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CHAPTER 8

NON-BORN–OPPENHEIMER CHEMISTRY: POTENTIAL SURFACES, COUPLINGS, AND DYNAMICS

Ahren W. Jasper
Department of Chemistry, University of Minnesota,
Minneapolis, MN 55455, USA

Brian K. Kendrick
Theoretical Division, Los Alamos National Laboratory,
Los Alamos, NM 87545, USA

C. Alden Mead
92 Bartram Road, Savannah, GA 31411, USA

Donald G. Truhlar
Department of Chemistry, University of Minnesota,
Minneapolis, MN 55455, USA
E-mail: truhlar@umn.edu

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1. Introduction

In a famous 1938 paper, Wigner wrote: "It seems that one can divide the elementary reactions into three groups. I would class into the first group those that do not change either the electronic quantum numbers of the colliding particles nor their chemical formula.... In the second group one could class all reactions which involve no jump in the electronic quantum numbers but change the chemical constitution.... The remaining third class deals with reactions which involve a jump in the electronic structure.... It is clearly the most general type and probably the most difficult of all."[1]

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The present chapter is concerned with this difficult third class; we call this area of chemistry "non-Born–Oppenheimer chemistry" in recognition of the classic work of Born and Oppenheimer[2] in analyzing the basis for the separation of electronic and nuclear motion when there is no change in the electronic quantum numbers. Collisions that either conserve or change the electronic quantum numbers are called electronically adiabatic and electronically nonadiabatic, respectively.

The work of Born and Oppenheimer[2] and later Born[3] and Born and Huang[4] developed the foundation for the separation of electronic and nuclear motion that underlies the modern theory of electronically adiabatic processes, and they also worked out the leading nonadiabatic coupling terms (NACTs). Section 2 begins by reviewing this fundamental theory for both electronically adiabatic and electronically nonadiabatic processes. A special topic that dominates many aspects of the considerations is the question of intersections of adiabatic potential energy surfaces, especially conical intersections. The key role of conical intersections in many photochemical processes was pointed out by Teller[5] in 1937.

Section 2 also presents a general multi-state approach that may be used to treat a wide variety of processes; this is called the generalized Born–Oppenheimer approximation. An important practical issue in the use of the generalized Born–Oppenheimer approximation is the choice of electronic basis states used to span the generalized Born–Oppenheimer finite electronic state space. Although the adiabatic electronic states are uniquely defined and are very useful for defining the space, they sometimes present practical difficulties when used for dynamics calculations because the NACTs that provide the coupling between electronically adiabatic states are multidimensional vectors with singularities, and they involve inconvenient differentiation of the electronic wave functions with respect to nuclear coordinates. These practical difficulties are not insuperable, and many useful calculations and discussions are based on the adiabatic representation. Nevertheless, there is also considerable interest in so-called diabatic bases in which the state coupling is dominated by nonsingular scalars that do not require the inconvenient differential operators mentioned above. Thus the final main subject of Sec. 2 is the question of adiabatic-to-diabatic transformations. The use of diabatic states is already implicit in the oldest dynamical theories of electronically nonadiabatic collisions,[6–8] but their systematics have been more slow in development.[9–38]

With potential energy surfaces and their couplings in either the adiabatic or the diabatic representation in hand, one may proceed to modeling or calculating the dynamics. In most cases an accurate quantum mechanical dynamical treatment is not computationally affordable or is otherwise not suitable, and one employs approximate "semiclassical" methods where the full dynamics of the system is approximated in some way using classical ideas.[39–41] Semiclassical mechanics may be rigorously defined as the small-$\hbar$ (or large-mass, high-temperature, etc.) limit of quantum mechanics, and semiclassical algorithms are often presented in this way. More often, however, semiclassical methods are obtained using the more intuitive procedure of incorporating quantum effects *ad hoc* into classical theories. Although semiclassical algorithms presented in this way may not be rigorously justified, the theoretical importance of the work lies in its ability to provide a physical picture (i.e., a language) for interpreting elusive quantum mechanical phenomena. The semiclassical picture that is provided aids in interpreting experimental results and in the search for more accurate approximate methods. Semiclassical methods for non-Born–Oppenheimer collisions have a long history.[6–8,42–46] The semiclassical approach is important from a practical point of view because it can be readily applied to large systems. It is likely that a fully-dimensional quantal treatment of a chemical system with more than a few atoms and a few electronic states will remain prohibitively expensive for some time, leaving semiclassical methods the task of modeling the bulk of chemically interesting phenomena. In Sec. 3.1, we describe several semiclassical trajectory methods that have been validated against accurate quantum mechanical results for realistic chemical systems. Specifically, we consider the time-dependent self-consistent field method, the trajectory surface hopping method, wave packet spawning, and their variants.

For systems with only two[17] or three[47–74] atoms, it is possible to solve the nuclear-motion Schrödinger equation accurately, for example, by propagating the solution of time-independent coupled-channel equations as a function of a radial[17,19,47–49] or hyperradial[50–52,55–58] coordinate, by a time-independent linear algebraic variational method,[59–74] or by propagating wave packets as a function of both time and coordinates.[53,54,75–79] Accurate quantum mechanical solutions for nuclear motion on coupled potential energy surfaces are of great fundamental interest, and they are also important for providing benchmark results that can be used to test semiclassical solutions. The use of accurate quantum dynamical methods to treat nuclear motion on coupled potential energy surfaces is discussed in Sec. 3.2.

2. Born–Oppenheimer Electronic Potential Energy Surfaces and Their Interactions

2.1. *The Born–Oppenheimer Expansion*

2.1.1. *Fundamentals*

Consider a molecular system with electronic coordinates designated collectively by r and nuclear coordinates designated by R, with an individual nuclear coordinate denoted by x_μ, x_ν, etc. The nuclear configuration space will be called $\Re$. We will use atomic units, in which the unit of length is the bohr, and the unit of energy is the hartree (twice the ionization energy of the ground-state hydrogen atom). In these units, the electronic mass, Dirac's $\hbar$, and the electronic charge are all unity, so that, in the nonrelativistic, spin-free case, the only parameters remaining in the Schrödinger equation are the masses of the various nuclei. We use mass-scaled coordinates in which all distances are scaled to the same reduced mass M, which is assumed to be the mass of the lightest nucleus in the molecule. The nonrelativistic, spin-free Schrödinger equation for the system may then be written symbolically as

$$\left\{-\frac{1}{2M}\nabla_R^2 + \hat{H}_{el}(R,r)\right\}\Psi(R,r) = E\Psi(R,r). \tag{1}$$

In Eq. (1), the Laplacian extends over all nuclear coordinates. The "electronic" Hamiltonian $\hat{H}_{el}(R,r)$ consists of all the terms in the Hamiltonian except nuclear kinetic energy, including the electronic kinetic energy as well as the electron–electron, electron–nuclear, and nuclear–nuclear interactions. The only parameter appearing in (1) is the nuclear mass M, and in atomic units M can be considered to be a large number, at least 1800. Thus, quantities calculated from Eq. (1) that are proportional to some negative power of M will normally be small in some sense, and those proportional to positive powers of M will be large, while quantities independent of M will be neither particularly large nor small, but *a priori* of order of magnitude unity.

In the method of Born and Oppenheimer,[2] as further developed by Born and Huang,[3,4] one makes use of the smallness of $1/M$ to obtain an approximate treatment which has been the basis for nearly all molecular theory to date. First, one treats $\hat{H}_{el}(R,r)$ as an operator in the electronic space depending parametrically on R and formally obtains its complete set of eigenfunctions $\phi_j(R,r)$ and eigenvalues $U_j(R)$:

$$\hat{H}_{el}(R,r)\phi_j(R,r) = U_j(R)\phi_j(R,r), \tag{2}$$

where the eigenfunctions $\phi_j(R,r)$ are required to be normalized in the electronic space for all R:

$$\int \phi_j^*(R,r)\phi_k(R,r)dr \equiv \langle j(R)|k(R)\rangle = \delta_{jk}. \tag{3}$$

The electronic eigenfunctions satisfying Eqs. (2) and (3) are called adiabatic electronic basis functions.

One then expands the full wave function $\Psi(R,r)$ as

$$\Psi(R,r) = \sum\nolimits_j \psi_j(R)\phi_j(R,r), \tag{4}$$

which on insertion into (1) yields the well-known coupled equations for the nuclear-motion wave functions $\psi_j(R)$:

$$\begin{aligned}&\left\{-\frac{1}{2M}\nabla^2 + U_j(R)\right\}\psi_j(R) + \sum\nolimits_k \left\{-\frac{1}{M}\vec{F}_{jk}(R)\cdot\nabla - \frac{1}{2M}G_{jk}\right\}\psi_k(R)\\ &\quad = E\psi_j(R)\end{aligned} \tag{5}$$

where

$$\vec{F}_{jk}(R) = \int \phi_j^*(R,r)\nabla_R\phi_k(R,r)\,dr \equiv \langle j(R)|\nabla k(R)\rangle; \tag{6}$$

$$G_{jk}(R) = \int \phi_j^*(R,r)\nabla_R^2\phi_k(R,r)\,dr \equiv \langle j(R)|\nabla^2 k(R)\rangle. \tag{7}$$

[The gradient operator is, like the Laplacian, multidimensional in the whole space $\Re$. Note that we sometimes omit the subscript R on the gradient and Laplacian operators where the function to which the operator is applied depends only on R.] Note that the sum in Eq. (5) contains both diagonal and off-diagonal terms, and that neglect of the off-diagonal terms would break Eq. (5) down into uncoupled Schrödinger equations, one for each electronic state j, with the $U_j(R)$ playing the role of effective nuclear potential energy functions, and therefore $U_j(R)$ is called a potential energy surface. We can also define matrices $\vec{\mathbf{F}}(R)$ [with components $\mathbf{F}_\mu(R)$] and $\mathbf{G}(R)$ with elements $\vec{F}_{jk}(R)$ [components $F_{\mu,jk}(R)$] and $G_{jk}(R)$. The quantities $F_{\mu,jk}$ and G_{jk} arise from the operation of nuclear momentum operators on electronic wave functions. The matrices $\vec{\mathbf{F}}(R)$ and $\mathbf{G}(R)$ are called nonadiabatic coupling matrices (NACMs). In Eq. (5), all NACMs are multiplied by the small quantity $1/M$, and we will refer to terms containing NACMs and a reciprocal of M as nonadiabatic coupling terms (NACTs). It should be clear that neglect of the terms containing NACMs is the mathematical translation of neglecting nuclear motion on the time scale of electronic

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In actually evaluating the NACMs, one must be careful in treating the origin of the electronic coordinates consistently.[6,80,81]

By differentiating Eq. (3) and making use of relations such as $\langle j(R)|\nabla k(R)\rangle = \langle \nabla k(R)|j(R)\rangle^*$ one easily obtains the following relations between the NACMs:

$$\vec{\mathbf{F}} + \vec{\mathbf{F}}^\dagger = 0; \tag{8}$$

$$\mathbf{G} + \mathbf{G}^\dagger + 2\vec{\mathbf{F}} \cdot \vec{\mathbf{F}} = 0; \tag{9}$$

$$\nabla \cdot \vec{\mathbf{F}} = \mathbf{G} + \vec{\mathbf{F}}^\dagger \cdot \vec{\mathbf{F}}; \tag{10}$$

$$(2\vec{\mathbf{F}} \cdot \nabla + \mathbf{G})^\dagger = 2\vec{\mathbf{F}} \cdot \nabla + \mathbf{G}; \tag{11}$$

$$\frac{\partial}{\partial x_\mu}\mathbf{F}_\nu - \frac{\partial}{\partial x_\nu}\mathbf{F}_\mu + [\mathbf{F}_\mu, \mathbf{F}_\nu] = 0, \tag{12}$$

where in obtaining Eq. (11) we have also made use of the anti-Hermitian character of the gradient operator.

With the aid of Eq. (10), the Schrödinger equation, Eq. (5), can be recast as follows:

$$\left\{\frac{1}{2M}[\vec{p} + \vec{\mathbf{A}}(R)]^2 + \mathbf{U}(R)\right\} |\Psi(R)\} = E|\Psi(R)\}, \tag{13}$$

where $\mathbf{U}(R)$ is the diagonal potential energy matrix with elements $U_j(R)$, $|\Psi(R)\}$ is a column vector with elements $\psi_j(R)$, $\vec{p} = -i\nabla$ is the nuclear momentum operator, and $\vec{\mathbf{A}}(R) = -i\vec{\mathbf{F}}$. It will be of importance later [in particular, in Eqs. (15) and (16)] that $\vec{\mathbf{A}}(R)$ appears to formally play the role of a vector potential, and in fact we have formulated Eq. (13) in terms of $\vec{\mathbf{A}}$ instead of $\vec{\mathbf{F}}$ precisely to emphasize that analogy.

2.1.2. *Hierarchy of Terms*

In the Born–Oppenheimer (BO) procedure, one takes advantage of the relative smallness of $1/M$ to obtain the leading terms in an asymptotic expansion[82,83] of the molecular wave function, energy, and other quantities of interest in powers of the small BO parameter $\kappa = (1/M)^{1/4}$. Here we present just a sketch of the procedure, referring the reader to the literature[2,4,84,85] for more details.

The NACM elements $F_{\mu,jk}$ and G_{jk} appearing in Eq. (5) are independent of κ and hence *a priori* of order of magnitude unity. However, they appear multiplied by $\kappa^4 = 1/M$, so there is hope that the contribution of these terms will be small. Therefore, we will provisionally neglect them, later estimating the magnitude of their contribution. At first we restrict our attention to low-lying states of a quasi-rigid molecule undergoing small vibrations about an equilibrium position.

With our provisional neglect of the NACTs, we can isolate a single electronic state, say state 0. The nuclear coordinates can be separated into translational and rotational coordinates that do not affect the potential energy and the internal (vibrational) coordinates upon which the potential energy U_0 depends. Assuming that U_0 has a minimum (equilibrium configuration), we take this as our origin and expand the potential energy in the neighborhood of the origin as a power series:

$$U_0(R) = U_0(0) + \frac{1}{2}\sum k_{\mu\nu}x_\mu x_\nu + \frac{1}{6}\sum k_{\mu\nu\sigma}x_\mu x_\nu x_\sigma + \cdots . \qquad (14)$$

The coefficients in the expansion (14) do not depend on κ, and their magnitude is thus considered to be of the order of unity. Keeping for the moment only the quadratic terms, we can find the normal modes, and are left with a series of uncoupled harmonic oscillators, each equivalent to a particle of mass $\sim M$ in a harmonic potential whose force constant is of the order of unity. In this approximation, then, the energy is just $U_0(0)$ plus a vibrational energy proportional to $\omega = \sqrt{k/M} \propto \kappa^2$. The rotational energy may be estimated by fixing the nuclei at the origin, and this energy is proportional to $1/M \propto \kappa^4$. According to standard harmonic oscillator theory, excursions from the origin are of order of magnitude κ meaning that corrections due to anharmonic terms in the potential energy and to vibrational–rotational interaction are also of higher order in κ.

What about the effect of the NACTs neglected up to now? The magnitude of these terms can be estimated using perturbation theory. Matrix elements of $\vec{\mathbf{F}}$ and $\mathbf{G}$ may also be expanded about the origin, with the leading terms equal to the values at the origin. The corrections to these terms will be higher order in κ because of the excursions being proportional to κ. Diagonal terms in $\vec{\mathbf{F}} \cdot \nabla$ will vanish in lowest order because diagonal elements of ∇ do so. There is a correction to the energy due to the diagonal part of $\mathbf{G}$, but this is proportional to κ^4 and is just a constant to this order. As for the off-diagonal part of $\vec{\mathbf{F}} \cdot \nabla$, this can be estimated by perturbation theory. The term couples a rovibrational state of one electronic level to another such state of another electronic level. Matrix elements of ∇ between vibrational states are proportional to $1/\kappa$, again because of the excursions being of order κ, and the whole thing is multiplied by κ^4. Thus, the matrix element is of order κ^3, with an energy denominator of order

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unity, resulting in a correction to the wave function of order κ^3 and to the energy of order κ^6.

To lowest order in κ, therefore, one is justified not only in neglecting the NACTs, but also in making the harmonic approximation for vibration and neglecting rotation–vibration interaction. This gives the wave function to zero order in κ and the energy through second order. To get the energy through fourth order, one must include a constant contribution from the diagonal elements of $\mathbf{G}$ (independent of vibrational and rotational quantum numbers), the first-order contribution of the quartic term in the potential energy, and the second-order contribution of the cubic term. Further corrections due to the NACTs and to higher-order anharmonicity and vibration–rotation interaction are of higher and higher order in κ. Thus, in making further corrections, it is in general necessary to consider all of these effects simultaneously. However, it often happens that different kinds of corrections, though of the same order in κ, depend differently on the quantum numbers. For instance, the energy correction due to the off-diagonal elements of $\vec{\mathbf{F}} \cdot \nabla$ is of sixth order, as is the second-order contribution of the quartic term in the potential energy; but the latter depends on the vibrational quantum number through the fourth power, the former only through the first. Thus, the $\vec{\mathbf{F}} \cdot \nabla$ coupling to this order furnishes an effective correction to the vibrational frequency, while the anharmonic term gives corrections of the sort more normally associated with anharmonicity.

In dealing with degrees of freedom other than vibrational, the main differences are the absence of analogs of the anharmonic corrections and the fact that the contribution of the gradient operator is not necessarily of order $1/\kappa$. For rotational degrees of freedom the contribution of the gradient operator is normally of order unity, while for translational degrees of freedom such as those that appear in scattering problems, its magnitude depends on that of actual nuclear momenta appearing in the problem. In most cases, this results in the contribution of the NACTs being of *higher* order in κ than is the case with vibrational degrees of freedom. Consider, for example, the generalization to scattering states and metastable states (such as those important for many unimolecular reactions and photodissociation processes). When the nuclear kinetic energy is low, the NACMs are of the order of magnitude of unity, just as for low-energy vibrational states. However, if the nuclear velocity is increased by a factor on the order of κ^2 (corresponding, for a proton or hydrogen atom, to a nuclear kinetic energy in excess of 10 keV), then the nuclear wave function varies rapidly with position and the $\vec{F}_{jk}$ factor in Eq. (5) is multiplied by a $\nabla\psi_k$ factor that is greater than unity by one or more orders of magnitude; in such a case the term containing $\vec{F}_{jk}$ is no longer negligible.

In summary, in the usual cases where the NACM is of order unity in atomic units, we are justified in neglecting the NACTs for low-energy bound states and low-energy dynamical processes, such as "slow collisions" but not for very high-energy collisions. As we will see below, the other case where the BO approximation is expected to fail is when $\vec{F}_{jk}$ itself is large. Then the BO approximation may fail even for low-energy nuclear motion states.

The above approach enables one to classify contributions to the wave function, energy, etc. according to the power of κ contained in each term. Thus, in the limit $\kappa \to 0$, the lowest-order terms dominate. In practice, κ can have values as large as about 0.15, so it is quite possible in a particular case for the coefficients to be such that, e.g. a given term proportional to κ^6 might be larger than another one proportional to κ^4.

2.2. *The Born–Oppenheimer Approximation*

In practice, based on the reasoning in Sec. 2.1, one often uses the term "Born–Oppenheimer approximation" to mean the one-state approximation, i.e. the neglect of all off-diagonal terms involving $\vec{\mathbf{F}}$ and/or $\mathbf{G}$, usually neglecting diagonal terms as well. All effects due to the off-diagonal $\vec{\mathbf{F}}$ and $\mathbf{G}$ terms are then called "BO corrections." We will adhere to this tradition, which usually results in a useful and accurate approximation. However, in calculating any effects that turn out to become small for small κ, one should never take for granted the justification for ignoring the BO corrections.

2.2.1. *Effective Schrödinger Equation*

If off-diagonal coupling is neglected, the coupled Eq. (5) or (13) become decoupled, and one can confine oneself to a single electronic state, say state 0. The nuclear wave function ψ_0 obeys the effective Schrödinger equation

$$\frac{1}{2M}\left\{(\vec{p}+\vec{A}_{00})^2+\sum_{k\neq 0}\vec{A}_{0k}\cdot\vec{A}_{k0}\right\}\psi_0+U_0\psi_0=E\psi_0. \tag{15}$$

In using Eq. (15), many workers omit the terms containing $\vec{A}$ matrix elements, while some include only the diagonal part. One sees that $\vec{A}_{00}$ behaves like an electromagnetic vector potential, while the summation over off-diagonal elements has the effect of a small correction (proportional to κ^4) to the potential energy U_0.

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The electronic eigenfunction ϕ_0 must obey Eqs. (2) and (3), but still may be subject to the transformation

$$\phi_0(R,r) \rightarrow \phi_0(R,r)e^{ig(R)}, \tag{16}$$

where $g(R)$ is any real function of R. The transformation (16) leaves (15) unchanged, except that the vector potential $\vec{A}_{00}$ undergoes the transformation

$$\vec{A}_{00} \rightarrow \vec{A}_{00} + \nabla g, \tag{17}$$

which is identical to a gauge transformation in electromagnetic theory. The transformation given by Eqs. (16) and (17) is thus often called a gauge transformation. As in electromagnetic theory, the gauge may be chosen for convenience in any particular problem.

Equation (15), together with appropriate boundary conditions, is an effective Schrödinger equation for the nuclear motion.

2.2.2. *Dependence of Electronic Wave Function on Nuclear Coordinates: Geometric Phase*

Up to now, we have omitted effects of electronic spin entirely. Nuclear spin will be neglected throughout. If spin is neglected, each electronic eigenfunction ϕ_j can be split into a spin part which plays no role in the calculation and an orbital part which can be chosen real. (That is, the eigenvalue equation that it satisfies does not require it to be complex, though it may be made complex through a gauge transformation. If this is done, the phase of the wave function still depends only on the nuclear coordinates.) If spin is included, the most important effect is the spin-orbit interaction, which in atomic units is proportional to the square of the fine structure constant, about 137^{-2} or roughly of order κ^4 for typical values of κ. Thus, although it is a small effect, it is likely to be larger than the BO corrections, and it is not inconsistent to include it within the one-state BO treatment.

If spin is included, one must distinguish between two cases: an even number of electrons with integer total electronic spin and an odd number of electrons with half-odd integer electronic spin. In the former case, it is a consequence of time-reversal invariance[86–89] that the electronic eigenfunctions can still in effect be chosen real, i.e. that all matrix elements of real operators are real. The case of an odd number of electrons with inclusion of spin is more complicated and will be discussed briefly in Sec. 2.5.

If the electronic wave function is chosen real, then it is defined up to an overall sign change by Eqs. (2) and (3) plus the reality condition.

Now imagine that the nuclear coordinates R are made to move continuously along a closed curve C in $\Re$. At each point along C, the electronic eigenfunction ϕ_j must satisfy Eqs. (2) and (3), and it also must vary smoothly and continuously with R. This still leaves open the possibility of a smoothly and continuously varying phase factor (gauge transformation) (16), but this is fixed if one also requires that ϕ_j remain real. When R has returned to its starting point, ϕ_j satisfies the same eigenvalue equation as at the beginning, is still normalized, and is still real, so it must be the same function as before, *except for a possible sign change*. The possibility of a sign change was recognized early on by Longuet-Higgins and coworkers,[90,91] and has later been recognized as a special case of the *geometric phase*, which has been of much interest in recent decades.[92–95]

If a sign change is possible, then (for each electronic eigenstate j) the set of closed curves in $\Re$ splits into two classes: Positive (+) curves in which no sign change occurs and negative (−) ones in which there is a sign change. Moreover, if a curve is continuously distorted, it can never change gradually from + to −; the change must be abrupt and discontinuous if it occurs at all. The situation is shown schematically in Fig. 1. Curve A is positive and curve B negative, even though they differ only infinitesimally from one another. If one goes counterclockwise around B and then clockwise around A, the net effect is a sign change, and also a traversal of the infinitesimally small curve enclosing the shaded area, which is therefore negative. The locus of the limit points of such infinitesimally small negative curves we call a *transition manifold* $\Im$. To determine the dimensionality of a transition manifold assuming that $\Re$ is of dimension n, consider an infinitesimally small negative circle, which with appropriate choice of coordinates may be

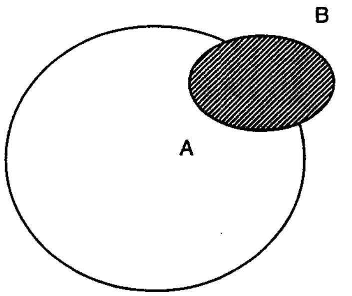

Fig. 1. The inside curve (A) is positive, and curve B on the outside is negative, even though they differ only by the infinitesimal curve enclosing the shaded area. This infinitesimal curve must therefore also be negative.

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described by $u = d\cos\theta$, $v = d\sin\theta$ (d very small). The center of the circle is a point in $\Im$, and it can be taken as the origin, with all coordinates set equal to zero. In the small neighborhood of the origin, then, what is the dimensionality of $\Im$? If it is of a dimension less than $(n-2)$, then it may be described in this neighborhood by the equations $u = v = w = \ldots = 0$. But if this is true, then the circle, while remaining in the uvw space, may be continuously deformed into a curve not encircling any part of $\Im$, and without crossing any part of $\Im$ in the process. On the other hand, if $\Im$ is of dimension more than $(n-2)$, then it either covers the entire space or divides it into two parts, and curves do not encircle it but are contained within it, or intersect it, etc. We conclude that *transition manifolds are of dimension* $(n-2)$.

2.3. *Conical Intersections and Geometric Phases*

2.3.1. *Conditions for Degeneracy*

The eigenvalues of $\hat{H}_{el}(R, r)$ do not depend on κ, so in general they, and differences between them, are of order unity in atomic units. Nevertheless, degeneracies can occur in submanifolds of $\Re$, and we will now investigate the conditions for these. In the well-known derivation, one first assumes that two states, say 1 and 2, are at least very nearly degenerate, so that in a small neighborhood the electronic Hamiltonian can be reduced to just the submatrix involving these two states. One can then choose a point at which states 1 and 2 are very nearly degenerate, take the eigenstates *at that point* as basis functions (not allowed to move with the nuclei in the small neighborhood), and consider the two-by-two effective Hamiltonian:

$$\hat{H}_{el}(R) = H_0(R)\mathbf{I} + \begin{pmatrix} u(R) & v(R) \\ v(R) & -u(R) \end{pmatrix}, \tag{18}$$

where $\mathbf{I}$ denotes the unit matrix, $H_0(R)$ is half the trace of the matrix, and $u(R)$ is half the difference between its diagonal elements. (We are continuing to assume that all matrix elements can be chosen real.) Evidently, the eigenvalues of the Hamiltonian (18) will be degenerate if and only if $u(R) = v(R) = 0$, meaning that R must satisfy *two* conditions in order for degeneracy to occur. In the case of diatomics, where the only "internal" coordinate (coordinate other than translation and rotation) on which the electronic energy depends is the internuclear distance, this leads to the well-known noncrossing rule for states of the same symmetry. For molecules with more than two nuclei, the number of internal coordinates is $3N-6$, where

N is the number of nuclei. Thus, for triatomic systems there can be degeneracy on a curve in the three-dimensional internal space, in tetratomics on a four-dimensional submanifold in the six-dimensional internal space, etc. The noncrossing rule and generalizations thereof have been discussed most thoroughly and elegantly by Longuet-Higgins,[96] with some further elaborations given by one of us.[89]

2.3.2. *Electronic Energy Eigenvalues and Eigenfunctions Near a Degeneracy: Conical Intersection Manifolds as Transition Manifolds*

To investigate the eigenvalues and eigenfunctions in the near neighborhood of a degeneracy, let us consider a polyatomic system and select as our origin a point in the manifold $u(R) = v(R) = 0$. Since this origin has been selected only based on the vanishing of u and v, it would be an improbable coincidence for either u or v to have vanishing gradient or for their gradients to be parallel. Accordingly, let x and y be a coordinates in the direction of the gradients of u and v, respectively. In the small neighborhood of the origin, therefore, the Hamiltonian has the form

$$\hat{H}_{el}(R) = H_0(R)\mathbf{I} + \begin{pmatrix} ax & by \\ by & -ax \end{pmatrix} \equiv H_0(R)\mathbf{I} + d\cdot\begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}. \tag{19}$$

The eigenvalues of this Hamiltonian are

$$E = H_0(R) \pm d, \tag{20}$$

with eigenfunctions

$$\begin{pmatrix} \cos\dfrac{\theta}{2} \\ \sin\dfrac{\theta}{2} \end{pmatrix}; \quad \begin{pmatrix} -\sin\dfrac{\theta}{2} \\ \cos\dfrac{\theta}{2} \end{pmatrix}. \tag{21}$$

In examining Eqs. (20) and (21), one notes first that the separation between the eigenvalues increases *linearly* with the distance from the degeneracy manifold. For this reason intersections of this kind are called conical intersections. They are to be distinguished from glancing intersections, in which the separation goes quadratically with distance from the intersection. Normally, a glancing intersection requires a coincidence, but an exception is a degenerate Π state of a linear triatomic, which splits on bending into two levels which are symmetric and antisymmetric under reflection in the plane of symmetry (Renner or Renner–Teller effect[97]).

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Another important thing to note is that the eigenfunctions (21) change sign when θ advances by 2π, i.e. when a closed path is traversed around the conical intersection. It follows that *conical intersection manifolds are transition manifolds.*

It should also be noted that these qualitative conclusions are rigorous, despite the apparently approximate nature of the Hamiltonian (19). The error incurred by using (19) shrinks to zero as one approaches the intersection, so the sign change certainly applies to infinitesimally small curves around the intersection. If such a curve is distorted continuously into a larger one, then it must remain negative unless in the course of distortion it crosses either this transition manifold or another one. Also, the conical nature of the intersection refers only to the behavior of the eigenvalues in the infinitesimal neighborhood of the intersection.

A special effect of a conical intersection is the case in which the degeneracy (perhaps only in a submanifold of the overall degeneracy manifold) is dictated by symmetry. In this case, Eq. (20) tells us that there will always be a nonzero gradient of the energy eigenvalues leading away from the symmetrical configuration (Jahn–Teller effect[86,98,99]).

2.3.3. *Nonadiabatic Coupling Terms, Conical Intersections, and Sign-Change Transitions*

By differentiating Eq. (2), using the definition given in Eq. (6), and taking matrix elements, it is easy to obtain the result

$$\vec{F}_{jk}(R) = \frac{\langle j(R)|\nabla \hat{H}_{el}(R)|k(R)\rangle}{U_k(R) - U_j(R)}, \tag{22}$$

where the above result applies only to off-diagonal elements j and k. Neither the numerator nor denominator of Eq. (22) depends on κ, so in general both are of order unity, so $\vec{F}_{jk}(R)$ will also normally be of order of magnitude unity. One frequently hears the statement that $\vec{F}_{jk}(R)$ will be small if the energy difference in the denominator is large enough. Of course this is true as far as it goes, but it must be clearly understood what is meant by "large enough". A "large" value for the denominator in atomic units would mean roughly an energy difference of thousands, or at least hundreds, of hartrees; in other words, one of the states would have to be very highly excited for this conclusion to apply. Of course, $\vec{F}_{jk}(R)$ may coincidentally be small (due to the numerator) for a particular region of a particular system, but one cannot simply assume that it is small without proof. Its *effect* is small in many cases because it appears multiplied by $1/M = \kappa^4$.

The vector NACM elements $\vec{F}_{jk}(R)$, then, will not normally be small. Can it be large, perhaps even singular? A little thought convinces one that the numerator will be large or singular only very rarely if at all. The operator whose matrix element is taken is basically the force exerted on a particular nuclear degree of freedom, for a given nuclear configuration. The singularities in the electron–electron and electron–nuclear forces are washed out in integrating to take the matrix element, while the nuclear–nuclear force is diagonal in the electronic states and thus does not contribute. The denominator, however, vanishes at a degeneracy, leading to a singularity. We conclude that $\vec{F}_{jk}(R)$ becomes singular at a conical (or glancing) intersection, but not elsewhere.

Moreover, it is easy to convince oneself that just this kind of singularity is necessary in order to have a transition manifold. From the definitions given above it is clear that

$$\nabla\phi_j(R) = \sum_{k\neq j} \phi_k(R)\vec{F}_{kj}(R). \tag{23}$$

Now consider an infinitesimally small circle of radius $d \rightarrow 0$ about a transition manifold. The circumference of the circle is just $2\pi d$, yet $\phi_j(R)$ undergoes a sign change, i.e. $\phi_j(R)$ changes by an amount of order unity. This means that at least one of the terms in the sum (23) must be singular of order $1/d$. But we have just seen that this kind of singularity occurs only at a conical intersection. We thus conclude that *conical intersection manifolds are the only transition manifolds.*

2.3.4. *Effects of Conical Intersections and Geometric Phase*

According to Eq. (21), a BO electronic wave function will not be single-valued as a function of R if the level with which it is associated experiences a conical intersection; and this double-valuedness will persist even in regions far from the intersection, as long as traversals of closed paths around the intersection are possible. In the one-state BO approximation, the full molecular wave function is approximated as

$$\Psi(R,r) \approx \psi_0(R)\phi_0(R,r). \tag{24}$$

Of course, $\Psi(R,r)$ must be single-valued, so something has to be done, either to ψ_0 or ϕ_0, to restore single-valuedness. We will consider two methods, both suggested previously.[91] Method (a), which has been used notably by Kuppermann and coworkers,[100–103] is to require that ψ_0 undergo a sign

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2.3.5. *Confluences*

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$$g(R) = \frac{\theta}{2} + f(R) \tag{25}$$

where $f(R)$ is any real function of R such that $\exp[if(R)]$ is single-valued. For example, $f(R)$ could be an integer multiple of θ, a function independent of θ, or a combination of these. If method (b) is used, then ψ_0 is subject to normal, single-valued boundary conditions, but

$$\vec{A}_{00} = \nabla g \neq 0, \tag{26}$$

so that the effective nuclear Hamiltonian in this case is that of a system of nuclei moving under the influence of a vector potential as well as the scalar potential $U_0(R)$. This vector potential is called the geometric vector potential. The two methods, of course, are completely equivalent. Additional considerations required to treat permutational symmetry when there are identical nuclei are discussed elsewhere.[91,104–109]

The geometric phase/vector potential clearly has consequences for chemical reactions and for properties of bound molecular systems, and there have been a number of theoretical studies of such effects.[94,99–103,105,110–119]

2.3.5. *Confluences of Conical Intersections*

In a nuclear internal space of n dimensions, we have seen that a conical intersection can occur on an $(n-2)$-dimensional manifold, and that this will also be a transition manifold. In general, moreover, there may be two or more distinct intersection manifolds, and in turn it is possible for two of these to intersect. Such "confluences" of intersection manifolds have been studied extensively by Yarkony.[36,120,121] Here we confine ourselves to a few simple remarks.

First, each manifold is of dimension $(n-2)$, so that, in the absence of symmetry, a point must satisfy two conditions (say $x = y = 0$) to be on one manifold, and two others (say $\xi = \eta = 0$) to be on the other. The confluence in this case consists of all points that are on both manifolds, and thus is of dimension $(n-4)$, with each point on the confluence satisfying four conditions (a confluence of larger dimensionality requires a coincidence, or the presence of symmetry). Since the dimensionality of the internal space is $n = 3N - 6$ for $N = 3$ nuclei, triatomics should exhibit no confluences, but confluences may occur of dimension 2 for $N = 4$, of dimension 5 for $N = 5$, etc.

Recall that the quantities that must vanish at an intersection are essentially the off-diagonal matrix element and the difference of the diagonal elements of the 2×2 Hamiltonian matrix. Thus, the quantities x, y, ξ, and η may be identified with these for the two separate manifolds. Each pair can also be formed into a complex number:

$$x + iy = re^{is}; \quad \xi + i\eta = \rho e^{i\sigma}. \tag{27}$$

The product of these two complex numbers will be a complex number that will vanish everywhere on either intersection manifold (but nowhere else) and whose real and imaginary parts may be taken respectively as half the difference of diagonal elements and the off-diagonal element of a model Hamiltonian matrix. We thus have for our model Hamiltonian

$$H = \begin{pmatrix} x\xi - y\eta & x\eta + y\xi \\ x\eta + y\xi & y\eta - x\xi \end{pmatrix} = r\rho \begin{pmatrix} \cos(s+\sigma) & \sin(s+\sigma) \\ \sin(s+\sigma) & -\cos(s+\sigma) \end{pmatrix}. \tag{28}$$

With eigenvalues

$$E = \pm r\rho \tag{29}$$

and eigenvectors

$$\begin{pmatrix} \cos\frac{1}{2}(s+\sigma) \\ \sin\frac{1}{2}(s+\sigma) \end{pmatrix}; \quad \begin{pmatrix} -\sin\frac{1}{2}(s+\sigma) \\ \cos\frac{1}{2}(s+\sigma) \end{pmatrix}. \tag{30}$$

For a tetratomic system there are six internal coordinates, and in the near neighborhood of the confluence we can take four of these to be x, y, ξ, and η. The other two, say u, and v play no role. The gradient of each eigenvalue vanishes at the confluence, but there are nonvanishing crossed second derivatives for all pairs of variables in which one is Latin and one is Greek:

$$\frac{\partial^2 E}{\partial x \partial \xi} = \frac{\partial^2 E}{\partial x \partial \eta} = \frac{\partial^2 E}{\partial y \partial \xi} = \frac{\partial^2 E}{\partial y \partial \eta} = 1. \tag{31}$$

A closed path cannot be considered as surrounding the confluence or not doing so, because the confluence is of too low dimension; any path can be distorted into any other without at any time touching the confluence.

But an example of a closed path around both intersections involving x, y, ξ, and η would be

$$x = \xi = \varepsilon \cos t; \quad y = \eta = \varepsilon \sin t, \tag{32}$$

with t advancing from zero to 2π. Here we find that $s = \sigma = t$, and $s + \sigma = 2t$, so there is no sign change. This should come as no surprise, since this path encloses an even number (two) of transition manifolds.

The above considerations apply to the usual case in which there is no symmetry. If symmetry is present, the situation is modified. Consider for example a triatomic system X_2Y, with two of the nuclei identical. If the two XY distances are equal, there is C_{2v} symmetry. Consider two electronic states that, in the C_{2v} configurations, have different symmetries under the C_2 rotation and/or the reflection in the plane. Let z denote the difference in the two XY distances, and let x and y be the other appropriately chosen internal coordinates, symmetric in the XY distances. Then, referring to Eq. (18), we have $v = zf(x, y, z)$, where $f(x, y, z)$ is even in z. An intersection will occur if either $u = z = 0$ or $u = f = 0$, and there can be a confluence of these intersections seams at the point where $u = z = f = 0$. In the infinitesimal neighborhood of such a confluence, the intersection will appear glancing for excursions in the uf place and conical in other directions.

2.4. *The Generalized Born–Oppenheimer Approximation*

2.4.1. *Introductory Comments*

The standard BO approximation is very accurate for a large class of molecular problems. However, its validity depends on the smallness of terms like

$$\frac{1}{M} \frac{\langle j, \tau_j | \vec{F}_{jk} \cdot \nabla | k, \tau_k \rangle}{U_k - U_j}, \tag{33}$$

where τ_j and τ_k denote quantum numbers of nuclear motion associated with electronic states j and k, respectively. As discussed in Sec. 2.1, the factor of $1/M$ in front normally guarantees the smallness of these terms, but exceptions can occur if one or both of the following holds: (a) the energy denominator becomes arbitrarily small, such as near a degeneracy; and/or (b) the nuclear energy is so large for the state $|k, \tau_k\rangle$ that the ∇ operator leads to a large matrix element. When terms such as Eq. (33) are large, we can usually still truncate the set of coupled Eqs. (5) to not just one electronic state but to two, three, or some other relatively small number of states (in practice, usually two, seldom more than three or four). This truncation to a few states rather than just one is called the generalized Born–Oppenheimer approximation.

Accordingly, we restrict ourselves not to one state, but to a subspace Q of dimension q in the electronic Hilbert space, spanned by q of the adiabatic states, and we will number the electronic states so that the first q of these are the chosen ones, the rest the excluded ones. This, we hope, will furnish an adequate basis for calculating molecular properties, at least within a given region of interest S in $\Re$.

It is important to recognize that not all regions of strong interaction of electronic states are associated with conical intersections. Conical intersections occur in manifolds of up to $n-2$ dimensions, whereas regions of strong interaction due to small adiabatic energy gaps may occur even in manifolds of $n-1$ or even n dimensions. Furthermore, regions of interaction or strong interaction due to small adiabatic energy gaps may also occur in dimensionality smaller than $n-2$ and may be important for initial conditions or other circumstances that lead to appreciable probabilities of the system visiting these regions.

The use of the generalized Born–Oppenheimer approximation is most well justified when there are no strong interaction regions between states in Q and states not in Q with appreciable nuclear wave function amplitude in the entire region of interest S. Accordingly, we require that there exists a positive number V, much larger than $1/M$, such that

$$|U_j(R)-U_k(R)|>V, \quad j\leq q,\ k>q,\ R\subset S. \tag{34}$$

Restricted to the subspace Q, the effective Schrödinger Eq. (13) (now again in terms of $\vec{\mathbf{F}}$ instead of $\vec{\mathbf{A}}$) takes the form

$$\left\{-\frac{1}{2M}\left[(\nabla+\vec{\mathbf{F}}^{(q)})^2+(\vec{\mathbf{F}}^{(od)}\cdot\vec{\mathbf{F}}^{(od)})^{(q)}+\mathbf{U}^{(q)}\right]\right\}\Psi^{(q)}=E\Psi^{(q)}, \tag{35}$$

where the superscript (q) denotes the part of a matrix restricted to Q, while (od) denotes the part coupling Q to its complement (i.e. coupling states $1,2,\ldots,q$ to the other states).

2.4.2. *Transformation of Electronic Basis*

In Eq. (35) the potential energy matrix $\mathbf{U}^{(q)}$ is diagonal, but the other terms on the left side are not. Since a solution will in any case contain contributions from more than one electronic state, there is no clear advantage in using the eigenfunctions of $\hat{H}_{el}(R)$ as basis functions; it may be useful

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to use other electronic functions as basis functions, chosen as linear combinations of the eigenfunctions of $\hat{H}_{el}(R)$. Accordingly, we define a unitary (real orthogonal) $q \times q$ matrix $\mathbf{S}(R)$, and make the transformation

$$\tilde{\phi}_j(R) = \sum_{k=1}^{q} \phi_k(R) S_{kj}(R). \tag{36}$$

The other quantities appearing in Eq. (35) are transformed as follows

$$\tilde{\vec{\mathbf{F}}}^{(q)} = \mathbf{S}^{\dagger}\vec{\mathbf{F}}^{(q)}\mathbf{S} + \mathbf{S}^{\dagger}\nabla\mathbf{S}; \tag{37}$$

$$\tilde{\mathbf{U}}^{(q)} = \mathbf{S}^{\dagger}\mathbf{U}^{(q)}\mathbf{S}; \tag{38}$$

$$\left(\tilde{\vec{\mathbf{F}}}^{(od)} \cdot \tilde{\vec{\mathbf{F}}}^{(od)}\right)^{(q)} = \mathbf{S}^{\dagger}\left(\vec{\mathbf{F}}^{(od)} \cdot \vec{\mathbf{F}}^{(od)}\right)^{(q)}\mathbf{S}. \tag{39}$$

2.4.3. *Strictly Diabatic Basis*

A particularly attractive possibility is to choose $\mathbf{S}$ in such a way that $\tilde{\vec{\mathbf{F}}} = 0$. An electronic basis with this property is called a *strictly diabatic basis* (as opposed to an adiabatic basis in which $\mathbf{U}^{(q)}$ is diagonal). Referring to Eq. (37), one sees immediately that this can be achieved if

$$\nabla\mathbf{S} = -\vec{\mathbf{F}}\mathbf{S}. \tag{40}$$

Taking mixed second partial derivatives of (40), one arrives at

$$\frac{\partial}{\partial x_\mu}\mathbf{F}_\nu^{(q)} - \frac{\partial}{\partial x_\nu}\mathbf{F}_\mu^{(q)} + \left[\mathbf{F}_\mu^{(q)}, \mathbf{F}_\nu^{(q)}\right] = 0 \tag{41}$$

as the condition for the existence of a solution of Eq. (40) and thus for the existence of a strictly diabatic basis, i.e. a strictly diabatic basis exists if Eq. (41) is satisfied, otherwise it does not. Because the left hand side is a kind of generalized curl, Eq. (41) is sometimes called the "curl condition." Equation (41) looks much like Eq. (12) restricted to Q, but it is not the same because Eq. (12) includes off-diagonal contributions. Separating Eq. (12) into diagonal and off-diagonal contributions, one easily finds

$$\frac{\partial}{\partial x_\mu}\mathbf{F}_\nu^{(q)} - \frac{\partial}{\partial x_\nu}\mathbf{F}_\mu^{(q)} + \left[\mathbf{F}_\mu^{(q)}, \mathbf{F}_\nu^{(q)}\right] = -\left[\mathbf{F}_\mu^{(od)}, \mathbf{F}_\nu^{(od)}\right]. \tag{42}$$

It is easy to verify that both right and left sides of Eq. (42) transform as $\mathbf{S}^{\dagger}\ldots\mathbf{S}$ under the transformation given in Eq. (36). Thus, while such a transformation can rearrange matrix elements, etc. it cannot make this expression small or zero. The conclusion is that, in general, *no strictly diabatic basis exists.*[10,21]

2.4.4. *Diabatic Bases*

Although there is no strictly diabatic basis, it may nevertheless be possible in certain problems to make the coupling less troublesome by means of a transformation like Eq. (36). Here one may speak of having achieved a "quasidiabatic" basis, by having (in some sense) removed part of the coupling, leaving the "nonremovable" part. Under suitable circumstances, this nonremovable part may be small enough to neglect, leaving only the scalar coupling arising from the off-diagonal matrix elements of the electronic Hamiltonian, which is often easier to work with than the vector NACMs that arise in the adiabatic representation. Since strictly diabatic bases do not exist, we follow the popular convention of just saying "diabatic" rather than "quasidiabatic" for any basis designed so as to reduce the effect of the NACMs in some particular problem, thus justifying their neglect at some level of approximation.

In particular, there is one troublesome part of the coupling that is always removable, and that is the part that becomes singular near a conical intersection. To see this, we need only note that the matrix elements entering into the right-hand side of Eq. (42) are all between states belonging to Q and those belonging to its complement, and according to Eqs. (22) and (34), these can never be singular. The singularities in the NACMs can therefore be removed by a transformation of the type described by Eq. (36). A neat way of doing this is to choose S so as to diagonalize the Q part of some nondegenerate operator $\hat{Z}$ other than the energy, e.g. a component of the dipole moment.[16,20,35] If this is done, the new NACMs within Q will evidently obey an equation analogous to Eq. (22), with $\hat{H}_{el}$ replaced by $\hat{Z}$, and if $\hat{Z}$ is nondegenerate they will never become singular.

2.4.5. *The Case* $q = 2$

If $q = 2$, the treatment becomes simpler. In this case, each component of $\vec{\mathbf{F}}^{(q)}$ is just a real antisymmetric 2×2 matrix:

$$\vec{\mathbf{F}}^{(q)} = \begin{pmatrix} 0 & \vec{f} \\ -\vec{f} & 0 \end{pmatrix} ; \tag{43}$$

the transformation matrix S is now a real orthogonal 2×2 matrix

$$\mathbf{S} = \begin{pmatrix} \cos\lambda & \sin\lambda \\ -\sin\lambda & \cos\lambda \end{pmatrix} ; \tag{44}$$

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$$\tilde{\vec{f}} = \vec{f} + \nabla\lambda; \tag{45}$$

Eq. (40) becomes

$$\nabla\lambda = -\vec{f}; \tag{46}$$

and the curl condition, Eq. (41), for the existence of a strictly diabatic basis is now

$$\frac{\partial}{\partial x_\mu} f_\nu - \frac{\partial}{\partial x_\nu} f_\mu = 0. \tag{47}$$

The curl condition now is just the familiar result from vector calculus that only a vector of zero curl can be the gradient of a scalar.

By making a Fourier transform, one can decompose f_μ as follows:

$$f_\mu = \frac{\partial}{\partial x_\mu}\Phi + \sum_{\nu=1}^{n} \frac{\partial}{\partial x_\nu} A_{\nu\mu}, \tag{48}$$

where n is the dimension of $\Re$, Φ is a scalar, and $A_{\nu\mu}$ are components of an antisymmetric tensor. The longitudinal (irrotational) term in Φ has zero curl and is removable, while the other transverse (solenoidal) term has zero divergence and is nonremovable. Equation (48) is a rather obvious n-dimensional generalization of Helmholtz's theorem.[122] Using the antisymmetry of $A_{\nu\mu}$, one easily derives the relations

$$\nabla \cdot \vec{f} = \nabla^2 \Phi \tag{49}$$

$$\frac{\partial}{\partial x_\mu} f_\nu - \frac{\partial}{\partial x_\nu} f_\mu = \sum_{\sigma=1}^{n} \frac{\partial}{\partial x_\sigma}\left(\frac{\partial}{\partial x_\mu} A_{\sigma\nu} - \frac{\partial}{\partial x_\nu} A_{\sigma\mu}\right). \tag{50}$$

Inserting Eq. (48) into Eq. (45), one sees how the transformation affects the two parts:

$$\tilde{\Phi} = \Phi + \lambda; \quad \tilde{A}_{\mu\nu} = A_{\mu\nu}. \tag{51}$$

It is now easy to see, at least in principle, how to choose λ so as to remove the longitudinal part. Referring to Eqs. (51) and (49), we see that removal of Φ requires that

$$\nabla^2 \lambda = -\nabla \cdot \vec{f}, \tag{52}$$

i.e. λ must satisfy a Poisson equation.

Based on the theory presented here, one expects that the singular part of the coupling can be removed, but that apart from this there is a nonremovable part that is, in general, of order unity. Numerical computations bear this out.[34,123–126] Reference 126 in particular makes use of the Poisson equation to decompose the coupling into removable and nonremovable parts.

Since, far from a conical intersection, the nonremovable coupling is in general of the same order of magnitude as the removable coupling, the *terms* that couple the nuclear motion due to the nonremovable part of the coupling will be of the order $1/M$ or κ^4, thus justifying the neglect of these terms and the usefulness of diabatic representations. The inconvenience of fully removing the nonremovable part when it is the same order of magnitude as the removable part may be more trouble than it is worth.[127] In general it may be better to take advantage of the arbitrariness of diabatic representations to simplify the calculation. Simplifying the adiabatic-to-diabatic transformation may facilitate other aspects of the calculation that are more important. When one considers regions of strong interaction that do not contain conical intersections, identifying the most important contributions to the nonadiabatic coupling may require careful system-specific analysis. This may, for example, involve an examination of orbital and configurational uniformity[11,14–18,23–25,27–33,38] of the electronic state functions.

It is also important to make a distinction between the "internal" nonadiabatic coupling, due to vibrations and relative translational motions, and Coriolis coupling due to rotation which has so far been mentioned only briefly. One obvious difference is that rotational degrees of freedom merely rotate the electronic eigenfunctions rigidly, while internal motions change the Schrödinger equation that they must satisfy. In a diatomic (either bound or unbound), $\partial/\partial s$ from relative momentum, where s is the internuclear distance, is the source of the internal part and rotational angular momentum is the source of the Coriolis part. In a diatomic, the internal part of the coupling conserves the electronic angular momentum quantum number Λ, while the Coriolis term couples states differing in Λ by ± 1. That illustrates one reason why diatomics are special, namely the internal part is one-dimensional and so it can be removed if we limit ourselves to Σ states.[12] A nice example of transforming coupled Σ states to a diabatic representation to remove the $\partial/\partial s$ and $\partial^2/\partial s^2$ coupling for a diatomic molecule is the recent work of Gadéa *et al.*[128] In triatomics, there is a mirror plane, and the symmetry under this reflection is conserved by internal and in-plane rotational degrees of freedom, while out-of-plane rotations change this symmetry from (+) to (−) and vice versa. In other polyatomics there is no symmetry in general. If, however, we have a quasi-rigid molecule whose equilibrium configuration possesses symmetry, then one can derive

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Coriolis coupling, when nonzero, is not removable in general although it may be zero in certain subspaces. For example, consider a diatomic molecule where a Σ state is close in energy to two Π states (Π_x and Π_y), and all other electronic states may be excluded. If the latitude angle θ causes motion in the space frame xz plane, the Σ and Π_x states will mix when θ is varied and

$$F_\theta = \frac{1}{s}\begin{pmatrix} 0 & -\alpha & 0 \\ \alpha & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{53}$$

where s was defined above as the internuclear distance, and α is a constant characteristic of the particular system. Upon varying the longitudinal angle ϕ, if the molecular axis lies in the space frame xy plane, Σ acquires Π_y character and vice-versa exactly as with Π_x in the θ case. But as the molecular axis approaches the space frame z axis (i.e. as θ approaches $\pi/2$ or $3\pi/2$), Σ is less and less affected by ϕ-motion while the two Π states rotate into each other. From these considerations, one may write

$$F_\phi = \frac{1}{s\sin\theta}\begin{pmatrix} 0 & 0 & -\alpha\sin\theta \\ 0 & 0 & -\cos\theta \\ \alpha\sin\theta & \cos\theta & 0 \end{pmatrix}. \tag{54}$$

The quantity that must vanish to satisfy the generalized curl condition, Eq. (41), is therefore

$$\frac{\partial F_\phi}{\partial\theta} - \frac{\partial F_\theta}{\partial\phi} + [F_\theta, F_\phi] = \begin{pmatrix} 0 & 0 & \alpha\cot\theta \\ 0 & 0 & \csc^2\theta - \alpha^2 \\ \alpha\cot\theta & -\csc^2\theta - \alpha^2 & 0 \end{pmatrix}, \tag{55}$$

and, since this is not zero, the coupling is not removable. Further discussion relevant to Coriolis coupling effects is available elsewhere.[17,45,81,129–142]

In Sec. 3, when we refer to the potential energy surfaces and their couplings, we mean either the adiabatic surfaces and the NACMs or the full nondiagonal diabatic potential energy matrix.

2.5. *Non-Abelian Case*

Many readers may already have been struck by the similarity between Eqs. (35) and (15), especially if the former is recast in terms of

$$\vec{p} = -i\nabla; \quad \vec{\mathbf{A}}^{(q)} = -i\vec{\mathbf{F}}^{(q)}. \tag{56}$$

The only difference is that in Eq. (35) the entity being acted upon is a column vector of nuclear wave functions rather than a single function; and that each component of the vector potential is now a matrix rather than a single number. A further generalization would be to allow complex numbers, something that has already appeared in our theory of gauge transformations. From this point of view, the q-dimensional case is called the non-Abelian case, because the components of the vector potential, taken at different places, are matrices that in general do not commute. The noncommuting vector potentials make the calculations more complicated. For example, there is no simple analog of Stokes' theorem for integrals of $\vec{\mathrm{A}}$ around closed curves.

It is easy to see now how various relations from the one-state case generalize to the non-Abelian case. The gauge transformation, Eqs. (16) and (17), for example, is replaced by Eqs. (36) and (37). Also, just as in the one-state case, attempts to avoid having a vector potential result in many-valuedness of the electronic basis functions (not just two-valuedness).

If two or more electronic states are degenerate over all of $\mathfrak{R}$, then we do not have the luxury of the one-state BO approximation even for portions of the space. As we have already seen, degeneracy of electronic states occurs normally only on an $(n-2)$-dimensional submanifold of $\mathfrak{R}$. But there are two exceptions to this.

The first exception, well-known in a way for years to molecular theorists[143] but first studied from this point of view by Moody, Shapere, and Wilczek,[132] is that of a diatomic molecule in a non-Σ state. This is also a special case of the two-state generalized BO approximation (Sec. 2.4.5), with a nonremovable coupling imposed by the spherical geometry of the rotational variables.

The second exception is the case of an odd number of electrons with spin included, where every electronic level is required by time-reversal symmetry to be doubly degenerate (this is called Kramers degeneracy).[87,88,95,144] Here the nature of the spin interaction forces us to accept complex numbers, and each component of the vector potential is a two-dimensional matrix, with different components at different points in $\mathfrak{R}$ not commuting. In this case one always has the 2-fold Kramers degeneracy but for two Kramers doublets to become degenerate, leading to a 4-fold degeneracy, requires that 5 conditions be satisfied. Thus, the relevant submanifold for this 4-fold degeneracy is of dimension $(n-5)$.[89] We refer the reader to the literature for more details on this topic.[95,144,145]

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3. Dynamics

3.1. *Semiclassical Trajectory Methods*

3.1.1. *General Considerations*

The term "semiclassical" is used in the literature in a variety of different contexts to signify that some combination of quantum mechanical and classical mechanical ideas are being used to simplify a problem or calculation. In the context of modeling the full-dimensional dynamics of electronically nonadiabatic chemical systems, the most useful and widespread approach is the use of what may be called the trajectory ensemble (TE) approximation.[42,43,146–154] Specifically, an ensemble of nuclear trajectories is evolved classically under the influence of a set of Born–Oppenheimer surfaces and their couplings, and the ensemble as a whole is supposed to simulate a wave packet or a particular slice of a wave packet.

The separation of nuclear (slow) and electronic (fast) degrees of freedom is the basis of the BO approximation, as discussed in Sec. 2, and a useful further approximation in many cases is to treat the slow degrees of freedom with classical mechanics. This approximation is expected to be completely valid only under much more limited circumstances, for example when the nuclei are much heavier than hydrogen and the experimental observables of interest are not sensitive to quantization of energy levels and wave function phases. However, the approximation can be very useful for approximate treatments even of problems involving hydrogen. Furthermore, we note that the partition of the nuclei as heavy particles and the electrons as light particles is not always the most convenient separation of time scales. Proton transfer, for example, may be modeled using an approach that considers the coordinates corresponding to the nuclear motion of the hydrogen nucleus as fast degrees of freedom while the remaining nuclear degrees of freedom are treated classically.[155,156] For clarity in this section, however, we will assume that all of the nuclear motions are treated as slow degrees of freedom.

The TE approximation is a reasonable starting point for performing approximate dynamics calculations, but there are obvious deficiencies, especially the lack of quantum effects such as zero-point energy and quantized vibrations, tunneling, coherence, and electronic state transitions. In this section, we will describe several methods for incorporating electronic state transitions into the TE scheme. We will also see how coherence and tunneling effects play a role in nonadiabatic transitions, and how these quantum effects may be treated within the context of nonadiabatic transitions. Of course, tunneling and coherence effects may be important independent of their role in nonadiabatic transitions. The TE methods discussed here explicitly treat only some of the quantum effects that are missing in the classical treatment of the nuclear motion, namely nonadiabatic transitions. This unequal treatment of quantum effects should not be thought of as a severe deficiency, but rather the TE approach allows one to isolate these effects and consider their importance for a given problem separately. This approach not only provides a more affordable means of computation but also provides insight into the role of quantum effects in molecular dynamics in general.

As mentioned above, the fundamental assumption behind the TE approximation is that the accurate quantum mechanical nuclear wave packet for the system can be represented as an ensemble of classical trajectories. The quantum wave packet has some inherent width in configuration and momentum space, whereas classical trajectories are delta functions in phase space. Equivalently, the position and momentum of a quantal particle has some uncertainty, whereas these quantities are fully determined in a classical system. An ensemble of trajectories (as opposed to a single trajectory) is therefore required to approximate the full quantal situation, where the initial conditions for each trajectory in the ensemble are distributed to mimic the accurate quantal wave packet. In this sense, each trajectory may be thought of as a basis function, and taken together, the ensemble of trajectories approximates the full nuclear wave packet. Alternatively, each trajectory may be thought of as a single chemical event governed by the probability distribution inherent in the spread of the quantum mechanical wave packet.

We note that before any dynamics may be carried out, one needs a reliable set of potential energy surfaces and their couplings, or one must be able to calculate these quantities from electronic structure calculations carried out "on-the-fly"; this latter approach is called direct dynamics. Obtaining potential energy surfaces and their couplings is often difficult and can be a significant source of error.[157–161] We will assume throughout this section, however, that accurate potential energies and their coupling terms are available or can be readily calculated.

A recent development that has had a significant impact on the development of nonadiabatic semiclassical theories has been the ability to obtain accurate converged quantum mechanical results for realistic systems.[17,47–74] This has allowed for the construction of a variety of three-body, two-state benchmark systems with which one may test (and systematically improve[67–74,154,162–165]) the various semiclassical methods that have been proposed. We will focus our attention on methods that have been validated

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in this way, and we note that although the semiclassical methods do not predict the accurate quantal results quantitatively, the results are usually within 20% of the quantal results,[154] allowing one to study trends and gain physical insight. Semiclassical methods have not been widely applied to systems larger than three atoms, mostly due to the lack of availability of accurate potential surfaces for these systems. As mentioned above, the semiclassical theories that will be discussed in detail in this section are readily applicable to large systems and may be immediately employed once potential energy surfaces and couplings become available for these systems.

3.1.2. *Self-Consistency of the Electronic and Nuclear Degrees of Freedom*

The coupled equations for the nuclear wave function derived above in Eq. (5) are interpreted semiclassically as follows: as the ensemble of nuclear trajectories evolves in time, the nuclear motion causes a change in the overall electronic state of the system (through $\vec{\mathbf{F}}$ and $\mathbf{G}$) which in turn results in a new effective potential energy felt by the trajectories, affecting the nuclear motion. As discussed in Sec. 2, this is the source of nonadiabatic electronic state changes, and in order to properly treat nonadiabatic effects, a self-consistent treatment of this nuclear-electronic coupling is necessary (i.e. the electronic and nuclear degrees of freedom must somehow be made to evolve simultaneously). Several methods for incorporating this self-consistency into a TE theory have been proposed, and before we discuss some of them specifically we will first consider the nuclear and electronic degrees of freedom separately.

Each nuclear trajectory in the ensemble evolves classically according to Hamilton's equations of motion[166]

$$\begin{aligned} \dot{P} &= -\nabla_R V(R) \\ \dot{R} &= P/M \end{aligned} \tag{57}$$

where R is now the collection of classical nuclear coordinates (i.e. $R(t)$ defines a classical trajectory through configuration space) scaled to mass M, P is the vector of the classical momenta associated with the components of R, and the over-dot indicates differentiation with respect to time. The semiclassical potential function V that appears in Eq. (57) will be explicitly defined later and must be carefully chosen such that the self-consistency discussed above is maintained.

We will now discuss the behavior of the electronic degrees of freedom along the classical trajectory. We make the generalized Born–Oppenheimer approximation and restrict our attention to q electronic states. We will ignore the coupling of the states in Q to the states in the complement of Q, and we may therefore drop the (q) superscript. The nuclear wave function $\psi_j(R)$ is approximated in the TE approach by a set of classical trajectories, i.e.

$$\psi_j(R) \rightarrow \sum_a c_j^a(t)\delta[R - R^a(t)], \tag{58}$$

where $\delta[R - R^a(t)]$ is a delta function in configuration space that follows the ath classical trajectory $R^a(t)$ in the ensemble, and the coefficient c_j^a is the probability amplitude that the electronic state of the system is state j at time t.

We note that the expansion coefficients c_j^a are complex quantities and the ensemble of trajectories may be used to simulate quantum coherence effects by allowing these coefficients to interfere with each other. We may differentiate between coherence effects that arise from trajectories in different electronic states interfering with each other (inter-state coherence) and those arising from trajectories in the same electronic state interfering with each other (intra-state coherence). Some researchers[167–173] use Eq. (58) as the starting point for including intra-state coherence effects into the TE approximation by replacing $\delta[R - R^a(t)]$ with some delocalized function. The various trajectories may then be propagated simultaneously and allowed to interfere with one another. These methods are promising, but remain to be tested on realistic chemical systems, and we will focus our attention on TE methods where the trajectories may be propagated independently. In this way the intra-state coherence is not included, but the computation is greatly simplified. We may therefore consider a single trajectory and drop the superscript a, keeping in mind that the final results of the simulation are obtained by averaging the results of an ensemble of trajectories that differ in their initial conditions as discussed above. The inter-state coherence may or may not be included in either type of method, depending on how the nonadiabatic effects are treated in the simulation. We will discuss the inter-state coherence below in the context of the specific TE methods.

Using Eq. (58) and explicitly indicating the time dependence, one can approximate Eq. (4) as

$$\Psi(t) = \sum\nolimits_j \bar{c}_j(t)\bar{\phi}_j[R(t), r] \tag{59}$$

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where the over-bar indicates a general electronic basis and can be either the adiabatic basis ϕ_j or some diabatic basis $\tilde{\phi}_j$. The electronic state of the system along the classical trajectory is given by the evolution of the coefficients $\bar{c}_j$. By substituting Eq. (59) into the time-dependent Schrödinger equation, one obtains coupled equations similar to those obtained earlier in Eq. (5),[146]

$$\dot{\bar{c}}_j = -\sum\nolimits_k \bar{c}_k(i\hbar^{-1}\bar{U}_{jk} + \dot{R}\cdot\bar{\vec{F}}_{jk}), \tag{60}$$

where we have neglected $\mathbf{G}$ and other small terms involving the gradient of $\bar{c}_j$. Note that if the adiabatic electronic basis is used, $\bar{\mathbf{U}}$ will equal the diagonal matrix $\mathbf{U}$, while if a diabatic basis is used, $\bar{\vec{\mathbf{F}}}$ will be neglected. Using Eq. (60), we can obtain an expression for the electronic state probability density as a function of time along the classical trajectory $R(t)$:[146]

$$\dot{\bar{\rho}}_{jj} = \sum_{k\neq j} 2\mathrm{Im}\hbar^{-1}(\bar{\rho}_{kj}\bar{U}_{kj}) + 2\mathrm{Re}(\bar{\rho}_{kj}\dot{R}\cdot\bar{\vec{F}}_{kj}), \tag{61}$$

where we have made use of Eq. (8) to simplify the expression, and the electronic state density matrix is defined by

$$\bar{\rho}_{jk} \equiv \bar{c}_j\bar{c}_k^*. \tag{62}$$

A similar (but slightly more complicated) expression[174] may also be written for the off-diagonal elements (coherences) of the electronic state density matrix. Note that the NACM $\vec{\mathbf{F}}$ appears in a dot product with the velocity of the trajectory, i.e. only the component of $\bar{\vec{\mathbf{F}}}$ in the direction of the nuclear motion is important in coupling the electronic states. Using Eq. (61) with suitable initial conditions, the electronic state probability density for each state j may be integrated along the with classical trajectory, i.e. along with Eq. (57).

We are now in a position to discuss the semiclassical potential energy function V that governs the trajectory. One may anticipate that V will be some function of the potential surfaces, their couplings, and the electronic state density matrix $\bar{\rho}$. Several semiclassical algorithms have been proposed with differing prescriptions for V and may be divided into two general categories: time-dependent self-consistent field methods and trajectory surface hopping methods. Each category will be discussed in some detail below.

3.1.3. *Time-Dependent Self-Consistent Field Methods*

The starting point for time-dependent self-consistent field (TDSCF) methods[69,71–74,148,154,162,163,175–183] is the quantum Ehrenfest theorem[184,185] which states that the expectation values of the position and momentum operators evolve according to classical equations of motion with a potential energy function given by the expectation value of the potential energy operator. We may define a "semiclassical Ehrenfest" (SE)[72,148,154,177] TE method in this way by taking the expectation value of the Hamiltonian using the time-dependent wave function given in Eq. (59), i.e.

$$V_{SE}(R) = \langle \Psi | H(R, r) | \Psi \rangle. \tag{63}$$

In a diabatic representation this becomes

$$V_{SE}(R) = \sum_{jk} \tilde{\rho}_{jk} \tilde{U}_{jk}(R). \tag{64}$$

We note briefly that an early version of the TDSCF method defined the semiclassical potential V as the expectation value of the Hamiltonian *averaged over all the trajectories in the ensemble.*[167–169] In this approach, the trajectories are not independent and are propagated simultaneously, and the semiclassical potential function may be considered to be a better representation of the quantum mechanical expectation value as it is averaged over all of the different parts of the wave function, i.e. over all the trajectories in the ensemble. An additional advantage of this type of method is that intra-state coherence effects are also included. However, as the system evolves in time the distribution of trajectories may become nonlocalized, and the mean-field approximation breaks down.[164] Using independent trajectories (as in the SE method) one loses intra-state coherence effects but gains the ability to model systems that feature divergent trajectories in phase space.

We return to our discussion of the SE semiclassical potential function defined by Eq. (63). Expectation values are unchanged by a unitary transformation of basis functions, and therefore V_{SE} could also be written in terms of the adiabatic electronic basis functions, and these two formulations are equivalent. The adiabatic coupling terms are often difficult to work with, and the SE method is usually discussed in the diabatic representation.[72,148,154,177] The computational implementation of the SE method involves integrating Eqs. (57) and (60) simultaneously using Eq. (64).

Additional insight into the SE method may be gained by recognizing that the expansion coefficients in Eq. (59) are complex quantities and may

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$$\tilde{c}_j = \frac{1}{\sqrt{2}}(\tilde{x}_j + i\tilde{p}_j), \tag{65}$$

where $\tilde{x}_j$ and $\tilde{p}_j$ are electronic variables that can be shown to behave like the position and momentum of a classical particle under the influence of the potential energy function given by Eq. (64), i.e.

$$\dot{\tilde{x}}_j = \frac{\partial V_{SE}}{\partial \tilde{p}} = \sum_k \tilde{p}_k \tilde{U}_{jk}; \tag{66}$$

$$\dot{\tilde{p}}_j = -\frac{\partial V_{SE}}{\partial \tilde{x}} = -\sum_k \tilde{x}_k \tilde{U}_{jk}. \tag{67}$$

In one sense Eqs. (66) and (67) are just the real and imaginary parts of Eq. (60) written in terms of the diabatic basis. More importantly, however, they allow the electronic variables to be dealt with in an entirely classical way such that the nuclear and electronic motions may be treated on equal footing.

To further illustrate the successes and failings of the SE method we will consider as an example a reactive system with two electronic states (labeled 0 and 1), vanishing electronic-state coupling for the isolated reactants and products, and initial conditions such that $\tilde{\rho}_{11} = 1$; $\tilde{\rho}_{00} = \tilde{\rho}_{01} = \tilde{\rho}_{10} = 0$, i.e. the system starts as a pure state in the excited electronic state (state 1). For a given trajectory in the ensemble, the semiclassical potential given by Eq. (64) is initially equal to the excited state potential, and the trajectory propagates in the pure excited state. When the trajectory enters a region of strong coupling, there is a flow of probability density between the electronic states (via Eq. (61)), and V_{SE} becomes a linear combination of the potential energy surfaces. In this strong interaction region, the potential energy felt by the SE trajectory is a weighted average of the potential energies felt by hypothetical trajectories in each electronic state. This situation allows the SE trajectory to be influenced by all of the electronic states at once and thus explicitly treats the coherence between the electronic states.

Unfortunately, the SE method as described above has many disadvantages that result from the mean-field assumption. Although at any instant along an SE trajectory it is physically meaningful for a system to be influenced by some average of the potential energies of all of the electronic states (i.e. it is meaningful to consider inter-state coherence), it is not physically meaningful for the nuclear *motion* corresponding to each electronic state to be described by a single trajectory. If the potential energies of the various electronic states are similar in topography and energy, then the nuclear motions in each state will be such that an average SE trajectory may provide a reasonable approximation. For many physically meaningful systems, however, this is not the case, and it is not possible for a single trajectory to approximate the motion in these different electronic states. An important consequence of this arises in the case of low-frequency events. A SE trajectory will be dominated by the character of the high-probability motions, and low-probability motions may not be properly explored. Furthermore, it is also not clear how to interpret the final state of a SE trajectory. In general, a SE trajectory will finish the simulation in a mixed (inter-state coherent) electronic state, whereas physically we expect isolated products to be in pure electronic states (if there is no electronic state coupling in the product region of phase space). The internal energy distribution of products in a mixed electronic state is not reliable because it does not correspond directly to the internal energy distribution of any single physically meaningful product.

Several modifications of the SE method have been suggested to remedy these deficiencies.[69,154,162,163,182,186,187] In keeping with our aim of discussing only those methods that have been tested using realistic systems, we will focus our discussion on the natural decay of mixing (NDM) method.[163,188] The NDM method is representative of the modified SE methods, which vary in their details but in general attempt to force the system into a pure electronic state (i.e. they force the inter-state coherent SE trajectory to decohere) as the system leaves the strong coupling region.

The NDM method starts from Eq. (64) but defines $\tilde{\rho}$ such that the system decoheres (dephases) to a pure electronic state in regions of vanishing coupling. The NDM electronic density matrix is defined like the SE density matrix, except that Eqs. (66) and (67) are replaced with

$$\dot{\tilde{x}}_j^{NDM} = \dot{\tilde{x}}_j + \dot{\tilde{x}}_j^{D}\,; \tag{68}$$

$$\dot{\tilde{p}}_j^{NDM} = \dot{\tilde{p}}_j + \dot{\tilde{p}}_j^{D}\,, \tag{69}$$

where $\tilde{x}_j$ and $\tilde{p}_j$ are the SE terms given in Eqs. (66) and (67), and $\tilde{x}_j^D$ and $\tilde{p}_j^D$ are responsible for dephasing. These terms are defined as

$$\dot{\tilde{\zeta}}_j^{D} = (\delta_{jK} - 1)\left(-\frac{\tilde{\zeta}_j}{2\tau_{jK}}\right) + \delta_{jK}\frac{\tilde{\zeta}_j}{2\tilde{\rho}_{jj}}\sum_{k\neq j}\frac{\tilde{\rho}_{kk}}{\tau_{jk}}, \tag{70}$$

where ζ is x or p, τ_{jk} is the decoherence (dephasing) time for coupled motions in states j and k, and K is the state towards which the system

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is collapsing. The target state K is allowed to change along the trajectory and is determined stochastically such that the fraction of trajectories in the ensemble that are decohering towards state K at any given time is equal to the ensemble average of the value of $\tilde{\rho}_{KK}$.

At any instant along the NDM trajectory, the system is decohering from each state j towards state a single state K at a rate $\sim 1/\tau_{jK}$. In the original formulation of the NDM method this rate was determined using the simple formula

$$\tau_{jK} = \frac{\hbar}{|\tilde{U}_j - \tilde{U}_K|} \frac{E}{T_{vib}}, \tag{71}$$

where E and T_{vib} are the total energy and vibrational energy of the system, respectively. Equation (71) is reasonable, and although it cannot be rigorously justified, it has been shown to work quite well for realistic chemical systems.[163] Other physical arguments would give

$$\tau_{jK} = \frac{\hbar}{|\tilde{U}_j - \tilde{U}_K|} \tag{72}$$

or a result depending on momentum components. Prezhdo and Rossky[181] derived a formula for the decoherence time by considerations based on Gaussian wave packets and Franck–Condon factors; however their result depends on the width of the Gaussian wave packet, which is not a fundamental property of the system.

A NDM trajectory behaves like a SE trajectory in strong coupling regions and collapses to a pure state asymptotically. The method retains the desirable feature of the SE method in that inter-state coherences are included when the electronic states are strongly coupled. Additionally, it is able to treat low-probability events and gives realistic product states. We note that the NDM method may also be formulated in the adiabatic representation[188] and that in contrast to the SE method, these adiabatic and diabatic formulations are not globally equivalent. However, because the method tends toward SE dynamics in strongly coupled regions, it is less sensitive to the adiabatic/diabatic choice than is the surface hopping approach which will be discussed below.

The NDM method is in many respects similar to the stochastic mean field (SMF) method of Prezhdo.[182] The SMF method is derived by considering a system coupled to the environment, and allowing the environment to continuously partially collapse the wave function, eventually resulting in a pure electronic state. The treatment of the decoherence effects leads to terms that involve random changes in the nuclear velocities, and these must be compensated for by rescaling the velocities such that energy is conserved (similar to a surface hop). The decoherence time scale is a parameter of the method, and the results may be sensitive to this parameter.

3.1.4. *Trajectory Surface Hopping Methods*

The trajectory surface-hopping approach has a long history[42,44,46,68,70,73,74,111,112,151–153,174,189–200] starting with Landau–Zener type approaches[42,190,191] where surface transitions were limited to pre-defined seams and later[194] generalized to include methods based on integrating the time-dependent quantities in Eq. (61) and allowing surface transitions anywhere that there is significant electronic state coupling. In general, the semiclassical potential is taken to be the diagonal element of the potential energy matrix $\bar{\mathbf{U}}$ that corresponds to the currently occupied state j, i.e.

$$V_{SH}(R) = \bar{U}_{jj}(R). \tag{73}$$

This single-surface propagation is interrupted by instantaneous surface transitions (called surface hops) to some other state k; these hops occur with some time-dependent probability g_{jk} that is integrated along the classical trajectory. The hopping probability g_{jk} may be defined in various ways, and we will discuss several of the prescriptions below.

The surface hopping method that has perhaps found the most use in physical applications is the molecular dynamics with quantum transitions method of Tully; we will call this Tully's fewest-switches (TFS) method.[174,197] Trajectories are propagated locally under the influence of a single-state potential energy function, and this propagation is interrupted at time intervals Δt with hopping decisions. A hopping decision consists of computing a probability for hopping from the currently occupied state j to some other state k, and the TFS method defines this hopping probability such that hopping is minimized in the sense that hopping only occurs when there is a net flow (in an ensemble averaged sense) of electronic state probability density out of the currently occupied state j. At each hopping decision, g_{jk} is computed and compared with a random number to determine if a hop occurs.

For clarity we will again consider a two-state system. The TFS hopping probability from state j to state k is defined as[174]

$$g_{jk}(t) = \max\left(0, -\frac{\dot{\bar{\rho}}_{jj}}{\bar{\rho}_{jj}}\Delta t\right), \tag{74}$$

where Δt is time interval between hopping decisions, and $\bar{\rho}_{jj}$ is given by Eq. (61). This formula for g_{jk} has several desirable properties. For example, the hopping probability is proportional to the step size Δt so the final results are not dependent on this parameter. Also, if the fraction F_j of trajectories in an electronic state is equal to $\bar{\rho}_{jj}$ at some time (say the start of the simulation), then F_j will equal to $\bar{\rho}_{jj}$ for all time t if hopping occurs according to Eq. (74) and *all hops that are called for by Eq. (74) are allowed.* The possibility of including hops that are not classically allowed by the original TFS scheme is discussed below. Most importantly perhaps, when using the TFS method, electronic transitions are minimized in that only as many trajectories as are necessary to retain the self-consistency of F_j and $\bar{\rho}_{jj}$ are allowed to hop. As discussed below, surface hops result in a discontinuous semiclassical potential energy function V_{SH}, and it is therefore desirable to minimize the number of surface hops.

In general, the potential energy of the currently occupied electronic state j and the state to which the system may hop k are not equal, i.e.

$$\Delta U \equiv \bar{U}_k - \bar{U}_j \neq 0, \tag{75}$$

and in order to conserve the total energy of the trajectory, the kinetic energy must be adjusted by ΔU. In practice, the adjustment is made by scaling the nuclear momentum in the direction of a unit vector called the hopping vector $\vec{h}$. The hopping vector is usually taken to be the direction of $\vec{F}_{jk}$, and this choice has been justified by both theoretical considerations[190,191,201,202] and numerical studies.[71,72] This choice for $\vec{h}$ is not as clear when the diabatic representation is being used, but $\vec{F}_{jk}$ (to be distinguished from $\tilde{\vec{F}}_{jk}$) is still commonly used to adjust the nuclear kinetic energy at a surface hop, even in the diabatic representation.

The TFS method may be implemented in either the adiabatic or the diabatic representation.[74,154] Initially, it was recommended that the adiabatic surfaces be used based on the idea that surface hops may provide a "diabatic passage" in the adiabatic representation and can thus model diabatic behavior, whereas surface hops between diabatic states cannot approximate motion on the adiabatic surfaces.[152] It was shown using numerical studies,[74,154] however, that the error in the TFS method may be reduced by using the diabatic representation if the diabatic surfaces are less coupled to each other than are the adiabatic surfaces. In this case the diabatic surfaces provide a better description of the uncoupled motion and therefore of the nonadiabatic process overall. A rule called the Calaveras County criterion has been developed, and it leads to the prescription that one should use the representation (adiabatic or diabatic) that gives the smaller number of attempted hops in TFS simulations. (One could equally well prescribe the representation that leads to the smaller number of hops in the FSTU surface-hopping method, which will described below.) The possibility of optimizing the electronic basis for surface hopping has also been explored by Herman.[203,204]

The accurate quantal picture is represented by a swarm of TFS trajectories, each hopping between the various electronic states at slightly different locations. In this way, the flow of probability density (which may occur over an extended region in phase space) is accurately modeled. One drawback of TFS method is the lack of the proper treatment of decoherence (intra-state and inter-state) effects. In the SE method, a single trajectory is used to represent the motion in all of the electronic states and the different motions were thus allowed to interfere. In the TFS method, several trajectories are required to model the nonadiabatic dynamics *even for a single initial condition.* (In practice, of course, each trajectory has different initial conditions, but the important point is that in contrast to the SE method where there is only one possible trajectory for each initial position and momentum, there are several possible trajectories for a single initial position and momentum in the TFS method which differ from each other in their hopping locations.) In order to properly treat inter-state coherence, the TFS trajectories would be required to interfere with each other, but they do not do so in the standard TFS method. This lack of decoherence effects can have a significant effect on the final results because the coherences $\bar{\rho}_{kj}$ show up in the expressions for $\bar{\rho}_{jj}$ in Eq. (61) and these quantities are used to compute the TFS hopping probabilities. The trade-off for this lack of inter-state coherence is the ability to model chemical processes that involve divergent trajectories on different electronic states.

A significant problem that must be dealt with when using the TFS formulation is the existence of classically forbidden electronic transitions, also called "frustrated hops".[68,70,74,165,199,200,205,206] The TFS algorithm may have a nonzero hopping probability g_{jk} in regions where the nuclear momentum is insufficient along $\vec{h}$ to allow for an energy adjustment that will conserve total energy, i.e. the energy gap between the occupied and target electronic states is less than the kinetic energy in the modes parallel to $\vec{h}$ and the system is hopping to a state with a higher potential energy than the currently occupied state. When a frustrated hop is encountered in the TFS method, it is either ignored or the momentum along $\vec{h}$ is reversed, and in both cases the trajectory does not change electronic states. Frustrated hops therefore destroy the self-consistency of F_j and $\bar{\rho}_{jj}$ built into the TFS method.

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The existence of frustrated hopping may be ascribed to two different sources: one is a deficiency of the TFS method, and the other is a deficiency of the TE approach in general. As discussed above, the TFS method does not properly treat decoherence effects. If, for example, an excited surface k is classically inaccessible the coherence term between the classically inaccessible state and the currently occupied state j ($\bar{\rho}_{jk}$) should be zero, i.e. there can be no coherence between two states if one state is completely unoccupied. From Eqs. (61) and (74) one can see that if $\bar{\rho}_{jk} = 0$, the hopping probability will also be zero. The TFS method does not correctly treat decoherence and $\bar{\rho}_{jk}$ may be nonzero even when state k is highly energetically forbidden, resulting in g_{jk} being finite when the target state is completely inaccessible. Frustrated hops caused by this lack of proper treatment of decoherence are therefore considered an artifact of the TFS formulation and are not physically meaningful.

We know, however, that quantum mechanically there is some probability density in regions of phase space that are classically forbidden due to tunneling. These tails of the nuclear wave function decrease exponentially, so we do not expect significant populations in "highly" classically forbidden regions, but these tails may be important for regions that are only "slightly" classically forbidden, i.e. regions that are somewhat close to classically accessible regions. These tails in the quantum mechanical wave function also contribute to the existence of frustrated hopping, and these frustrated hops must be somehow allowed to switch electronic states in order to model the proper nonadiabatic dynamics. Frustrated hopping can be a severe problem, affecting anywhere from 10–80% of hopping trajectories for several realistic systems that have been recently studied.[70,165]

The fewest-switches with time-uncertainty (FSTU) method[165] has been developed to correct this deficiency without explicitly including tunneling or coherence effects. The FSTU method is identical to the TFS method except when a frustrated hop is encountered. If a FSTU trajectory $R(t)$ experiences a frustrated hop at time t_0, the trajectory is allowed to hop at time t_h [or equivalently at the geometry $R(t_h)$], where t_h is determined by selecting the closest time to t_0 (either forward or backward in time) such that: (1) a hop at $R(t_h)$ is classically allowed, and (2) the difference between t_0 and t_h is small enough that

$$|t_0 - t_h|\Delta E \leq \hbar/2, \tag{76}$$

where ΔE is the amount of energy that the system would have to "borrow" to hop at time t_0. This treatment is clearly inspired by the time-energy uncertainty relations,[207] and these nonlocal hops can be thought of as approximating those parts of the quantal system that borrow energy and tunnel into classically forbidden regions. If a suitable t_h cannot be found that meets the above criteria, then the frustrated hopping attempt is ignored. The cutoff in Eq. (76) allows us to separate and treat differently those frustrated hops caused by tunneling (and are therefore physically meaningful) and those that are caused by the improper treatment of decoherence (and are not physically meaningful).

We note another type of surface-hopping method that may be applied to physically meaningful systems. Early formulations of surface hopping[42,197] defined g_{jk} to be zero everywhere except at a predefined, localized transition seam. This approach has been extensively studied and extended by Zhu and Nakamura[208,209] (ZN) by using idealized hopping seams and has recently been tested against accurate quantum mechanics on a realistic three-atom system.[210] We will outline and discuss the method briefly for a two-state system. First, the transition seam is defined as the line of minimum energy gaps between the electronic states. Trajectories from an ensemble are propagated, and whenever a trajectory crosses the transition seam, the hopping probability g_{jk}^{ZN} is computed. The hopping probability is a function of the energies of the potential energy surfaces and the kinetic energy of the trajectory in the direction perpendicular to the seam. The ZN form of g_{jk}^{ZN} may be derived as a generalization of the analytic form given by Landau and Zener[6,7,46,152] which is valid only if one assumes a constant translational energy and diabatic coupling. When a surface hop occurs, the momentum of the trajectory is adjusted to conserve energy with $\vec{h}$ taken to be a unit vector perpendicular to the transition seam. If a hopping attempt is classically forbidden, the hop is allowed to occur nonlocally. Inter-state coherence effects are treated accurately within the context of the nonadiabatic effects being limited to a hopping seam.

The ZN method is mathematically elegant and physically illuminating as to the processes of nonadiabatic energy transfer at transition seams. The problem of identifying the transition seam and restricting transitions to idealized seams limits the applicability of the ZN methods when one considers large or complex chemical systems; in particular, the assumption of constant diabatic coupling as one crosses a seam is a serious limitation. An earlier trajectory surface hopping scheme employing idealized seams was presented by Stine and Muckerman[211] and is criticized elsewhere.[212]

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3.1.5. *Approximate Wave Packet Methods*

The methods described in the previous sub-sections were obtained by adding quantum corrections to classical mechanics. Another approach to developing semiclassical methods (advocated especially by Heller[213,214]) is to start with the accurate time-dependent quantum theory and to simplify it until it is affordable. The spawning method of Levine, Martinez, and coworkers[215,216] (called full-multiple spawning or FMS) is an example of a such a method that may be applied to chemical systems. Recently a well defined, minimal version of spawning called FMS-M has been presented.[164] It has been systematically tested[164] against accurate quantum mechanics, and so we will discuss it briefly here.

The initial state of the system for a FMS-M calculation is constructed from a relatively small set of Gaussian-shaped wave packets. The number of initial wave packets can be much less than the number of trajectories used in the simulations described above because each wave packet has some width. One must be careful, however, to be sure that the phase space of the reactants is adequately sampled, and that the phase space remains properly sampled over the course of the simulation. This is often difficult and remains a significant drawback to the spawning method and to wave packet methods in general. The initial wave packets are propagated along a classical trajectory located at the center of the Gaussian. The wave packets periodically "spawn" new wave packets on other electronic surfaces, and meanwhile electronic state population density is allowed to flow between the wave packets on different surfaces. An attractive feature of spawning is that the algorithm adds new wave packets as needed on-the-fly, and in this sense it is more efficient that simply saturating the phase space with wave packets. A seeming advantage of the FMS method is that one does not make arbitrary assumptions about where a hop occurs or what component of the nuclear momentum to change when a hop occurs. However these decisions are replaced by an equally arbitrary set of choices concerning the placement of spawned packets, and as a result the method has a strong underlying similarity to surface hopping. Nevertheless, the FMS-M method can treat both inter-state and intra-state coherence effects and some tunneling effects, and it remains an attractive area of research.

3.2. *Quantum Mechanical Methods*

3.2.1. *General Considerations*

Accurate quantum dynamics calculations are of fundamental interest and provide important benchmarks for the approximate but more practical semiclassical trajectory methods discussed in Sec. 3.1. For systems with two or three atoms, an accurate quantum mechanical treatment of the nuclear motion on coupled electronic potential energy surfaces is computationally feasible. The computational requirements typically scale as N_b^3 (or at best N_b^2) where N_b denotes the size of the basis set. If $n_b(i)$ denotes the size of the basis set required for an accurate quantum mechanical calculation on the ith electronic potential energy surface and d the denotes the number of coupled electronic states, then $N_b = \sum_{i=1}^{d} n_b(i)$. If the same basis set is used for each electronic state (i.e. all $n_b(i)$ are equal), the computational requirements scale as d^3. In this case, the computational requirements for two coupled electronic states ($d = 2$) are 8 times larger than a calculation on a single (uncoupled) electronic potential energy surface. Often a smaller basis set can be used for the excited electronic state, and when this is the case a two-state calculation is less than 8 times more expensive than a single-state calculation. Furthermore, a fully converged cross section or bimolecular reaction rate involves contributions from a large number of partial waves. A separate calculation is required for each value of total angular momentum J and inversion parity P. If k denotes the size of the basis set for $J = 0$ and if one uses complete sets of angular momentum projection quantum numbers, one has $N_b = k(J + 1)$ (for $J + P$ even). In such cases the computational requirements scale as J^3. However, one can often truncate the basis set for larger values of J to some maximum value Ω of the component of total angular momentum along a body-frame z axis.[217] In this case the size of the basis set remains constant for $J > \Omega$ which makes the calculations much more affordable for large J. Since the computational requirements increase significantly when more electronic states are included, most of the accurate quantum mechanical studies to date are limited to $d = 1$ when $J \geq 0$ or to $d = 2$ with $J = 0$. However, recent improvements in the numerical methods coupled with the current generation of parallel supercomputers make calculations with $d > 1$ and $J \geq 0$ more practical.

If the non-diagonal coupling cannot be neglected, we must solve the generalized Born–Oppenheimer Eq. (35). As discussed in Secs. 2.4.2–2.4.4,

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a transformation to a diabatic electronic basis is often desirable. This transformation removes the singular part of the vector NACTs that arises in the adiabatic representation, leaving a "nonremovable" part. In some cases the nonremovable part may be small enough to neglect, leaving only the scalar coupling arising from the off-diagonal matrix elements of the diabatic electronic Hamiltonian. All of the converged quantum mechanical treatments of polyatomic nonadiabatic dynamics to date utilize a diabatic electronic representation and ignore the nonremovable part of the vector NACTs.

3.2.2. *Computational Methodology*

We will restrict our attention in this section to triatomic systems, which have six nuclear degrees of freedom, excluding the center-of-mass motion. Three of these degrees of freedom correspond to internal motion which we will denote as x. The other three degrees of freedom give the orientation of the body frame (BF) relative to the space frame (SF) and are usually taken to be the three Euler angles, which we will denote as $\hat{x} = (\alpha, \beta, \gamma)$.

The first computational approach which we will discuss in detail is based on the symmetrized hyperspherical coordinates $x = (\rho, \theta, \varphi)$.[218–222] The radial coordinate ρ corresponds to a symmetric stretch motion, the polar angle θ represents a bending type motion where $\theta = \pi/2$ corresponds to linear geometries and $\theta = 0$ corresponds to T-shaped arrangements (equilateral triangles for equal mass nuclei), and the azimuthal angle φ corresponds to an internal kinematic rotation (i.e. a pseudo-rotational motion). The BF z axis is chosen perpendicular to the plane of the triatomic molecule, and the BF x and y axes are chosen to lie along the instantaneous principal axes of inertia (i.e. the $\vec{Q}$ and $\vec{q}$ vectors of Ref. 223). The collective set of coordinates is denoted by $R = (\rho, \theta, \varphi, \alpha, \beta, \gamma)$ or $R = (x, \hat{x})$. The relevant nuclear Schrödinger equation is solved in two steps.[223] In the first step, the radial variable ρ is partitioned into a large number of "sectors" and the 5D surface (angular) differential equation is solved with ρ fixed at the center of each sector. This step is independent of the scattering energy. The surface function solutions are used to compute the potential coupling and overlap matrices which appear in the coupled-channel (CC) radial equations. In the second step, the CC radial equations are solved at each scattering energy using a log-derivative[224–226] propagation technique. Once one has solved the CC radial equation, one can apply the boundary conditions to the log-derivative matrix at large ρ to obtain the scattering matrix.[223]

The surface function solutions are obtained by diagonalizing the 5D surface differential equation, and this is usually the most computationally demanding step. However, if more than about 200 scattering energies are required then the propagation step can become the most computationally demanding step. The 5D surface function solutions are expanded in terms of a hybrid basis set consisting of a discrete variable representation (DVR)[227–229] in the hyperangle $\tilde{\theta} = \pi - 2\theta$, a finite basis representation (FBR) in the azimuthal angle φ, and the appropriate set of normalized Wigner $\tilde{D}(\alpha, \beta, \gamma)$ functions.[230] The hybrid basis set accurately treats both of the Eckart[231,232] singularities which occur in the kinetic energy operator at the north pole ($\theta = 0$) and equator ($\theta = \pi/2$) of the 2D hypersphere in (θ, φ) (see Ref. 230 for more details). An accurate treatment of these singularities is crucial for obtaining accurate scattering results especially at the higher scattering energies associated with nonadiabatic dynamics.[230] (We note that these singularities do not arise in some other solution methods, e.g. Refs. 59–64, discussed below.) The hybrid basis set is also highly parallelizable so that parallel supercomputers can be utilized.[230,233,234]

If the non-diagonal coupling can be neglected, then Eq. (15) is valid and a single electronic state (usually the ground state) is sufficient. Most single-surface dynamics calculations also ignore the vector potential terms in Eq. (15). However, if the ground electronic state exhibits a conical intersection with an excited electronic state, then $\vec{A}_{00}$ can be non-zero [see Eq. (26)]. If the energy of the nuclear motion is sufficient so that the nuclear wave function has appreciable amplitude along a closed path around the conical intersection, the effects of the geometric phase can be important.[91] If one uses a diabatic representation, the geometric phase is included automatically. If one uses an adiabatic representation there are two ways to proceed. First, accurate solution methods have been developed to solve Eq. (15) with a non-zero $\vec{A}_{00}$.[138,139] These methods have been applied to the $H + O_2 \rightarrow OH + O$ reaction,[112,138,139,235,236] the $H + D_2 \rightarrow HD + D$ reaction,[233] and the $H + H_2 \rightarrow H_2 + H$ and $D + H_2 \rightarrow HD + H$ reactions.[237] The same methodology has also been used to include geometric phase effects in calculations of the vibrational spectra for HO_2[112] and Na_3.[236,238] Alternatively, as noted in Sec. 2.3.4, the geometric phase can be accounted for by solving Eq. (15) with a zero $\vec{A}_{00}$ and double-valued boundary conditions on ψ_0. This is the approach used by Kuppermann and coworkers.[100–103] One of us has recently implemented the double-valued basis set approach in calculations on the $H + H_2$ reaction (and its isotopic variants) and has verified that it gives identical results to those based on the vector potential

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approach.[237] However, these geometric phase results are quite different than those of Kuppermann and coworkers[100–103] and will be discussed in detail elsewhere.[237]

One possibly desirable way to proceed is to remove the entire longitudinal part of the nonadiabatic coupling. As discussed in Sec. 2.4.5, in order to remove the longitudinal part of the vector NACMs, one must solve the Poisson Eq. (52) for λ as a function of the nuclear coordinates. One can then apply the transformation matrix of Eq. (44) to the adiabatic electronic basis to obtain an effective Schrödinger equation for the nuclear motion with non-singular (transverse) NACMs and a non-diagonal electronic potential matrix [i.e. Eq. (35) but expressed in terms of the transformed quantities given in Eqs. (37)–(39)]. Abrol and Kuppermann[126] have implemented these steps for the H_3 system. The relevant 3D Poisson equation in terms of (ρ, θ, φ) was solved with appropriate boundary conditions using the MUDPACK[239,240] library of subroutines. If one considers all six nuclear degrees of freedom, then a 6D Poisson equation in terms of $(\rho, \theta, \varphi, \alpha, \beta, \gamma)$ must be solved. A meshless solution method based on the Moving Least Squares (MLS) approach could be used in this case.[241]

Obtaining accurate numerical solutions of the Poisson equation can be computationally demanding and may require more work than solving the original nuclear Schrödinger equation. Fortunately, accurate solutions to the Poisson equation are not usually needed because it is expected to often be a reasonable strategy to only remove the singularities in the longitudinal part of $\vec{\mathbf{F}}$ that occur at conical intersections. It is hard to make general arguments to justify the extra effort required to remove the longitudinal part of $\vec{\mathbf{F}}$ far from an intersection because, far from a conical intersection, the nonremovable coupling is in general the same order of magnitude as the removable coupling [see the discussion below Eq. (52)]. For example, in the H_3 system a conical intersection between the ground and first excited electronic states occurs at $\theta = 0$ (equilateral triangles) for all ρ. Thus, one can choose $\lambda = -\varphi/2$ which is a solution of Eq. (46) in an infinitesimal region near the conical intersection.[241] Furthermore, this choice for λ gives rise to an electronic basis which is single-valued around the conical intersection.[242] However, since the transformation involves $\varphi/2$ instead of $3\varphi/2$, the nuclear permutation symmetry must be treated with care.[91] As the radial distance from the conical intersection increases, $\vec{\mathbf{F}}$ will contain non-zero longitudinal and transverse components,[243] but neither of these are singular. Even when one has successfully removed the troublesome singularities in $\vec{\mathbf{F}}$, the Eckart[231,232] singularities may still be present for some choices of coordinates, and an accurate numerical solution must also account for them.[230]

For X_3 systems with a single conical intersection located at equilateral triangle (D_{3h}) geometries (such as H_3), there is an alternative approach for treating the singular NACMs without a transformation to a diabatic electronic basis via $\lambda = -\varphi/2$. In this approach a complex single-valued adiabatic electronic basis is used, and there are non-zero diagonal matrix elements of $\vec{\mathbf{F}}$ (see Secs. 2.2, 2.3, and Ref. 242). The singularities in the diagonal matrix elements of $\vec{\mathbf{F}}$ can be grouped together with the Eckart singularities, and all of the singularities can then be accurately treated numerically by a suitable choice of Jacobi polynomials in the hyperangle θ.[230] One can show that the exact single-surface (uncoupled) nuclear wave functions approach zero at the conical intersection so that matrix elements of the singular terms in the non-diagonal coupling elements of $\vec{\mathbf{F}}$ should cause no problems.[242] We also note that the treatment of the nuclear permutation symmetry is more straightforward in this approach.[91,242]

The adiabatic approach described above has the advantage that modifications of the existing computer codes are relatively straightforward to implement to treat two coupled adiabatic electronic potential energy surfaces, and one does not have to solve a Poisson equation. It also avoids an adiabatic-to-diabatic transformation. One simply adds one more index to the surface function basis set that labels the adiabatic states and duplicates the code in the matrix-vector multiply routine (which is used by the Lanzcos diagonalizer) so that one part acts on the vector components associated with the excited electronic state, and the other part acts on the vector components associated with the ground electronic state. The computer code for the two parts are identical except for the matrix elements of the adiabatic electronic potential energy surfaces. One then adds one more part which computes the contributions due to the non-diagonal matrix elements of $\vec{\mathbf{F}}$ (i.e. the coupling between the two adiabatic electronic states). One must also write a subroutine which computes the matrix elements of the non-diagonal terms in $\vec{\mathbf{F}}$ with respect to our basis set in (θ, φ). This subroutine is called prior to the diagonalization step. The log-derivative propagation algorithm can be generalized to handle radial coupling terms which also contain a first derivative with respect to ρ,[112] as can the Magnus algorithm, the R-matrix method, and other numerical schemes.[19] Applying boundary conditions for scattering problems requires the addition of an electronic label on the asymptotic diatomic states. If the coupling between the relevant electronic states vanishes asymptotically (e.g. for large ρ or a

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large value of the distance between any two separating subsystems), then the appropriate boundary conditions involve adding an electronic label to the single surface boundary conditions. However, if the coupling does not vanish asymptotically, it must be taken into account when computing the relevant asymptotic wave functions and energies.[65,80,81] The initial and final scattering states will then be some linear superposition of these coupled basis states.

For other triatomic molecules (i.e. ABC, AB_2, and more complicated X_3 molecules such as O_3), the location of the conical intersection of interest is not always fixed at $\theta = 0$. Thus, in the adiabatic approach the singularities in the diagonal matrix elements of $\vec{\mathbf{F}}$ cannot be grouped with the Eckart singularities. For these more general situations a transformation to a diabatic basis is probably the best approach. However, even for these more complicated systems, we can remove the troublesome singularities in $\vec{\mathbf{F}}$ without having to solve a Poisson equation (see Sec. 2.4.4). Once a suitable λ has been evaluated, one can implement the transformation of Eq. (44) and solve Eq. (35). The modifications to our existing computer codes are similar to those discussed above. However, the diabatic electronic potential energy matrix contains non-diagonal matrix elements with respect to the electronic label, and there are no diagonal matrix elements in $\vec{\mathbf{F}}$ (or $\tilde{\vec{\mathbf{F}}}$).

Several other methods based on a variety of different approaches are also available for quantum mechanical nonadiabatic dynamics calculations. Some calculations propagate the solution of the time-independent coupled-channel equations as a function of the hyperradius[50–52,55–58,141] and are similar to the hyperspherical approach discussed above. The treatment of Kamisaka *et al.*[50] utilized a 3×3 Diatomics-in-Molecules (DIM) potential matrix to fit *ab initio* data for the DH_2^+ system. The adiabatic representation is obtained by diagonalizing this matrix. The dynamics were carried out for zero total angular momentum ($J = 0$) on the three diabatic states using the DIM matrix to represent the interaction. The nonadiabatic transitions were observed to give rise to non-statistical behavior in the resonance spectrum. The work by Schatz and Drukker[51,141] investigated the effects of spin-orbit and Coriolis coupling in the $Cl(^2P) + HCl$ and $O(^1D) + H_2$ reactions. For the former reaction, rate constants were evaluated using the separable rotation approximation with the accurate $J = 1/2$ calculations as reference. The activation energy was found to increase by about 30% of the atomic $^2P_{1/2} - {}^2P_{3/2}$ energy difference. More recent work on this same reaction was undertaken by Whiteley *et al.*[52] including three coupled potential energy surfaces. Takayanagi and Kurosaki[56] have investigated the $Br(^2P_{1/2}) + H_2$ reaction using a 2 × 2 diabatic model. They found that electronically nonadiabatic transitions from $Br(^2P_{1/2}) + H_2(v)$ to $Br(^2P_{3/2}) + H_2(v+1)$ effectively occur in the entrance region of the potential energy surface but that the contribution of the electronically nonadiabatic reaction $Br(^2P_{1/2}) + H_2(v) \rightarrow HBr + H$ is small. Takayanagi *et al.*[55] investigated the $(D+H_2)^+$ system using a 3×3 DIM potential matrix; they compared the quantum mechanical results to a quasiclassical trajectory surface hopping method and found generally good agreement. Takayanagi[58] has recently investigated the $O(^1D) + H_2$, D_2, and HD reactions including three electronic states. Electronically nonadiabatic transitions were found to be very important, but the effects of isotopic substitution were relatively minor. Aquilanti *et al.*[57] obtained converged quantum mechanical dynamics using a hyperspherical coordinate approach for the $F + H_2$ system.

Other coupled-channel calculations include those of Yang and Alexander.[47] They constructed a 4 × 4 diabatic electronic potential matrix and investigated the effects of nonadiabatic coupling in the predissociation dynamics of the $CN(X^2\Sigma^+, A^2\Pi)Ne$ complex. The calculated resonance energies were found to be in reasonably good agreement with the experimental data. However, some of the calculated predissociation lifetimes did not agree well with the experimental data, and the discrepancies were attributed to uncertainties in *ab initio* electronic potential energy surfaces. Gilibert and Baer[48] studied the effect of spin-orbit coupling for the $F(^2P_{3/2,1/2}) + H_2 \rightarrow HF + H$ reaction using model potential energy surfaces. One of their main findings was that weak electronic diabatic coupling terms significantly affect the reaction process taking place on the lower adiabatic potential energy surface. This same reaction was later studied by Alexander *et al.*[49] using accurate *ab initio* potential energy surfaces. They reached the opposite conclusion. That is, the overall dynamics of the $F + H_2$ are well described by calculations on a single, electronically adiabatic potential energy surface.

Accurate quantum mechanical nonadiabatic dynamics calculations have also been performed using a time-independent linear algebraic variational method[59–74]. In this method (called the outgoing wave variational principle or OWVP[63,244]), the Schrödinger equation is solved by expanding the outgoing scattering waves in terms of internal-state channel functions for each asymptotic chemical arrangement. The full Hamiltonian for each chemical arrangement is partitioned into a distortion Hamiltonian that contains some of the channel–channel coupling and a coupling potential that contains the

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remainder of the channel–channel coupling. The solution to the Schrödinger equation can be written in integral form where the first term in the solution is called the distorted-wave and is obtained by solving the distorted wave Schrödinger equation numerically using finite differences. The contribution to the scattering matrix from the coupling potential is obtained variationally using a dynamically adapted basis set. Using this two-step scheme, the full scattering matrix is written as the sum of two terms, where the first term is the distorted-wave Born approximation for the scattering matrix obtained using the distorted-wave functions, and the second term is the contribution from the coupling potential.

Early treatments employing the OWVP method focused on the nonreactive quenching process $\mathrm{Na}(3p) + \mathrm{H}_2 \rightarrow \mathrm{Na}(3s) + \mathrm{H}_2$ for zero[59–62] and unit[62] total angular momentum. Convergence was demonstrated[59,62] by obtaining the same results using two entirely different methods—R-matrix propagation[245,246] and the outgoing wave variational principle.[63,244] Accurate quantum mechanical calculations were also obtained for the reactive collisions $\mathrm{H}+\mathrm{HBr} \rightarrow \mathrm{H}_2+\mathrm{Br}(^2P_{1/2})$ and $\mathrm{H}+\mathrm{HBr} \rightarrow \mathrm{H}_2+\mathrm{Br}(^2P_{3/2})$.[64] The competition between electronically nonadiabatic reaction and electronic-to-vibrational energy transfer was investigated for the $\mathrm{Br}(^2P_{1/2}) + \mathrm{H}_2 \rightarrow \mathrm{HBr} + \mathrm{H}$ reaction.[65] Calculations for a series of three-body model systems exhibiting avoided crossings in the vicinity of the reaction barrier showed strong nonadiabatic effects on reaction probabilities due to funnel resonances.[66] OWVP calculations have been performed more recently on a variety of model systems, and these results have been used as benchmarks to assess the validity of the semiclassical approaches discussed in Sec. 3.1. The benchmarks include three qualitatively different types of chemical systems: (1) systems with conical intersections,[67,68,71,72,74] (2) systems with diabats that cross and adiabats that do not intersect,[69] and (3) systems with wide regions of weak coupling where the diabats and adiabats do not cross.[70,73] This set of benchmark calculations includes reactive[67,69,70,72,73] and nonreactive[71,72] scattering collisions as well as unimolecular excited-state decay processes.[68,74]

Other quantum mechanical methods propagate wave packets as a function of both time and coordinates.[53,54,75–79] The study by Gray *et al.*[53] investigated the dynamics of the $\mathrm{O}(^1D) + \mathrm{H}_2 \rightarrow \mathrm{OH} + \mathrm{H}$ reaction including two diabatic electronic states. They found that nonadiabaticity is not an important issue if the initial wave packet starts on the ground electronic state. However, if the initial wave packet starts on the excited electronic state, then long range electronic transitions can occur. Wave packets have also been used to study the photodissociation of ozone.[54] In this study, a 2×2 diabatic potential matrix was computed using *ab initio* methods. The nonadiabatic coupling was found to be exceedingly strong so that the dissociation processes were very fast (within one symmetric stretch period). The photodissociation of collinear HF$\cdots$Na van der Waals complexes has also been investigated using wave packets.[75] The quantum calculations showed a substantial isotope effect. Comparing the quantum results with those of several semiclassical theories showed that none of them were in even qualitative agreement with the half lives and branching ratios inferred from this kind of wave packet simulation. Converged quantum results using wave packets have also been obtained for the unimolecular dissociation of the spin-orbit coupled N_2O[76,77] system and the HCO[78] and HNO[79] systems including Renner–Teller coupling.

Many of the quantum mechanical methods discussed above treat the nonadiabatic coupling using a diabatic representation and ignore the nonremovable part of the vector NACMs. Since the nonremovable coupling is not always negligible, a complete treatment of nonadiabatic coupling should include it.

4. Concluding Remarks

We reviewed the fundamental theory for both electronically adiabatic and electronically nonadiabatic processes. The nonadiabatic coupling matrices (NACMs) which appear in the coupled equations for the nuclear motion are *a priori* of order magnitude unity. However, in the terms (called nonadiabatic coupling terms or NACTs) in which these coupling matrices appear in the coupled equations for the nuclear motion, they are multiplied by the small quantity $1/M$ so that a power series expansion for the molecular wave function, energy, and other quantities of interest in terms of $\kappa = (1/M)^{1/4}$ is possible. For low-energy bound states and low-energy dynamical processes, the off-diagonal matrix elements of the NACTs can often be neglected, and we have a situation which is usually referred to as the "Born–Oppenheimer approximation" in which the nuclear motion is governed by the effective potential generated by a single adiabatic electronic state.

However, even under the Born–Oppenheimer approximation there can be additional complications due to conical intersections, even if the nuclear-motion wave function is significantly different from zero only in regions where the NACTs are negligible and the Born–Oppenheimer approximation is valid, provided that the nuclear wave function has significant amplitude along the whole length of a path enclosing a conical intersection. A conical intersection causes the real adiabatic electronic wave function to change sign for any closed path in the nuclear parameter space which encircles a conical intersection (i.e., is double-valued). This sign change is a special case of the geometric phase. Since the total molecular wave function must be single-valued, the nuclear wave function must also be double-valued and a correct theoretical treatment must take this into account. One approach applies a phase transformation on the real electronic basis to give a single-valued *complex* electronic basis. The effective Schrödinger equation for the nuclear motion contains a vector potential (i.e., a non-zero diagonal NACT) and the nuclear wave functions are single-valued. Another approach is to implement the double-valuedness directly into the nuclear wave functions by implementing suitable boundary conditions on the basis functions. There is no vector potential in this approach. A third approach is to use diabatic representations that include the geometric phase implicitly so that it need not be dealt with explicitly. If implemented fully (including the residual nonadiabatic coupling in the diabatic case and including all nonadiabatic coupling in the adiabatic case), all three approaches will give the same results for physical observables.

A conical intersection (degeneracy) between two adiabatic electronic states occurs in submanifolds of the nuclear parameter space. The number of conditions or constraints which define these submanifolds is two. Thus, the dimensionality of these submanifolds is $n-2$ where $n = 3N-6$ for $N \geq 3$ nuclei. Any closed path in the nuclear parameter space which encircles a conical intersection manifold results in a sign change on the two relevant real adiabatic electronic wave functions (i.e., conical intersection manifolds are transition manifolds). Furthermore, by considering the singular properties of the NACMs, we have shown that conical intersection manifolds are the *only* transition manifolds. In general, there may be more than one conical intersection manifold and it may be possible that two of these intersect. Such intersections are called "confluences" and the number of conditions which must be satisfied for them to occur is 4, leaving $n - 4$ degrees of freedom on the confluence. The number of conditions can be further reduced to 3 in the presence of symmetry.

For high-energy bound states and high-energy dynamical processes or when two or more electronic states are degenerate or nearly degenerate for any nuclear geometry where the nuclear wave function has significant amplitude, the off-diagonal matrix elements of the NACTs cannot be ignored, and we must include more than one electronic state. However, in many cases we can still limit attention to a finite number of electronic states, and in such cases we have a situation that is referred to as the "generalized Born–Oppenheimer approximation". We investigated the effects of a unitary transformation on the relevant adiabatic electronic subspace and showed that a strictly diabatic basis (i.e. a basis for which the NACMs are identically zero) does not exist. However, there is one troublesome part of the NACMs that can be removed by a suitable transformation, and that is the part that becomes singular near a conical intersection. The nonremovable part is, in general, of order unity, and because it appears multiplied by $1/M$, it is often neglected. The corresponding electronic basis is often referred to as a quasidiabatic or diabatic basis. For a two-dimensional electronic subspace, we showed how to decompose the coupling into longitudinal (irrotational) and transverse (solenoidal) parts. The longitudinal part contains the singular terms and is removable. However, in order to completely remove the longitudinal part of the coupling, a Poisson equation must be solved. Since, far from a conical intersection, the non-removable coupling is in general the same order of magnitude as the removable coupling, we do not necessarily need to solve a Poisson equation and remove all of the longitudinal coupling. Instead, we can take advantage of the arbitrariness of the diabatic representation to remove only the troublesome singular terms.

Our discussion of semiclassical methods focused mainly on methods in which an ensemble of trajectories represents, in some sense, a quantum mechanical wave packet or a slice through such a wave packet, and we presented detailed discussions only of semiclassical methods that have been tested against accurate quantum dynamics for full-dimensional three-body problems. In order to properly treat nonadiabatic effects, a self-consistent treatment of the nuclear-electronic coupling is necessary. We considered trajectory ensemble (TE) methods where the trajectories may be propagated independently and derived the coupled equations for the time evolution of the coefficients representing the probability amplitudes for the relevant electronic states. We discussed two general categories of semiclassical algorithms with differing prescriptions for the potential energy function V: time-dependent self-consistent field (TDSCF) methods and trajectory surface hopping (TSH) methods.

The TDSCF methods are based on a semiclassical version of the quantum Ehrenfest theorem. In the semiclassical Ehrenfest (SE) approach, the potential energy felt by the SE trajectory is a weighted average of the potential energies felt by hypothetical trajectories in each electronic state. Thus, the coherence effects between the electronic states are treated in this

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approach. However, the SE approach has many disadvantages that result from the mean-field assumption. In particular, a SE trajectory will finish the simulation in a mixed electronic state, whereas physically we expect isolated products to be in pure electronic states (assuming that the electronic states chosen as a basis are uncoupled in the product region of phase space). Several modifications of the SE method have been proposed to overcome these problems. We discussed the natural decay of mixing (NDM) method which modifies the time derivatives of the density matrix elements by adding a dephasing term. The dephasing terms cause the mixed states to decohere or collapse into a pure electronic state asymptotically, and this mimics what happens in quantum mechanical wave packet treatments due to the dephasing of different parts of the wave packet.

In the TSH methods the potential is taken to be the diagonal element of the potential energy matrix that corresponds to the currently occupied electronic state. The single-surface propagation is interrupted by instantaneous surface transitions (called surface hops) to some other electronic state. These hops occur with some time-dependent probability, and we discussed several ways of defining this hopping probability. Tully's fewest-switches (TFS) method minimizes the number of surface hops, and either the adiabatic or diabatic representation is used depending upon which representation gives the fewest number of attempted hops in the TFS simulation. (This criterion is called the Calaveras County criterion.) Unlike the SE approach, the TFS method does not treat inter-state coherence effects. Also, a significant problem that must be dealt with when using the TFS approach is the existence of classically forbidden electronic transitions or "frustrated hops". Some frustrated hops originate from the inability of the TFS method to properly treat decoherence effects and are considered to be an artifact of the TFS method. However, many frustrated hops are due to quantum mechanical tunneling effects and should be somehow accounted for. We discussed the fewest switches with time-uncertainty (FSTU) method, which addresses this deficiency without explicitly including tunneling or coherence effects. This approach is inspired by the time-energy uncertainty relations and allows us to separate and treat differently those frustrated hops caused by tunneling and those that are caused by the improper treatment of decoherence.

We also discussed another surface hopping method which defines the hopping probability to be zero everywhere except at a predefined, localized, idealized transition seam. Inter-state coherence effects are treated accurately within the context of the nonadiabatic effects being limited to such an idealized hopping seam. However, the transition seam becomes harder to identify for large or complex systems, and restricting transitions to an idealized seam limits the applicability of this approach. We also discussed approximate wave packet methods which approximate the solution of the accurate time-dependent Schrödinger equation such that the calculations are computationally affordable. In particular the full multiple spawning (FMS) method and its well defined minimal version, FMS-M, were discussed. This approach spawns (creates) new wave packets as needed on-the-fly and can treat both inter-state and intra-state coherence effects and some tunneling effects.

We began our discussion of accurate quantum mechanical methods by discussing the scaling of the computational cost as a function of the number of atoms, the number of electronic states, and the total angular momentum quantum number J and by noting that all of the nonadiabatic quantum mechanical studies to date have been limited to systems with two or three atoms, two electronic states, and $J = 0$ or 1. We discussed in detail a coupled-channel approach based on body-frame symmetrized hyperspherical coordinates that may be used for computing the nuclear dynamics for triatomic molecules. This method accurately treats the Eckart singularities that occur in body-frame coordinate systems. An accurate treatment of these singularities is crucial for obtaining accurate scattering results in body-frame coordinate systems especially at the high collision energies associated with nonadiabatic dynamics. This method is also highly parallelizable so that the full power of the latest generation of parallel supercomputers can be utilized.

If the off-diagonal NACTs can be neglected, then the nuclear dynamics can be confined to a single adiabatic electronic potential energy surface. However, if a conical intersection occurs, additional complications due to the geometric phase arise. In particular, a vector potential (i.e. a nonzero diagonal NACT) can appear in the nuclear Schrödinger equation. We discussed recent calculations which include geometric phase effects by solving the nuclear Schrödinger equation with a vector potential.

If the off-diagonal NACTs cannot be neglected, then we must include more than one electronic state and solve a generalized Born–Oppenheimer equation. Furthermore, the NACMs contain troublesome singularities at conical intersections. For two electronic states, we can solve a Poisson equation to determine an adiabatic-to-diabatic transformation angle λ as a function of the internal nuclear coordinates. This approach removes *all* of the longitudinal (irrotational) part of the NACMs including the singular terms.

However, an accurate solution to the Poisson equation can be computationally challenging. An alternative approach is to take advantage of the arbitrariness of diabatic representations and choose an appropriate functional form for the angle λ which removes *only* the singular terms. We discussed how such an approach could be implemented for the H_3 molecule. From simple X_3 systems such as H_3 where the conical intersection happens to occur at the same location as one of the Eckart singularities, one can also solve the problem directly in the adiabatic representation (i.e. a transformation to a diabatic basis is not required) by choosing an appropriate set of Jacobi polynomials in the hyperangle θ.

We also discussed several quantum mechanical nonadiabatic dynamics calculations of both bimolecular and unimolecular processes that are based on a variety of other methods, such as a time-independent coupled-channel approach that propagates the solution as a function of a radial or hyperradial coordinate, a time-independent linear algebraic method, and a time-dependent wave packet approach. The linear algebraic method, in particular, has proved to be a powerful method for solving a variety of electronically nonadiabatic dynamics problems.

Quantum mechanical treatments are important for understanding the fundamental mechanisms associated with electronically nonadiabatic chemical reactions. They are also important for benchmarking the approximate but more computationally practical semiclassical methods. However, much work remains to be done, such as extending the benchmark calculations to higher values of total angular momentum to obtain fully converged cross sections and reaction rates and generalizing the quantum mechanical methods to include treatment of the nonremovable part of the vector NACMs.

Acknowledgments

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References

1. E. Wigner, *Trans. Faraday Soc.* 34, 29 (1938).
2. M. Born and R. Oppenheimer, *Ann. Phys.* 84, 457 (1927).

3. M. Born, *Festschrift Gött. Nachr. Math. Phys.* K1, **1** (1951).
4. M. Born and K. Huang, *The Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954).
5. E. Teller, *J. Phys. Chem.* **41**, 109 (1937).
6. L. D. Landau, *Phys. Z. Sowjet.* **2**, 46 (1932).
7. C. Zener, *Proc. Roy. Soc. (London)* **A137**, 696 (1932).
8. E. C. G. Stückelberg, *Helv. Phys. Acta* **5**, 369 (1932).
9. H. Hellman and J. K. Syrkin, *Acta Phys. Chem. USSR* **2**, 4331 (1935).
10. A. D. McLachlan, *Mol. Phys.* **4**, 417 (1961).
11. W. Lichten, *Phys. Rev.* **164**, 131 (1967).
12. F. T. Smith, *Phys. Rev.* **179**, 111 (1969).
13. R. D. Levine, B. R. Johnson and R. B. Bernstein, *J. Chem. Phys.* **50**, 1694 (1969).
14. T. F. O'Malley, *Adv. Atom. Mol. Phys.* **7**, 223 (1971).
15. R. W. Numrich and D. G. Truhlar, *J. Phys. Chem.* **79**, 2745 (1975).
16. A. Macias and A. Riera, *J. Phys.* **B11**, L489 (1978).
17. B. C. Garrett and D. G. Truhlar, *Theor. Chem. Adv. Perspectives* (New York) **6A**, 215 (1981).
18. J. B. Delos, *Rev. Mod. Phys.* **53**, 287 (1981).
19. B. C. Garrett, M. J. Redmon, D. G. Truhlar and C. F. Melius, *J. Chem. Phys.* **74**, 412 (1981).
20. H.-J. Werner and W. Meyer, *J. Chem. Phys.* **74**, 5802 (1981).
21. C. A. Mead and D. G. Truhlar, *J. Chem. Phys.* **77**, 6090 (1982).
22. M. Baer, in *Theory of Chemical Reaction Dynamics*, ed. M. Baer (CRC, Boca Raton, 1988), Vol. 2, p. 219.
23. T. Pacher, L. S. Cederbaum and H. Köppel, *J. Chem. Phys.* **89**, 7367 (1988).
24. V. Sidis, *Adv. Chem. Phys.* **82**, 187 (1992).
25. T. Pacher, L. S. Cederbaum and H. Köppel, *Adv. Chem. Phys.* **84**, 293 (1993).
26. J. Hendekovic, *Croat. Chem. Acta* **56**, 3751 (1983).
27. F. Spiegelman and J. P. Malrieu, *J. Phys.* **B17**, 1259 (1984).
28. F. X. Gadéa and M. Pélissier, *J. Chem. Phys.* **93** 545 (1990).
29. T. Pacher, H. Köppel and L. S. Cederbaum, *J. Chem. Phys.* **95**, 6668 (1991).
30. R. Cimiriglia, in *Time-Dependent Quantum Molecular Dynamics*, eds. J. Broeckhove and L. Lathouwers (Plenum, New York, 1992), pp. 11–26.
31. P. Cattaneo and M. Persico, *Chem. Phys.* **214**, 49 (1997).
32. R. Thürwächter and P. Halvick, *Chem. Phys.* **221**, 33 (1997).
33. G. J. Atchity and K. Ruedenberg, *Theor. Chem. Acc.* **97**, 47 (1997).
34. R. D. Sadygov and D. R. Yarkony, *J. Chem. Phys.* **109**, 20 (1998).
35. D. R. Yarkony, *J. Phys. Chem.* **A102**, 8073 (1998).
36. D. R. Yarkony, *J. Chem. Phys.* **112**, 2111 (2000).
37. H. Köppel, J. Gronki and S. Mahapatra, *J. Chem. Phys.* **115**, 2377 (2001).
38. Hisao Nakamura and D. G. Truhlar, *J. Chem. Phys.* **115**, 10353 (2001); **117**, 5576 (2002); **119**, in press.
39. W. H. Miller, *Adv. Chem. Phys.* **26**, 69 (1974); **30**, 77 (1975).

---

40. W. R. Ge
(Plenum,
41. M. S. Chi
(Plenum,
42. J. C. Tully,
43. Hiroki Nak
44. S. Chapma
45. Hiroki Nak
R. E. Wya
46. E. E. Nikit
47. M. Yang a
48. M. Gilibert
49. M. H. Ale
109, 5710
50. H. Kamisa
116, 654 (
51. G. C. Scha
52. T. W. J.
Chem. Che
53. S. K. Gray
A103, 944
54. H. Flöthma
Phys. **107**,
55. T. Takaya
(2000).
56. T. Takayan
57. V. Aquilan
85, 368 (2
58. T. Takayan
59. D. W. Sch
D. G. Truh
60. S. L. Mielk
Soc. **115**, 6
61. S. L. Mielk
tum Chem.
62. G. J. Tawa
Phys. **100**,
63. G. J. Tawa
Vib. Collis
64. S. L. Mielk
Lett. **234**,
65. S. L. Mielk
(1995).
66. T. C. Allisi
Soc. Farad

(1951).
ystal Lattices (Oxford
).
'R **2**, 4331 (1935).
Chem. Phys.* **50**, 1694
9, 2745 (1975).
v. Perspectives* (New
F. Melius, *J. Chem.*
: (1981).
)90 (1982).
ed. M. Baer (CRC,
'hys.* **89**, 7367 (1988).
Chem. Phys.* **84**, 293
(1984).
(1990).
'hys.* **95**, 6668 (1991).
:r Dynamics*, eds. J.
)92), pp. 11–26.
)7).
(1997).
97, 47 (1997).
9, 20 (1998).
s.* **115**, 2377 (2001).
115, 10353 (2001);
(1975).

---

40. W. R. Gentry, in *Atom-Molecule Collision Theory*, ed. R. B. Bernstein (Plenum, New York, 1979), pp. 391–425.
41. M. S. Child, in *Atom-Molecule Collision Theory*, ed. R. B. Bernstein (Plenum, New York, 1979), pp. 427–465.
42. J. C. Tully, *Ber. Bunsenges. Physik. Chem.* **77**, 557 (1973).
43. Hiroki Nakamura, *Adv. Chem. Phys.* **82**, 243 (1992).
44. S. Chapman, *Adv. Chem. Phys.* **82**, 423 (1992).
45. Hiroki Nakamura, in *Dynamics of Molecules and Chemical Reactions*, eds. R. E. Wyatt and J. Z. H. Zhang (Dekker, New York, 1996), pp. 473–529.
46. E. E. Nikitin, *Annu. Rev. Phys. Chem.* **50**, 1 (1999).
47. M. Yang and M. H. Alexander, *J. Chem. Phys.* **107**, 7148 (1997).
48. M. Gilibert and M. Baer, *J. Phys. Chem.* **99**, 15748 (1995).
49. M. H. Alexander, H. J. Werner and D. E. Manolopoulos, *J. Chem. Phys.* **109**, 5710 (1998).
50. H. Kamisaka, W. Bian, K. Nobusada and Hiroki Nakamura, *J. Chem. Phys.* **116**, 654 (2002).
51. G. C. Schatz, *J. Phys. Chem.* **99**, 7522 (1995).
52. T. W. J. Whiteley, A. J. Dobbyn, J. N. L. Connor and G. C. Schatz, *Phys. Chem. Chem. Phys.* **2**, 549 (2000).
53. S. K. Gray, C. Petrongolo, K. Drukker and G. C. Schatz, *J. Phys. Chem.* **A103**, 9448 (1999).
54. H. Flöthmann, C. Beck, R. Schinke, C. Woywood and W. Domcke, *J. Chem. Phys.* **107**, 7296 (1997).
55. T. Takayanagi, Y. Kurosaki and A. Ichihara, *J. Chem. Phys.* **112**, 2615 (2000).
56. T. Takayanagi and Y. Kurosaki, *J. Chem. Phys.* **113**, 7158 (2000).
57. V. Aquilanti, S. Cavalli, D. De Fazio and A. Volpi, *Int. J. Quantum Chem.* **85**, 368 (2001).
58. T. Takayanagi, *J. Chem. Phys.* **116**, 2439 (2002).
59. D. W. Schwenke, S. L. Mielke, G. J. Tawa, R. S. Friedman, P. Halvick and D. G. Truhlar, *Chem. Phys. Lett.* **203**, 565 (1993).
60. S. L. Mielke, G. J. Tawa, D. G. Truhlar and D. W. Schwenke, *J. Am. Chem. Soc.* **115**, 6436 (1993).
61. S. L. Mielke, G. J. Tawa, D. G. Truhlar and D. W. Schwenke, *Int. J. Quantum Chem. Symp.* **27**, 621 (1993).
62. G. J. Tawa, S. L. Mielke, D. G. Truhlar and D. W. Schwenke, *J. Chem. Phys.* **100**, 5751 (1994).
63. G. J. Tawa, S. L. Mielke, D. G. Truhlar and D. W. Schwenke, *Adv. Mol. Vib. Collision Dynam.* **2B**, 45 (1994).
64. S. L. Mielke, G. J. Tawa, D. G. Truhlar and D. W. Schwenke, *Chem. Phys. Lett.* **234**, 57 (1995).
65. S. L. Mielke, D. G. Truhlar and D. W. Schwenke, *J. Phys. Chem.* **99**, 16210 (1995).
66. T. C. Allision, S. L. Mielke, D. W. Schwenke and D. G. Truhlar, *J. Chem. Soc. Faraday Trans.* **93**, 825 (1997).

67. M. S. Topaler, T. C. Allison, D. W. Schwenke and D. G. Truhlar, *J. Phys. Chem.* **A102**, 1666 (1998).
68. M. D. Hack, A. W. Jasper, Y. L. Volobuev, D. W. Schwenke and D. G. Truhlar, *J. Phys. Chem.* **A103**, 6309 (1999).
69. Y. L. Volobuev, M. D. Hack, M. S. Topaler and D. G. Truhlar, *J. Chem. Phys.* **112**, 9716 (2000).
70. A. W. Jasper, M. D. Hack and D. G. Truhlar, *J. Chem. Phys.* **115**, 1804 (2001).
71. M. S. Topaler, M. D. Hack, T. C. Allison, Y.-P. Liu, S. L. Mielke, D. W. Schwenke and D. G. Truhlar, *J. Chem. Phys.* **106**, 8699 (1997).
72. M. S. Topaler, T. C. Allison, D. W. Schwenke and D. G. Truhlar, *J. Chem. Phys.* **109**, 3321 (1998); **110**, 687(E) (1999); **113**, 3928(E) (2000).
73. Y. L. Volobuev, M. D. Hack and D. G. Truhlar, *J. Phys. Chem.* **A103**, 6225 (1999).
74. M. D. Hack, A. W. Jasper, Y. L. Volobuev, D. W. Schwenke and D. G. Truhlar, *J. Phys. Chem.* **A104**, 217 (2000).
75. Y. Zeiri, G. Katz, R. Kosloff, M. S. Topaler, D. G. Truhlar and J. C. Polanyi, *Chem. Phys. Lett.* **300**, 523 (1999).
76. Hisao Nakamura and S. Kato, *J. Chem. Phys.* **110**, 9937 (1999).
77. Hisao Nakamura and S. Kato, *J. Chem. Phys.* **112**, 1785 (2000).
78. J. Weiß, R. Schinke and V. A. Mandelshtam, *J. Chem. Phys.* **113**, 4588 (2000).
79. J. Weiß and R. Schinke, *J. Chem. Phys.* **115**, 3173 (2001).
80. R. J. Buenker and Y. Li, *J. Chem. Phys.* **112**, 8318 (2000).
81. A. K. Belyaev, A. Dalgarno and R. McCarroll, *J. Chem. Phys.* **116**, 5395 (2002).
82. H. Jeffreys and B. S. Jeffreys, *Methods of Mathematical Physics*, 3rd Edition (Cambridge University Press, Cambridge, 1956), Chapter 17.
83. E. T. Whitaker and G. N. Watson, *A Course of Modern Analysis*, 4th Edition (Cambridge University Press, Cambridge, 1958), Chapter VIII.
84. C. J. Ballhausen and A. E. Hansen, *Ann. Rev. Phys. Chem.* **23**, 15 (1972).
85. C. A. Mead in *Mathematical Frontiers in Computational Chemical Physics*, ed. D. G. Truhlar (Springer-Verlag, New York, 1988), pp. 1–17.
86. H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce and R. A. Sack, *Proc. Roy. Soc.* (London) **A244**, 1 (1958).
87. K. Gottfried, *Quantum Mechanics* (Benjamin, New York, 1966), Vol. 1, Sec. 39.
88. D. G. Truhlar, C. A. Mead and M. A. Brandt, *Adv. Chem. Phys.* **33**, 295 (1975).
89. C. A. Mead, *J. Chem. Phys.* **70**, 2276 (1979).
90. G. Herzberg and H. C. Longuet-Higgins, *Discuss. Faraday Soc.* **35**, 77 (1963).
91. C. A. Mead and D. G. Truhlar, *J. Chem. Phys.* **70**, 2284 (1979); **78**, 6344(E) (1983).
92. M. V. Berry, *Proc. Roy. Soc.* (London) **A392**, 45 (1984).

---

93. A. Sha
entific,
94. J. W.
(1990).
95. C. A.
96. H. C.
97. E. Ren
98. H. A.
99. M. S.
259 (1
100. B. Lep
101. A. Ku
102. A. Ku
R. E.
103. A. Ku
104. C. A.
105. T. C.
(1985).
106. S. P. K
107. T. C.
Mead,
108. S. P. K
109. B. Ken
110. A. Aue
111. J. Scho
112. B. Ken
113. E. E.
114. S. Adh
115. H. von
P. Seb
(1999).
116. A. J. C
117. S. Adhi
118. H. Koi
112, 8
119. M. Kei
J. Che
120. D. R.
121. D. R.
122. See, e.
(Acade
123. D. R.
124. N. Mat
125. R. Abr
115, 4
126. R. Abr

93. A. Shapere and F. Wilczek, eds., *Geometric Phases in Physics* (World Scientific, Singapore, 1989).
94. J. W. Zwanziger, M. Koenig and A. Pines, *Annu. Rev. Phys. Chem.* **41**, 601 (1990).
95. C. A. Mead, *Rev. Mod. Phys.* **64**, 51 (1992).
96. H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London) **A344**, 147 (1975).
97. E. Renner, *Z. Phys.* **92**, 938 (1934).
98. H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London) **A161**, 220 (1937).
99. M. S. Child and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London) **A254**, 259 (1961).
100. B. Lepetit, Z. Peng and A. Kuppermann, *Chem. Phys. Lett.* **166**, 572 (1990).
101. A. Kuppermann and Y.-S. M. Wu, *Chem. Phys. Lett.* **205**, 577 (1993).
102. A. Kuppermann, in *Dynamics of Molecules and Chemical Reactions*, eds. R. E. Wyatt and J. Z. H. Zhang (Dekker, New York, 1996), pp. 411–472.
103. A. Kuppermann and Y.-S. M. Wu, *Chem. Phys. Lett.* **349**, 537 (2001).
104. C. A. Mead, *Chem. Phys.* **49**, 23 (1980).
105. T. C. Thompson, D. G. Truhlar and C. A. Mead, *J. Chem. Phys.* **82**, 2392 (1985).
106. S. P. Keating and C. A. Mead, *J. Chem. Phys.* **82**, 5102 (1985).
107. T. C. Thompson, G. Izmirlian Jr., S. J. Lemon, D. G. Truhlar and C. A. Mead, *J. Chem. Phys.* **82**, 5597 (1985).
108. S. P. Keating and C. A. Mead, *J. Chem. Phys.* **86**, 2152 (1987).
109. B. Kendrick and C. A. Mead, *J. Chem. Phys.* **102**, 4160 (1995).
110. A. Auerbach, N. Manini and E. Tosatti, *Phys. Rev.* **B49**, 12998 (1994).
111. J. Schoen and H. Köppel, *J. Chem. Phys.* **103**, 9292 (1995).
112. B. Kendrick and R. T Pack, *J. Chem. Phys.* **106**, 3519 (1997).
113. E. E. Nikitin, *J. Chem. Phys.* **107**, 6748 (1997).
114. S. Adhikari and G. D. Billing, *Chem. Phys. Lett.* **289**, 219 (1998).
115. H. von Busch, V. Dev, H.-A. Eckel, S. Kasahara, J. Wang, W. Demtroder, P. Sebald and W. Meyer, *Phys. Rev. Lett.* **81**, 4584 (1998); **82**, 3560(E) (1999).
116. A. J. C. Varandas, H. G. Yu and Z. R. Xu, *Mol. Phys.* **96**, 1193 (1999).
117. S. Adhikari and G. D. Billing, *Chem. Phys.* **259**, 149 (2000).
118. H. Koizumi, I. B. Bersuker, J. E. Boggs and V. Z. Polinger, *J. Chem. Phys.* **112**, 8470 (2000).
119. M. Keil, H.-G. Krämer, A. Kudell, M. A. Baig, J. Zhu and M. Demtröder, *J. Chem. Phys.* **113**, 7414 (2000).
120. D. R. Yarkony, *J. Chem. Phys.* **109**, 7047 (1998).
121. D. R. Yarkony, *Mol. Phys.* **99**, 1463 (2001).
122. See, e.g., G. Arfken, *Mathematical Methods for Physicists*, 3rd Edition (Academic Press, New York, 1985), pp. 78–84.
123. D. R. Yarkony, *J. Chem. Phys.* **105**, 10456 (1996).
124. N. Matsunaga and D. R. Yarkony, *J. Chem. Phys.* **107**, 7825 (1997).
125. R. Abrol, A. Shaw, A. Kuppermann and D. R. Yarkony, *J. Chem. Phys.* **115**, 4640 (2001).
126. R. Abrol and A. Kuppermann, *J. Chem. Phys.* **116**, 1035 (2002).

127. B. K. Kendrick, C. A. Mead and D. G. Truhlar, *Chem. Phys.* **277**, 31 (2002).
128. F. X. Gadéa, H. Berriche, O. Roncero, P. Villarreal and G. Delgado Barrio, *J. Chem. Phys.* **107**, 10515 (1997).
129. J. H. Van Vleck, *Phys. Rev.* **33**, 467 (1929).
130. Y. B. Band and K. F. Freed, *Chem. Phys. Lett.* **79**, 238 (1981).
131. P. Archirel and P. Habitz, *Chem. Phys.* **78**, 213 (1983).
132. J. Moody, A. Shapere and F. Wilczek, *Phys. Rev. Lett.* **56**, 893 (1986).
133. S. Lee and K. F. Freed, *J. Chem. Phys.* **87**, 5772 (1987).
134. B. Zygelman, *Phys. Lett.* **A125**, 476 (1987).
135. R. Jackiw, *Int. J. Mod. Phys.* **A3**, 285 (1988).
136. B. Zygelman, *Phys. Rev. Lett.* **64**, 256 (1990).
137. A. Bohm, B. Kendrick and M. E. Loewe, *Int. J. Quantum Chem.* **41**, 53 (1992).
138. B. Kendrick and R. T. Pack, *J. Chem. Phys.* **104**, 7475 (1996).
139. B. Kendrick and R. T. Pack, *J. Chem. Phys.* **104**, 7502 (1996).
140. T. A. Barckholtz and T. A. Miller, *Int. Revs. Phys. Chem.* **17**, 435 (1998).
141. K. Drukker and G. C. Schatz, *J. Chem. Phys.* **111**, 2451 (1999).
142. M. H. Alexander, G. Capecchi and H.-J. Werner, *Science* **296**, 715 (2002).
143. See, e.g. R. de L. Kronig, *Band Spectra and Molecular Structure* (Cambridge University Press, Cambridge, 1930).
144. C. A. Mead, *Phys. Rev. Lett.* **59**, 161 (1987).
145. J. Schoen and H. Köppel, *J. Chem. Phys.* **108**, 1503 (1998).
146. J. C. Tully, in *Dynamics of Molecular Collisions*, ed. W. H. Miller (Plenum, New York, 1976), Part B, pp. 217–267.
147. D. G. Truhlar and J. T. Muckerman, in *Atom-Molecule Collision Theory*, ed. R. B. Bernstein (Plenum, New York, 1979), pp. 505–566.
148. H.-D. Meyer and W. H. Miller, *J. Chem. Phys.* **70**, 3214 (1979).
149. L. M. Raff and D. L. Thompson, in *Theory of Chemical Reaction Dynamics*, ed. M. Baer (CRC, Boca Raton, 1985), Vol. 3, pp. 1–121.
150. E. A. Gislason, G. Parlant and M. Sizun, *Adv. Chem. Phys.* **82**, 321 (1992).
151. M. F. Herman, *Ann. Rev. Phys. Chem.* **45**, 83 (1994).
152. J. C. Tully, in *Modern Methods for Multidimensional Dynamics Computations in Chemistry*, ed. D. L. Thompson (World Scientific, Singapore, 1998), pp. 34–72.
153. J. C. Tully, *Faraday Discuss. Chem. Soc.* **110**, 407 (1998).
154. M. D. Hack and D. G. Truhlar, *J. Phys. Chem.* **A104**, 7917 (2000).
155. S. Hammes-Schiffer and J. C. Tully, *J. Chem. Phys.* **101**, 4657 (1994).
156. S. Hammes-Schiffer, *J. Phys. Chem.* **A102**, 10443 (1998).
157. J. O. Hirschfelder and W. J. Meath, *Adv. Chem. Phys.* **12**, 3 (1967).
158. B. H. Lengsfield III and D. R. Yarkony, *Adv. Chem. Phys.* **82**, 1 (1992).
159. S. Mahapatra, H. Köppel, L. S. Cederbaum, P. Stampfuss and W. Wenzel, *Chem. Phys.* **259**, 211 (2000).
160. J. F. Stanton, *J. Chem. Phys.* **115**, 10382 (2001).
161. D. Xie, H. Guo and K. A. Peterson, *J. Chem. Phys.* **115**, 10404 (2001).
162. M. D. Hack and D. G. Truhlar, *J. Chem. Phys.* **114**, 2894 (2001).
163. M. D. Hack and D. G. Truhlar, *J. Chem. Phys.* **114**, 9305 (2001).

---

164. M. D. Hac
Martinez, *J*
165. A. W. Jasp
5424 (2002)
166. H. Goldstei
167. R. B. Gerb
168. V. Buch, R.
169. R. Alimi, R.
Chem. Phys
170. C. C. Mart
171. J. C. Buran
172. S. Nielsen,
173. A. Donoso,
174. J. C. Tully,
175. D. A. Mich
176. J. Durup,
177. A. Garcìa-
(1992).
178. G. Stock, *J.*
179. X. Sun and
180. X. Sun and
181. O. V. Prezh
182. O. V. Prezh
183. D. A. Mich
184. P. Ehrenfes
185. L. I. Schiff,
1968), pp.
186. O. V. Prez
187. E. R. Bittn
188. A. W. Jasp
J. Chem. P
189. A. Bjerre a
190. R. K. Prest
191. J. C. Tully
192. W. H. Mill
193. P. J. Kuntz
194. N. C. Blais
195. N. C. Blais,
196. G. Parlant
197. J. C. Tully,
198. P. J. Kuntz
199. U. Müller a
200. J.-Y. Fang
201. M. F. Herm
202. D. F. Coke
203. M. F. Herm

164. M. D. Hack, A. M. Wensmann, D. G. Truhlar, M. Ben-Nun and T. J. Martinez, *J. Chem. Phys.* **115**, 1172 (2001).
165. A. W. Jasper, S. N. Stechmann and D. G. Truhlar, *J. Chem. Phys.* **116**, 5424 (2002).
166. H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, 1957), p. 362.
167. R. B. Gerber, V. Buch and M. A. Ratner, *J. Chem. Phys.* **77**, 3022 (1982).
168. V. Buch, R. B. Gerber and M. A. Ratner, *Chem. Phys. Lett.* **101**, 44 (1983).
169. R. Alimi, R. B. Gerber, A. D. Hammerich, R. Kosloff and M. A. Ratner, *J. Chem. Phys.* **93**, 6484 (1990).
170. C. C. Martens and J.-Y. Fang, *J. Chem. Phys.* **106**, 4918 (1997).
171. J. C. Burant and J. C. Tully, *J. Chem. Phys.* **112**, 6097 (2000).
172. S. Nielsen, R. Kapral and G. Ciccotti, *J. Chem. Phys.* **112**, 6543 (2000).
173. A. Donoso, D. Kohen and C. C. Martens, *J. Chem. Phys.* **112**, 7345 (2000).
174. J. C. Tully, *J. Chem. Phys.* **93**, 1061 (1990).
175. D. A. Micha, *J. Chem. Phys.* **78**, 7138 (1983).
176. J. Durup, *Chem. Phys. Lett.* **173**, 537 (1990).
177. A. Garcìa-Vela, R. B. Gerber and D. G. Imre, *J. Chem. Phys.* **97**, 7242 (1992).
178. G. Stock, *J. Chem. Phys.* **103**, 10015 (1995).
179. X. Sun and W. H. Miller, *J. Chem. Phys.* **106**, 916 (1997).
180. X. Sun and W. H. Miller, *J. Chem. Phys.* **106**, 6346 (1997).
181. O. V. Prezhdo and P. J. Rossky, *J. Chem. Phys.* **107**, 825 (1997).
182. O. V. Prezhdo, *J. Chem. Phys.* **111**, 8366 (1999).
183. D. A. Micha, *J. Phys. Chem.* **A103**, 7562 (1999).
184. P. Ehrenfest, *Z. Phys.* **45**, 455 (1927).
185. L. I. Schiff, *Quantum Mechanics*, 3rd Edition (McGraw-Hill, New York, 1968), pp. 28–30.
186. O. V. Prezhdo and P. J. Rossky, *J. Chem. Phys.* **107**, 5863 (1997).
187. E. R. Bittner and P. J. Rossky, *J. Chem. Phys.* **107**, 8611 (1997).
188. A. W. Jasper, M. D. Hack, A. Chakraborty, D. G. Truhlar and P. Piecuch, *J. Chem. Phys.* **115**, 7945 (2001).
189. A. Bjerre and E. E. Nikitin, *Chem. Phys. Lett.* **1**, 179 (1967).
190. R. K. Preston and J. C. Tully, *J. Chem. Phys.* **54**, 4297 (1971).
191. J. C. Tully and R. K. Preston, *J. Chem. Phys.* **55**, 562 (1971).
192. W. H. Miller and T. F. George, *J. Chem. Phys.* **56**, 5637 (1972).
193. P. J. Kuntz, J. Kendrick and W. N. Whitton, *Chem. Phys.* **38**, 147 (1979).
194. N. C. Blais and D. G. Truhlar, *J. Chem. Phys.* **79**, 1334 (1983).
195. N. C. Blais, D. G. Truhlar and C. A. Mead, *J. Chem. Phys.* **89**, 6204 (1988).
196. G. Parlant and E. A. Gislason, *J. Chem. Phys.* **91**, 4416 (1989).
197. J. C. Tully, *Int. J. Quantum Chem. Symp.* **25**, 299 (1991).
198. P. J. Kuntz, *J. Chem. Phys.* **95**, 141 (1991).
199. U. Müller and G. Stock, *J. Chem. Phys.* **107**, 6230 (1997).
200. J.-Y. Fang and S. Hammes-Schiffer, *J. Phys. Chem.* **A103**, 9399 (1999).
201. M. F. Herman, *J. Chem. Phys.* **81**, 754 (1984).
202. D. F. Coker and L. Xiao, *J. Chem. Phys.* **102**, 496 (1995).
203. M. F. Herman, *J. Chem. Phys.* **110**, 4141 (1999).

204. M. F. Herman, *J. Chem. Phys.* **111**, 10427 (1999).
205. J.-Y. Fang and S. Hammes-Schiffer, *J. Chem. Phys.* **110**, 11166 (1999).
206. See, endnote 39 in S. Hammes-Schiffer and J. C. Tully, *J. Chem. Phys.* **101**, 4657 (1994).
207. J. J. Sakurai, *Modern Quantum Mechanics* (Addison-Wesley, Redwood City, 1985), pp. 78–80.
208. C. Zhu, K. Nobusada and Hiroki Nakamura, *J. Chem. Phys.* **115**, 3031 (2001).
209. C. Zhu, H. Kamisaka and Hiroki Nakamura, *J. Chem. Phys.* **115**, 1136 (2001).
210. C. Zhu, H. Kamisaka and Hiroki Nakamura, *J. Chem. Phys.* **116**, 3234 (2002).
211. J. R. Stine and J. T. Muckerman, *J. Chem. Phys.* **65**, 3975 (1976).
212. C. A. Mead and D. G. Truhlar, *J. Chem. Phys.* **84**, 1055 (1986).
213. E. J. Heller, *J. Chem. Phys.* **62**, 1544 (1975).
214. E. J. Heller, *J. Chem. Phys.* **75**, 2923 (1981).
215. T. J. Martinez, M. Ben-Nun and R. D. Levine, *J. Phys. Chem.* **100**, 7884 (1996).
216. T. J. Martinez, M. Ben-Nun and R. D. Levine, *J. Phys. Chem.* **101**, 6839 (1997).
217. S. L. Mielke, G. C. Lynch, D. G. Truhlar and D. W. Schwenke, *Chem. Phys. Lett.* **213**, 10 (1993).
218. F. T. Smith, *J. Chem. Phys.* **31**, 1352 (1959).
219. F. T. Smith, *Phys. Rev.* **120**, 1058 (1960).
220. A. J. Dragt, *J. Math. Phys.* **6**, 533 (1965).
221. W. Zickendraht, *Ann. Phys.* **35**, 18 (1965).
222. R. C. Whitten and F. T. Smith, *J. Math. Phys.* **9**, 1103 (1968).
223. R. T. Pack and G. A. Parker, *J. Chem. Phys.* **87**, 3888 (1987).
224. B. R. Johnson, *J. Comput. Phys.* **13**, 445 (1973).
225. B. R. Johnson, *J. Chem. Phys.* **67**, 4086 (1977).
226. F. Mrugala and D. Secrest, *J. Chem. Phys.* **78**, 5954 (1983).
227. J. C. Light, I. P. Hamilton and J. V. Lill, *J. Chem. Phys.* **82**, 1400 (1985).
228. Z. Bacic, R. M. Whitnell, D. Brown and J. C. Light, *Comput. Phys. Comm.* **51**, 35 (1988).
229. Z. Bacic, J. D. Kress, G. A. Parker and R. T. Pack, *J. Chem. Phys.* **92**, 2344 (1990), and references therein.
230. B. K. Kendrick, R. T Pack, R. B. Walker and E. F. Hayes, *J. Chem. Phys.* **110**, 6673 (1999).
231. C. Eckart, *Phys. Rev.* **46**, 383 (1934).
232. C. Eckart, *Phys. Rev.* **47**, 552 (1935).
233. B. K. Kendrick, *J. Chem. Phys.* **112**, 5679 (2000); **114**, 4335(E) (2001).
234. B. K. Kendrick, *J. Chem. Phys.* **114**, 8796 (2001).
235. V. J. Barclay, C. E. Dateo, I. P. Hamilton, B. Kendrick, R. T. Pack and D. W. Schwenke, *J. Chem. Phys.* **103**, 3864 (1995).
236. B. Kendrick, *Int. J. Quantum Chem.* **64**, 581 (1997).

237. B. Kendric
Spectroscop
Scientific, S
238. B. Kendric
239. J. C. Adan
240. J. C. Adan
241. T. Belytsch
Methods A
242. C. A. Meac
243. A. J. C. Va
J. Chem. P
244. Y. Sun, D.
4857 (1990
245. J. C. Light
246. M. J. Unek
and Techni
(STEF, Ca

237. B. Kendrick, in *Conical Intersections: Electronic Structure, Dynamics, and Spectroscopy*, eds. W. Domcke, D. R. Yarkony and H. Köppel (World Scientific, Singapore, 2003).
238. B. Kendrick, *Phys. Rev. Lett.* **79**, 2431 (1997).
239. J. C. Adams, *Appl. Math. Comput.* **34**, 113 (1989).
240. J. C. Adams, *Appl. Math. Comput.* **43**, 79 (1991).
241. T. Belytschko, Y. Krongauz, D. Organ, M. Fleming and P. Krysl, *Comput. Methods Appl. Mech. Eng.* **139**, 3 (1996).
242. C. A. Mead, *J. Chem. Phys.* **78**, 807 (1983).
243. A. J. C. Varandas, F. B. Brown, C. A. Mead, D. G. Truhlar and N. C. Blais, *J. Chem. Phys.* **86**, 6258 (1987).
244. Y. Sun, D. J. Kouri, D. G. Truhlar and D. W. Schwenke, *Phys. Rev.* **A41**, 4857 (1990).
245. J. C. Light and R. B. Walker, *J. Chem. Phys.* **65**, 4272 (1976).
246. M. J. Unekis, D. W. Schwenke, N. M. Harvey and D. G. Truhlar, in *Methods and Techniques in Computational Chemistry: METECC-94*, ed. E. Clementi (STEF, Cagliari, 1993), Vol. C, p. 1.