].
53. D. Secrest and B. R. Johnson, *J. Chem. Phys.* **45**, 4556 (1966).
54. D. Beck, V. Ross, W. Schepper, *Phys. Rev. A* **19**, 2173 (1979); K. Bergmann, V. Hefter, J. Witt, *J. Chem. Phys.* **72**, 4777 (1980).
55. R. Schinke and J. M. Bowman, in *Molecular Collision Dynamics*, J. M. Bowman, Ed. (Springer-Verlag, Heidelberg, 1983); R. Schinke, *J. Phys. Chem.* **90**, 1742 (1986).
56. W. H. Miller, *J. Chem. Phys.* **54**, 5386 (1971); J. D. Doll and W. H. Miller, *ibid.* **57**, 5019 (1972); C. W. McCurdy and W. H. Miller, *ibid.* **73**, 3191 (1980).
57. W. H. Wong and R. A. Marcus, *ibid.* **55**, 5663 (1971); J. R. Stine and R. A. Marcus, *ibid.* **59**, 5145 (1973); H. Kreek, R. L. Ellis, R. A. Marcus, *ibid.* **62**, 913 (1975).
58. J. W. Duff and D. G. Truhlar, *ibid.* **63**, 4418 (1975).
59. A. P. Clark, *J. Phys. B* **6**, 1153 (1973).
60. C. C. Rankin and W. H. Miller, *J. Chem. Phys.* **55**, 3150 (1977); T. F. George and W. H. Miller, *ibid.* **56**, 5722 (1972); *ibid.* **57**, 2458 (1972); J. D. Doll, T. F. George, W. H. Miller, *ibid.* **58**, 1343 (1973); S. M. Hornstein and W. H. Miller, *ibid.* **61**, 745 (1974).
61. S. F. Wu and R. D. Levine, *Mol. Phys.* **25**, 937 (1973).
62. J. M. Bowman and A. Kuppermann, *J. Chem. Phys.* **59**, 6524 (1973).
63. J. J. Tyson, R. P. Saxon, J. C. Light, *ibid.*, p. 363.
64. J. W. Duff and D. G. Truhlar, *Chem. Phys.* **4**, 1 (1974).
65. J. R. Stine and R. A. Marcus, *Chem. Phys. Lett.* **29**, 575 (1974).
66. J. D. Doll, *J. Chem. Phys.* **61**, 954 (1974); D. R. Dion and J. D. Doll, *Surf. Sci.* **58**, 415 (1976).
67. R. I. Masel, R. P. Merrill, W. H. Miller, *Phys. Rev. B* **12**, 5545 (1975); *J. Chem. Phys.* **64**, 45 (1976); *J. Vac. Sci. Tech.* **13**, 355 (1976).
68. D. E. Fitz and R. A. Marcus, *J. Chem. Phys.* **59**, 4380 (1973); *ibid.* **62**, 3788 (1975); A. F. Turfa, D. E. Fitz, R. A. Marcus, *ibid.* **67**, 4463 (1977).
69. I. Rusinek and R. E. Roberts, *ibid.* **65**, 872 (1976); *ibid.* **68**, 1147 (1978).
70. A. F. Turfa and H. F. P. Knapp, *Chem. Phys.* **62**, 75 (1981).
71. S. K. Gray and M. S. Child, *Mol. Phys.* **51**, 189 (1984).
72. G. C. Corey and A. D. Smith, *J. Chem. Phys.* **83**, 5663 (1985).
73. H. Massmann and J. O. Rasmussen, *Nucl. Phys. A* **243**, 155 (1975); H. Massmann, P. Ring, J. O. Rasmussen, *Phys. Lett.* **57B**, 417 (1975).
74. T. Koeling and R. A. Malfliet, *Phys. Rep.* **22C**, 181 (1975); S. Levit, V. Smilansky, D. Pelte, *Phys. Lett.* **53B**, 39 (1974).
75. C. W. McCurdy and W. H. Miller, *J. Chem. Phys.* **67**, 463 (1977).
76. R. A. Marcus and M. E. Coltrin, *ibid.*, p. 2609.
77. B. C. Garrett, D. G. Truhlar, A. F. Wagner, T. H. Dunning, Jr., *ibid.* **78**, 4400 (1983); B. C. Garrett and D. G. Truhlar, *ibid.* **79**, 4931 (1983).
78. R. A. Marcus, *ibid.* **57**, 4903 (1972); H. Kreek, R. L. Ellis, R. A. Marcus, *ibid.* **61**, 4540 (1974).
79. J. N. L. Connor, *Mol. Phys.* **25**, 181 (1973); *ibid.* **26**, 1371 (1973); *ibid.* **27**, 853 (1974); *ibid.* **31**, 33 (1976).
80. T. Uzer and M. S. Child, *ibid.* **46**, 1371 (1982); T. Uzer, J. T. Muckerman, M. S. Child, *ibid.* **50**, 1215 (1983).
81. W. H. Miller, *J. Chem. Phys.* **55**, 3146 (1971); *ibid.* **58**, 1664 (1973).
82. R. M. Stratt and W. H. Miller, *ibid.* **67**, 5894 (1977).
83. E. P. Wigner, *Phys. Rev.* **40**, 749 (1932); H. S. Green, *J. Chem. Phys.* **19**, 955 (1951); T. Kihara, Y. Midzuno, T. Schizume, *J. Phys. Soc. Jpn.* **10**, 249 (1955).
84. W. H. Miller, *J. Chem. Phys.* **62**, 1899 (1975); S. Chapman, B. C. Garrett, W. H. Miller, *ibid.* **63**, 2710 (1975).
85. S. Coleman, *Phys. Rev. D* **15**, 2929 (1977); C. G. Callan, Jr., and S. Coleman, *ibid.* **16**, 1762 (1977); J. P. Sethna, *Phys. Rev. B* **25**, 5050 (1982); A. O. Caldeira and A. J. Leggett, *Ann. Phys. (NY)* **149**, 374 (1983).
86. M. G. Gutzwiller, *J. Math. Phys.* **12**, 343 (1971).
87. W. H. Miller, *J. Chem. Phys.* **63**, 996 (1975).
88. R. F. Dasher, B. Hasslacher, A. Neveu, *Phys. Rev. D* **10**, 4114 (1974).
89. L. D. Landau, *Phys. Z. Sowjetunion* **2**, 46 (1932); C. Zener, *Proc. R. Soc. London Ser. A* **137**, 696 (1932); E. C. G. Stuckelberg, *Helv. Phys. Acta* **5**, 369 (1932).
90. R. E. Olson and F. T. Smith, *Phys. Rev. A* **3**, 1607 (1971).
91. J. C. Tully and R. K. Preston, *J. Chem. Phys.* **55**, 562 (1971).
92. W. H. Miller and T. F. George, *ibid.* **56**, 5637 (1972).
93. J. P. Davis and P. Pechukas, *ibid.* **64**, 3129 (1976).
94. R. P. Saxon and B. Liu, *ibid.* **67**, 5432 (1977).
95. W. H. Miller and C. W. McCurdy, *ibid.* **69**, 5163 (1978).
96. H. D. Meyer and W. H. Miller, *ibid.* **70**, 3214 (1979).
97. R. L. Whetton, G. S. Ezra, E. R. Grant, *Annu. Rev. Phys. Chem.* **36**, 277 (1985).
98. C. W. McCurdy, H. D. Meyer, W. H. Miller, *J. Chem. Phys.* **70**, 3177 (1979).
99. H. D. Meyer and W. H. Miller, *ibid.* **71**, 2156 (1979).
100. A. E. Orel, D. P. Ali, W. H. Miller, *Chem. Phys. Lett.* **79**, 137 (1981); D. P. Ali and W. H. Miller, *ibid.* **103**, 470 (1984).
101. W. H. Miller and A. E. Orel, *J. Chem. Phys.* **74**, 6075 (1981).
102. S. K. Gray and W. H. Miller, *Chem. Phys. Lett.* **93**, 341 (1982).
103. D. P. Ali and W. H. Miller, *J. Chem. Phys.* **78**, 6640 (1983); *Chem. Phys. Lett.* **105**, 501 (1984).
104. H. D. Meyer, *Chem. Phys.* **82**, 199 (1983).
105. J. C. Tully, personal communication.
106. J. W. Zwanziger *et al.*, *Chem. Phys. Lett.* **120**, 106 (1985).
107. Supported by the Department of Energy under contract DE-AC03-76SF00098 and by NSF grant CHE84-16345.