MOLECULAR DYNAMICS BEYOND THE ADIABATIC APPROXIMATION:
New Experiments and Theory

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INTRODUCTION

At the heart of the quantum mechanical description of molecular structure and dynamics lies the adiabatic or Born-Oppenheimer approximation (1, 2). Starting with an assumption of separability of time scales for nuclear and electronic motion, a familiar picture emerges of nuclei subject to well-defined forces corresponding to the potential energy surface for a particular electronic state. Although the well-established success of these ideas in the areas of molecular spectroscopy (3–5) and reaction dynamics (6–9) is likely to secure the adiabatic approximation as a continuing foundation of molecular science, the range of dynamical processes that lies within its scope is far from complete. Recent experimental and theoretical advances in particular are beginning to yield a coherent understanding of several phenomena that, far from requiring minor corrections to the adiabatic approximation for their explanation, by their very nature exist entirely outside its framework. Examples of importance in diverse areas of chemistry and physics range from the dynamics of radiationless decay (10–15) and nonadiabatic processes in chemical reactions (16–19) to the spectroscopy of excited (20–23) and ionized (24–26) states of isolated molecules, from single collision electronic energy transfer (27–41) to exciton (42) and soliton (43) dynamics and spin-lattice relaxation (44). Specialized reviews on these topics are available.
In this article we adopt a much narrower view, concentrating on nonadiabatic bound states. Considerable recent progress has been made in this area, with a strong and very profitable interaction between theory and experiment. By emphasizing some theoretically tractable models that though simple are capable of quantitatively interpreting state-of-the-art spectroscopic measurements, we hope to provide the basis for an appreciation of the role of nonadiabatic coupling in the wider contexts noted above. We endeavor in particular to use the treatment of nonadiabatic states to illuminate the nature of the simpler or less rich dynamics obtained in the limit that the adiabatic approximation is valid.

In the past few years a number of monographs and review articles have been devoted to subjects closely related to the material discussed here. Among these, special attention is drawn to the following:

1. First is the recent text of Bersuker (19). Aside from being a sound review of the principles of molecular dynamics, this work is also extremely important because it extends beyond the formal chemical physicist's viewpoint of eigenstates and energy level patterns and makes contact with qualitative molecular orbital theories that are of widespread use in organic and inorganic chemistry. It is accompanied by an exhaustive bibliography of work up to 1979 (45).

2. The recent reviews by Köppel et al (46, 47) draw special attention to the novel effects encountered when more than one vibrational mode interacts with electronic states. From this starting point Köppel et al have been led to apply the statistical theory of energy level spacings to characterize complex vibrational manifolds, and to identify important applications in the field of irreversible radiationless decay.

3. Judd (48) and Carrington (49) have reviewed the qualitative form of adiabatic potential surfaces in the vicinity of intersections. (See also 50–56.) This work generally uses group theory to deduce the form of the surface, but leaves off at the point at which an explicit connection with nonadiabatic dynamics must be made.

4. Nonadiabatic processes in the solid state are covered in the classic work of Davydov (42) (see also 43), in Engelman's comprehensive text (44), and in Bersuker & Polinger's review of cooperative effects and phase transitions (57). Reviews in more peripheral areas are cited below.

Our review of nonadiabatic bound states begins with a discussion of a quantum formalism first developed over 25 years ago. This formalism has recently been remarkably successful in providing a complete quantitative analysis of a molecular vibronic spectrum, as discussed below. However, the intractability of the quantum approach for treating larger systems remains an outstanding problem. Experimental manifestations of bound
state nonadiabaticity are reviewed next, with an emphasis on isolated molecules. Two exceptionally promising developments are highlighted, both relating to Rydberg states. Finally, several semiclassical theories of nonadiabatic processes are briefly reviewed, and vibronic dynamics in the vicinity of a conical intersection are explored within the framework of the classical electron model.

QUANTUM THEORY OF NONADIABATIC MOLECULAR STATES

The quantum theory of molecular bound states beyond the adiabatic approximation has until recently remained well ahead of experiment in the investigation of spectroscopic and dynamical consequences of nonadiabaticity. This situation is now rapidly changing, as shown by advances described in the next section. In view of the nature of the experimental work discussed there, attention is restricted here to effects that occur in isolated polyatomic molecules; this leaves ample scope for treatment of an interesting range of new and unexpected phenomena.

A long-standing difficulty in the theory has been the lack of a simple means for visualizing the effects of nonadiabaticity. This has been partially remedied by several recent calculations (58–61a) of nuclear probability densities corresponding to exact vibronic states; comparison of these densities with those derived from purely adiabatic functions, as discussed below for triazine; and by the development of classical analog hamiltonians for studying nonadiabatic dynamics in multimode systems.

The discussion to follow is a brief account of theoretical work directed toward (a) understanding the implications of electronic degeneracy and the consequent structural instabilities in molecules such as X₃ (X = Li, Cu, Na, Ag, K) or planar C₅H₅ and C₆H₆⁺; (b) the nature of vibronic states in the vicinity of degeneracies, and the most useful representations for describing electronic state evolution; (c) problems of localization due to effects of higher-order couplings; (d) interpretation of complex spectra in nonadiabatic systems and extraction of nonadiabaticity parameters from experiment; and (e) extension to multimode problems and related phenomena such as radiationless electronic decay.

Reviews of the theory of molecular bound states beyond the adiabatic approximation have been given by Longuet-Higgins (62), Kolos (63), Özkan & Goodman (64), Bishop & Cheung (65), and Lathouwers & Van Leuven (66). Various aspects of fully quantum mechanical approaches to nonadiabatic transitions in molecular collisions have been reviewed by Baer (38, 40), Garrett & Truhlar (35), Rebentrost (36), Tully (17), Child (30–32), Macias & Riera (41), and Kleyn, Los & Gislason (39). Several
definitions of the term "vibronic coupling" have been discussed in the useful article by Azumi & Matsuzaki (67).

**General Formalism**

Most of the important manifestations of nonadiabaticity are present in the simplest case of a symmetry-based electronic degeneracy; hence we consider this class of problem in some detail [the results are extendable to treat less symmetrical cases (68)].

In the absence of electronic degeneracy, a good approximation to the molecular wavefunction is the familiar Born-Oppenheimer or adiabatic product of electronic and nuclear functions. In the vicinity of an \( n \)-fold degeneracy, known to be ubiquitous in the space spanned by polyatomic vibrational coordinates (54, 69–72), it is therefore natural to invoke an expansion in some \( n \)-dimensional electronic basis. These general considerations can be formalized as follows: The time-independent spin-free Schrödinger equation for an isolated molecule is written:

\[
[T_N + H_e(Q)]\Psi_n(q, Q) = E_n \Psi_n(q, Q),
\]

where \( T_N \) is the nuclear kinetic energy operator, and \( H_e(Q) \) is the remainder of the full molecular Hamiltonian:

\[
H_e(Q) = T_e + U_{ee} + U_{eN} + U_{NN}.
\]

Note that this electronic Hamiltonian, \( H_e(Q) \), depends parametrically on the nuclear coordinates, denoted collectively by \( Q \). Terms in Eq. 2 are the electronic kinetic energy, the interelectronic repulsion potential, electron-nuclear attraction, and internuclear repulsion, respectively. Separation into coupled vibrational equations can be effected using either of two distinct strategies:

One involves the use of *diabatic* states (62, 73). The exact molecular wavefunction is expanded as follows:

\[
\Psi_n(q, Q) = \sum \psi_k(q; Q_0) \chi_k(Q),
\]

where the orthonormal electronic states \( \psi_k \) are defined by solving the electronic Schrödinger equation at a chosen *reference* configuration \( Q_0 \):

\[
H_e(Q_0) \psi_k(q) = E_k^0 \psi_k(q).
\]

The vibrational wavefunctions \( \chi_k \) are determined by a set of coupled equations with Hamiltonian matrix elements

\[
H_{kk'} = T_N \delta_{kk'} + \langle \psi_k | H_e(Q) | \psi_{k'} \rangle.
\]
Note that the nuclear kinetic energy is diagonal in the diabatic basis, and the matrix elements of $H_e(Q)$ can be further expanded to give:

$$H_{k,k'} = (T_N + E_k^0 + \Delta U_{NN}) \delta_{kk'} + \langle \psi_k | \Delta U_{eN} | \psi_{k'} \rangle.$$  

Each diagonal element therefore defines an effective vibrational hamiltonian, consisting of the nuclear kinetic energy operator plus the Hellmann-Feynman (74, 75) potential for nuclear motion given by the internuclear repulsions and the attraction to the electronic charge distribution $[\psi_k^* \psi_k]$. These vibrational hamiltonians neglect, however, all response of the electronic state to changing nuclear configuration. The neglected off-diagonal coupling terms derive from the $\Delta U_{eN}$ term, and it is therefore the change in the electron-nuclear attractive potential with nuclear configuration that induces mixing of diabatic basis states, giving rise to both adiabatic and nonadiabatic correlation of electronic and nuclear motion.

We note that greatly improved forms of diabatic bases for practical solution of Eq. 1 are possible (46, 47, 76–78).

An alternative strategy is to expand $\Psi(q, Q)$ using a basis of adiabatic electronic states:

$$\Psi_n(q, Q) = \sum \psi_m(q ; Q) \chi_m(Q),$$

where the $\psi_m(q ; Q)$ are solutions of the electronic Schrödinger equation

$$H_e(Q)\psi_m(q ; Q) = E_m(Q)\psi_m(q ; Q)$$

and depend parametrically on the nuclear coordinates $\{Q\}$. Expansion 7 is the Born-Huang series (2), and the electronic eigenvalues $E_m(Q)$ define the usual adiabatic potential surfaces. A set of coupled equations can be obtained for the adiabatic vibrational amplitudes, $\chi_m$, where the coupling is now induced by off-diagonal matrix elements of the nuclear kinetic energy (61a,b).

Diabatic states are in many ways more convenient for practical calculations, because they correspond to fixed electronic configurations, whereas adiabatic electronic states and associated potential energy surfaces emerge naturally from quantum chemistry computations (41).

**Two-State Systems**

The simplest case of a symmetry-induced two-fold electronic degeneracy ($n = 2$) interacting with a single doubly-degenerate vibrational mode, such as the trigonal-molecule $E \times e$ problem, is important in the interpretation of spectra discussed in the next section, and, additionally, it illustrates several general and unusual consequences of nonadiabaticity. To first order, the corresponding adiabatic surfaces show a linear divergence from the
degeneracy point, characteristic of a conical intersection (69); addition of a harmonic restoring force leads to the familiar cylindrically symmetric sombrero picture shown in Figure 1. Addition of higher-order coupling terms breaks the cylindrical symmetry by putting three-fold symmetric ripples in the surfaces. Forms of adiabatic potential sheets in the vicinity of crossings have been studied in the comprehensive papers of Liehr (50–52) and others (49, 53–56).

The exact vibronic levels of the model $E \times \varepsilon$ problem are easily obtained numerically (62, 79) by employing a diabatic basis of functions that are degenerate at the point of symmetry. Denoting the pair of diabatic functions $\psi_{\pm}$, where $\psi_+ = \psi^*$, the coupled vibrational equations are (in reduced units)

$$
\begin{pmatrix}
    p^2/2 & kpe^{-i\phi} \\
    kpe^{i\phi} & p^2/2
\end{pmatrix}
\begin{pmatrix}
    \chi_+ \\
    \chi_-
\end{pmatrix}
= W
\begin{pmatrix}
    \chi_+ \\
    \chi_-
\end{pmatrix}
$$

where $p$ and $\phi$ are polar vibrational coordinates and $k$ is the linear distortion constant. The energy levels $W$ are functions of $D = \frac{1}{2}k^2$ (the distortion energy) as shown in Figure 2.

The eigenstates of this system are characterized by a good half-integer quantum number $j$ (79). This is a remarkable result that merits some discussion.

Diagonalizing the electronic hamiltonian in the basis of the two diabatic

![Figure 1](image-url)  
*Figure 1* Adiabatic potential energy surfaces for a degenerate electronic state linearly coupled by a doubly-degenerate vibrational mode. Coupling splits the isotropic paraboloid to give the familiar conical intersection of the linear Jahn-Teller $E \times \varepsilon$ problem.
states results in adiabatic functions:
\[
\psi_{\text{upper,lower}}^{\text{AD}} = [\mp e^{-i\phi/2}\psi_+ + e^{i\phi/2}\psi_-].
\]

It is easily seen that these functions change sign upon encircling the conical intersection in nuclear configuration space, i.e. \(\phi \to \phi + 2\pi\). This is a general result (72, 80–86). Since the complete vibronic wavefunction \(\Psi\) must be single-valued, this implies that the associated vibrational amplitudes \(\chi_{\text{upper,lower}}\) must also change sign upon circling the point of degeneracy. As a consequence of this sign change, in the linear limit the internal rotation quantum number \(j\) can take on only half-integer values \((1/2, 3/2, \ldots)\) as stated above. The distinctive character of the level spectrum that results has recently been confirmed for the first time by direct observation (87).

The occurrence of half-integer quantum numbers in systems without spin implies a topological or Kramers-type degeneracy, and is currently of interest in a wide variety of fields. For example, we note the growing literature on quantization (and fractional quantization) of the Hall conductance in two-dimensional solids (85). Wilczek & Zee (84) have given a general discussion of the origin of fractional quantization, and derive a formula predicting half-integer quantum numbers for two-level systems (when adiabatic energies diverge linearly from the degenerate point). The appearance of half-integer quantum numbers is important for the implementation of semiclassical descriptions of nonadiabatic phenomena.

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**Figure 2**  Correlation diagram giving the relative energies of the exact vibronic levels of the linear \(E \times e\) hamiltonian (Eq. 9) as a function of the distortion parameter, \(D = 1/2k^2\).
In a series of papers, Mead (88–90) and Mead & Truhlar (80, 91) have examined the consequences of these general results in scattering and bound-state problems. Mead noted that the form of the adiabatic functions (Eq. 10) corresponds to a particular choice of gauge in the vibrational problem. It is possible to eliminate the sign change of vibrational amplitudes, but at the expense of introducing a vector potential term into the vibrational Hamiltonian. This result has been termed the Molecular Aharonov-Bohm Effect because of its formal similarity to the well-known interference effect discussed by Aharonov & Bohn (92). The work of Mead and others shows that there are subtleties and surprises in the theory of vibronic interactions, and that care must be taken when assessing the validity of any approximation scheme (61).

**Higher-Order Effects and Localization**

Several characteristic features of the linear case just described disappear when quadratic coupling or other symmetry lowering is allowed. These additional coupling terms are important for the $E \times \varepsilon$ problem in vibronic states for which there are large vibrational displacements. There is both a loss of the free adiabatic pseudorotation of Figure 1, and a splitting of the degeneracies of states in which $j$ (taken customarily to be positive unless otherwise noted) is $3/2 \mod 3$. These effects have now been characterized experimentally by means of observed $j = 3/2$ splittings in trifluorobenzene cation (93) and the ion cores of benzene (94) and cyclohexane (95) Rydberg states. A quantitative account of the effects of higher-order coupling on the positions and intensities of optical transitions has been given for the $3s^1E'$ Rydberg state of sym-triazine (87, 96).

Inclusion of quadratic coupling terms in the $E \times \varepsilon$ system leaves the diagonal matrix unchanged but alters the upper off-diagonal element to read:

$$kpe^{-i\phi} + 1/2g\rho^2 e^{2i\phi},$$

where the parameter $g$ measures the strength of the quadratic coupling. The corresponding adiabatic surfaces are

$$E(\rho, \phi) = 1/2\rho^2 \mp k\rho \left( 1 + \frac{g\rho}{k} \cos (3\phi) + \frac{g^2\rho^2}{4k^2} \right)^{1/2}.$$  

For small ratios, $g\rho/k$, the energies reduce to the simple form:

$$E = 1/2[\rho^2 \mp g\rho^2 \cos (3\phi)] \mp k\rho$$

to good approximation, and show directly the three-fold symmetry.

The splitting of degeneracies for $j = 3/2 \mod 3$ for small $g$ is due to above-barrier reflection in the three-fold symmetric angular potential.
Asymptotically for large $g$ the lowest state derived from $j = 3/2$ becomes degenerate with the ground $j = 1/2$ pair, corresponding to localization in three deep minima. A small energy gap between the near three-fold degenerate levels, due to tunneling, implies strong localization and near-static distortions from the symmetrical configuration, in which case nonadiabatic effects are relatively unimportant. The magnitude of the tunneling splitting determines the time scale on which a measurement will show the molecule to be symmetrical. The concept of localization is of central importance in the interpretation of temperature-dependent ESR spectra of the alkali trimers $X_3$ (97–99). A uniform semiclassical treatment of tunneling splittings for deep states in the $E \times \epsilon$ problem has been given by Karkach & Osherov (100).

**Cone-States or Resonances in Two-Level Systems**

The successful treatment of low-lying states of the conical intersections in terms of adiabatic approximations with correct boundary conditions suggests that a similar model might work for some higher states. In particular, there has been speculation dating from the work of Longuet-Higgins et al (79, 101–105) that some stationary states exist on the upper cone. [Thompson et al (61) refer to these as “cone states” whereas lower-surface states are called “hat-states.”] However, a thorough analysis by Sloane & Silbey (106) showed that no exact wavefunctions are accurately described by states of the upper conical surface, and Köppel & co-workers (107–110) have extensively described the role of simple conical intersections in ultrafast electronic decay. Nevertheless, this idea remains attractive because it is known that in order to account for the facts of molecular spectroscopy, for some energy gap the adiabatic Born-Oppenheimer approximation must work well for excited states. Indeed, these very facts motivated Born & Heisenberg (111) and later Born & Oppenheimer (1) to attempt to separate electronic and nuclear motion.

The absence of simple resonant or cone states in the Sloane-Silbey treatment has therefore not deterred further searching. Very recently, Thompson et al (61) have found a close correspondence between exact and adiabatic energies for large distortions and higher angular momentum states. They give, in addition, one example of an exact wavefunction of the $j = 5/2$ type showing remarkable localization within the classical turning points of the upper conical surface. Such a discovery, if shown to be general, has wide implications, because these states would be regarded as precursors to the type of excited electronic states observed in conventional spectroscopy, and they should be semiclassically quantizable.

This observation leads us to the final topic of this section, that of multimode nonadiabatic states and their relation to spectral complexity and irreversible electronic decay.
Multimode Vibronic Interactions and Radiationless Electronic Decay

It is not possible to generalize very easily the above discussion to multimode systems (systems of two degenerate or degenerate plus non-degenerate vibrations) because of the occurrence of highly complex level spacings and coupled nuclear dynamics even in deep adiabatic states. Some of the simplest unusual features were first described for trigonal molecules by Sloane & Silbey (106) and by Scharf & Jortner (112), but a full exposition awaited the work of Cederbaum, Köppel and co-workers (46, 47).

To see the source of the complexity, note first that the major change in the diabatic formulation above is in the off-diagonal elements, which for multiple modes become

\[ \sum_{\alpha} k_{\alpha} \rho_{\alpha} \exp(-i \phi_{\alpha}) \]

where \( \{\alpha\} \) is the set of modes. The adiabatic energies are coupled to give the lower adiabatic surface:

\[ E_{\text{AD lower}}^{\text{lower}} = \frac{1}{2} \sum_{\alpha} \lambda_{\alpha} \rho_{\alpha}^{2} - \left[ \sum_{\alpha} k_{\alpha} \rho_{\alpha}^{2} + 2 \sum_{\alpha > \beta} k_{\alpha} k_{\beta} \rho_{\alpha} \rho_{\beta} \cos(\phi_{\alpha} - \phi_{\beta}) \right]^{1/2} \]

where \( \lambda \) are the harmonic force constants of the modes. This evidently leads to highly correlated dynamics even at lowest energies (motion in one mode "tunes" the conical intersection in another). For this linear-distortion approximation the surviving quantum number \( J \) is a sum of those from individual modes and takes on the half-integer values characteristic of the two-level electronic system. The difficulty of this problem is reflected by the facts that (a) even for only three modes, to obtain exact eigenfunctions pushes the limit of present computational capabilities, and (b) no solutions of the adiabatic approximation, Eq. 15, have been given. It is therefore necessary to seek statistical approaches such as that suggested by Haller et al (113, 114) or to look to semiclassical methods. Work in the latter direction is reviewed in the final section below.

More generally, Cederbaum and co-workers have demonstrated success in multimode problems using the diabatic representation with potentials fitted to ab initio quantum chemical calculations (47, 76). Using the Lanczos method with simplifying assumptions derived from the precise spectroscopy of the situation at hand, they have been able to treat the previously intractable optical spectrum of \( \text{NO}_2 \) (114) and the photoelectron spectrum of \( \text{C}_2\text{H}_4^+ \) (109). Their work in this area represents an important advance for the interpretation of complicated molecular spectra.

In \( \text{C}_2\text{H}_4^+ \), two spin-doublet states are coupled by vibrations of the \( D_{2d} \)
(conical-intersection) type. The surfaces in the spectroscopically observable zone are so widely split that it had previously been believed that the two photoelectron bands were due to independent adiabatic states. Köppel & co-workers' reassignment (109) establishes clearly that this is not the case. Moreover, model calculations show (107) that starting a nuclear wavepacket on the upper surface yields decay on a time scale of a single vibrational period, and offers no evidence for stationary states.

The spectral line pattern in C₂H₄⁺ is very complex, and in the analogous case for neutral NO₂ a statistical analysis has been carried out to show that nearest neighbor level spacing statistics are described quite well by the Wigner distribution (115) [or, better, by a Brody distribution (116)], as found in the spectra of complex nuclei and nonlinear quantum systems whose classical limit is chaotic (117–125). For these small-molecule cases there is thus a strong connection between spectral complexity due to conical intersections and the "decay" or radiation-emission behavior observed. Köppel & Meyer (110) have pursued this point further in a recent paper exploring the connection among fluorescence yields, ultrafast decay, and nonadiabaticity as it appears most simply in doublet molecules (where spin interconversions are unimportant). Other than the apparent cone states uncovered by Thompson et al (61), as yet little evidence has emerged from theoretical work for resonance spectra in nonadiabatic model problems. Clearly, this will be a major line of future work. In a similar vein, conical intersections are important in mediating chemical reactions or decompositions, and when many modes are present a statistical theory is appropriate. Toward this end, Lorquet and co-workers (126–128a) have generalized transition state theory to nonadiabatic states and applied it to the decomposition of C₂H₄⁺.

EXPERIMENTAL OBSERVATIONS ON THE
STRUCTURE AND DYNAMICS OF
NONADIABATIC STATES

The section above outlines how one can model potential energy surfaces, and, more importantly, calculate quantum states in the vicinity of conical intersections. The formulation is general, but the specific case most easily treated is one in which the degenerate electronic term is well isolated energetically, with strong restoring forces preventing very large amplitude nuclear motions from the intersection. Such systems are most often associated with single-hole or single-electron degeneracies.

Quantum states derived from this simplest electronic configuration offer an excellent opportunity to probe the coupling of electronic and nuclear motion. The pattern of energy levels characteristic of a given system can be
understood with the help of correlation diagrams and a knowledge of likely deviations from simple limiting cases. It now remains to ask what experimental methods can provide detailed information for a range of vibronic systems. Considering typical energy spacings between vibronic states, it is clear that optical spectroscopy is a prime candidate, with the most direct and unambiguous information coming from isolated molecules in a single specified initial quantum state. A sketch of the range of experimental systems for which nonadiabatic effects are found confirms this expectation.

Survey of Nonadiabatic Effects: Rationale for an Experimental Approach

The extreme sensitivity of vibronic states to perturbations has become one of the best known consequences of an electronic degeneracy. Both the relatively large-amplitude nuclear motions and electronic mixings are known to be easily influenced by environment (129), as underlined by the sustained interest in the cooperative Jahn-Teller effect (130). This implies that if we hope to study the individual vibronic states, as opposed to bulk response properties of nonadiabatic bound state systems, then it is essential that the molecule be isolated.

The ground states of stable molecules contain an even number of electrons and are usually totally symmetric electronic terms. Open-shell polyatomics of sufficient symmetry often have electronic degeneracies, but as illustrated by work on metal trimers (60, 131), the reactivities of such systems generally require extraordinary measures in preparation and isolation. Many transition metal complexes have degenerate ground terms, but most of these are observed only in the solid state and solution. Consequently, strong nonadiabatic effects are rare in the lower vibronic levels of the ground electronic terms of most molecules that can be readily isolated. At higher energies, near thresholds for chemical reactions or unimolecular dissociation, strong vibronic effects can indeed be expected. However, the associated surface intersections, although often critically important in the reaction dynamics of such systems (132), usually do not have high symmetry and involve complex and very large amplitude nuclear vibrations. Thus, one cannot look to ground terms of stable molecules as a source of few-state nonadiabatic effects.

Among the valence excited states of many molecules having some symmetry, a great number involve degenerate or near-degenerate electronic terms. It is perhaps noteworthy that few of these known excited states have a settled-upon interpretation (see for example 11). By definition, valence states involve the strong interaction of at least two electrons or electrons and holes. In the spectroscopy of such systems it is also common for both
the initial and final molecular orbitals to be degenerate, so that the excited state contains four closely related terms, two of which are degenerate. In such cases a description of the consequent vibronic coupling requires at least a four-state treatment. Similar considerations apply to the ground states of cyclobutadiene and cyclo-octatetraene, where the two highest electrons derive from the same degenerate molecular orbital (133).

The extraordinary complexity of such (valence) multielectron degenerate configurations is reflected in the long history (134–136) of effort on the lowest electronic transition in cyclopentadienyl radical $\text{C}_5\text{H}_5$. The ground state of $\text{C}_5\text{H}_5$ has the simple one-hole configuration, $(e^-)^3$, but its first excited terms derive from the configuration $(e^-)^2(e^+)^1$, which produces no less than eight coupled states from the three-electron interaction. The numerous attempts to assign this spectrum serve as an indication of the complexity of degenerate valence states in general.

The easiest way to introduce a single hole in a set of degenerate orbitals is simply to remove an electron. The resulting ionic term has no inherent reason to be strongly coupled to any other, and recent experiments confirm that the spectroscopy of ionized states indeed offers one of the best opportunities for finding essentially pure two-state nonadiabatic problems in molecular bound states (25, 26, 137, 138). Thus, it is not surprising that the most substantial experimental developments in the understanding of the two-state dynamic Jahn-Teller problem have come from advances in the spectroscopy of ions: vibrationally-resolved photoelectron spectroscopy (138–140) and, more recently, laser-induced fluorescence. The former has until very recently been limited by electron velocity resolution to offer only marginal separation of vibronic bands. The latter has great potential but most ion-excited states do not fluoresce.

One of the major exceptions is the family of halobenzene cations that has been studied in great detail from this point of view over the past five years by Miller, Bondybey, and co-workers (25, 26, 137, 141–144) and by Leach, Cossart-Magos, and co-workers (145–148). Hexafluorobenzene cation has provided one of the most comprehensive tests of the two-state Jahn-Teller model to date (149), although its transition system still presents some difficulties, as one between valence states (in this case of the ion).

On balance, valence complexities, together with the related problem of low fluorescence quantum yields, must be viewed as a fundamental limitation of optical spectroscopy as a general means for determining the vibronic structure of ions. Thus, the greatest long-term potential for the universal study of ion ground states appears to lie with photoelectron techniques, especially in their most recent form as laser multiphoton photoelectron spectroscopies (150–152). It is now believed that a resolution near $10 \text{ cm}^{-1}$ will soon be possible.
A simpler, entirely optical method of studying ions is through the spectroscopy of molecular Rydberg states, in which one electron is excited to high-lying orbitals of the Coulomb potential (153). To a good approximation, the excited electron has a negligible effect on the vibronic structure and dynamics of the ion core (see below), so that the level patterns accessed, and even the vibronic intensities, match those of the ionic state of the core. Until about eight years ago, however, the study of the vibronic structure of molecular Rydberg states was extremely limited in scope. With the development of high peak power tunable dye lasers in the mid-1970s came the means to perform nonlinear spectroscopy on the high-lying states of atoms and molecules. In this realm, particularly for multiphoton ionization spectroscopy, Rydberg state resonances play a featured role (154). It is therefore easy to see that the excitation to Rydberg levels of molecules whose highest-lying molecular orbitals are degenerate or near-degenerate offers a most promising means of studying two-state non-adiabatic phenomena.

A major advantage of this approach is that, like photoelectron spectroscopy, the molecule is excited from the ground vibronic states of the neutral about which there is much prior information. Thus, the nonadiabatic effects observed can be straightforwardly associated with the ionized state. The major advantage compared with the current practice of photoelectron spectroscopy is resolution; structure of the Rydberg state is probed at the \( n \) photon resolution of the laser (typically \( \approx 1 \text{ cm}^{-1} \)). To complete the connection between the Rydberg spectroscopy of the molecule and the vibronic structure of the ion, it remains only to justify the above assertion concerning the separability of the ion-Rydberg electron subsystems.

**Strong Vibronic Coupling in Molecular Rydberg States**

An exceedingly simple and useful way to look at vibronically active Rydberg states is in terms of a strong coupling limit for the degenerate ion core (155). In this limit the dominant vibronic coupling is that within the core, so that, neglecting rotation, the molecular ion and Rydberg electron form noninteracting subsystems, except for the fact that the Rydberg electron is governed by the symmetric average field of the ion and is orthogonal with respect to core orbitals. This is clearly an idealized limit, and such a separation is only appropriate when the magnitude of the vibronic coupling in the core is much greater than both the dependence of the Rydberg electronic energy on nuclear positions (for small amplitude vibrations) and Rydberg-valence interactions at the configuration level.

For a given Rydberg state, the zeroth-order vibronic energy levels appropriate to this separation are simply those of the cationic subsystem
shifted down by the Rydberg term value. Band intensities in optical spectra of Rydberg states also find a match with corresponding photoelectron spectra. Within this limit electronic and vibrational moments separate, and the vibrational part corresponds precisely to the Franck-Condon factor expression for the set of transitions from the ground state of the molecule to the vibronic levels of the ground state ion.

Symmetries of these individual vibronic levels, though, are a composite, determined by the direct product of the ion core vibronic state symmetry and the orbital symmetry of the Rydberg electron. One implication of this is that nondegenerate Rydberg states of a degenerate ion core will arise only as part of an electronic quartet, which remains four-fold degenerate in the ideal-Rydberg limit. This results in a substantial reduction in the number of distinct Rydberg series that can be expected, as degeneracies and splittings introduced by the Rydberg electron are considered in a coupling hierarchy that proceeds on a core-vibronic, term-by-term basis. Recognition of this hierarchy, with its symmetry implications for optical transitions, is critical for the proper assignment of Rydberg states and associated vibronic structure in symmetric molecules.

This spectral simplification is one consequence of the idealized Rydberg limit and its approximate sum hamiltonian (155, 156). Other predictions include quantum defects that carry for given series from convergence with one ionization potential to all others, and an excited state lifetime determined solely by radiative decay. Deviation from this limit with respect to these latter observables, which in itself often constitutes a form of strong nonadiabaticity, is reviewed below. For the present, we turn to an examination of the completeness of this separation as a window on the core and the nonadiabaticity derived from its conical intersection.

**Structure of Nonadiabatic Bound States: Benzene and Sym-triazine**

There are two general sets of criteria against which one can easily judge the ideal Rydberg-limit as an accurate predictor of the vibronic structure of degenerate core Rydberg states. With an extensive data set spanning many series, the degree to which vibronic structure conforms, series to series, with the highest available resolution photoelectron spectrum, together with the magnitudes of quartet splittings, will give one indicator of how far Rydberg electron-core interactions carry the system from simple separability. Another test, for a vibronic system that is simple enough, is to check spectral positions and intensities within a single electronic state for internal consistency against the best available theoretical calculation. Benzene and triazine in turn offer cases of each of these tests. At the same time these
important systems provide interesting examples of dynamical distortions in highly symmetrical rigid molecules, which by classical rules of bonding would be expected to retain high symmetry (133).

**BENZENE** By analogy to the halobenzene cations, we can expect benzene to present a multimode vibronic coupling problem. This is confirmed both by two-photon Rydberg spectra (94, 156–158) and moderately well-resolved conventional (159) as well as laser photoelectron spectra (150). This fact makes a definitive confirmation and interpretation of observed vibronic structure by direct calculation difficult. However, the size of the data set combined with the availability of the photoelectron spectrum provides the means for a test of the first kind.

In conformity with ideal expectations, degenerate Rydberg states of this system that arise in zeroth order as products of the degenerate core ($^{2}E_{1g}$) with nondegenerate Rydberg orbitals (for example $nsa_{1g}$), show readily assignable structure in Jahn-Teller active and symmetric modes, and this structure is virtually identical to that of the photoelectron spectrum. Rydberg states derived from degenerate hydrogenic orbitals provide an even more sensitive test. As noted above, in the limit of vanishing Rydberg-core interaction, the simple product of orbital- with core-degeneracy will double the degeneracy of all such vibronic levels. A great many of these are accidental degeneracies, and any perturbation (configuration interaction or vibration-Rydberg coupling) will strongly mix zeroth-order states and produce characteristic splittings.

Such splittings are observed, but with one exception all are exceedingly small (156). Typical is the 15 cm$^{-1}$ splitting of the $E_{2g}-A_{1g}$ components of the 3$d_{1}$ origin. The exception is the 3$p_{1}$ origin, for which the measured splitting is 160 cm$^{-1}$ (94, 157, 160), a value that perhaps reflects the special significance of this state as derived from the lowest degenerate Rydberg orbital.

This generally favorable picture of the ideal-Rydberg limit for the vibronic structure of benzene Rydberg states is supported by the small magnitudes of other deviations, such as origin perdeuteration shifts and trends in vibrational frequencies. Thus, it is with reasonable confidence that the Rydberg data can be combined with the specific though much lower resolution photoelectron spectrum to provide a qualitative picture of vibronic coupling in the $^{2}E_{1g}$ C$_{6}$H$_{6}^{+}$ ion matching in completeness that for substituted benzene cations. Main conclusions at the current level of understanding are as follows:

1. The dynamical Jahn-Teller effect in the $^{2}E_{1g}$ benzene cation is inherently multimode, involving at least Jahn-Teller modes $v_{8}$ and $v_{9}$. In benzene-$h_{6}$, $v_{6}$ dominates, with a total stabilization energy of about 250 cm$^{-1}$. 
Greater apparent $v_9$ activity is seen for $-d_6$, a result consistent with multimode coupling expectations (106). In both cases the number of active modes is far smaller than that for the halo benzene cations.

2. Higher order Jahn-Teller effects are quite small, leaving single-mode vibronic angular momentum largely unquenched.

3. A Renner effect in the out-of-plane mode $v_{16}$ has been observed and characterized for the first time (94, 161). The observation of interferences in combination states with Jahn-Teller active $v_6$, as predicted by theory (162), sheds further light on multimode quenching and coupling of vibronic angular momentum in nonadiabatic states.

SYM-TRIAZINE The two-photon absorption spectrum of $\text{sym-C}_3\text{N}_3\text{H}_3$ shows a set of sharp vibronic bands associated with a clear origin ($T_0 = 55,791 \text{ cm}^{-1}$; $55,882 \text{ cm}^{-1}$, $-d_3$) (87). These bands, pictured for triazine-$h_3$ in Figure 3, are readily assigned to the lowest $3s^1E'$, Rydberg state. With its totally symmetric Rydberg orbital and degenerate ion core, the limiting picture just confirmed for benzene predicts this state to be Jahn-Teller active. Analysis shows that it is, with coupling dominated by strong activity in a single normal coordinate, the lowest frequency $e'$ mode, $v_6$, a ring-bending vibration. This simplicity presents a unique opportunity. All other known examples of nonadiabatic states for which resolved vibronic spectra have been recorded for isolated molecules are multimode systems. With its strong single-mode conical intersection, the $3s^1E'$ state of triazine offers a chance to (a) visualize the dynamics of nonadiabatic bound state vibronic motion in an active vibrational space of manageable dimensionality, and (b) quantitatively test the few-parameter numerical coupling theories reviewed above, from which can also be obtained accurate vibronic wavefunctions.

Comparison of the spectrum in Figure 3 with the correlation diagram in Figure 2 shows that a description in terms of simple linear coupling with $k \approx 2.2$ gives a good account of level positions through the conical intersection and above, thus allowing the confident first-order assignment of all the bands of the spectrum. Linear coupling alone, however, fails to predict the observed intensities (the spectrum shows strong bands that would be forbidden for strictly linear coupling) and certain distinctive splittings. Inclusion of quadratic terms with $g = 0.046$ and optimization of $k$ to 2.14 gives quantitative and sensitive agreement with both positions and intensities of all measured bands (96, 163).

With this coupling strength, the zero-point and first few excited levels of the active mode, $v_6$, lie substantially below the conical intersection. Simple calculation shows that the exact level structure for such conditions is reasonably well described by the eigenvalues of the adiabatic lower surface Born-Oppenheimer (or more correctly Born-Huang) hamiltonian. Motion
in these lower states can thus be viewed in very simple terms, as approximately that of a free internal rotor built on a radial harmonic oscillator with a level structure (79):

\[ E(v, j) = \omega(v + 1/2) + Aj^2 \]

where \( \omega \) is the fundamental frequency and \( A \) is the rotational constant. The latter term is determined by the amplitude of the trough, \( \rho_0 = k/\lambda \), via \( A = h^2/2m\rho_0^2 \), where for the present case \( \rho_0 = 0.26 \, \text{Å} \) and \( A \) is calculated to be 80 cm\(^{-1}\). Importantly, it is found that this rotational constant gives a precise account of the deepest few rotor states, so long as the angular momentum quantum number \( j \) is taken to be a half-odd integer. This observation constitutes the first direct confirmation of the appropriateness.

![Figure 3](image_url)

*Figure 3* Two-photon absorption spectrum of the \( 3s^1E' \) Rydberg state of *sym*-triazine. The *stick figure* indicates theoretical positions and intensities for bands assigned in terms of approximate \( j \) quantum number as: 1/2 (origin), 5/2, 1/2, 7/2, 5/2, 1/2, 11/2, reading from the left. (Cf Figure 2: 3/2 bands are forbidden. These and symmetric fundamentals and combinations are suppressed.)
of the choice of phase implied by the electronic basis functions of Eq. 10 in forming the proper adiabatic limiting wavefunctions. It is interesting to note that the energy of the first excited state of this adiabatic-limit pseudorotation is 160 cm⁻¹, which corresponds to an extraordinary low frequency of $5 \times 10^{12}$ sec⁻¹ for internal motion in a molecule as rigid as triazine. The level structures predicted by each of the models discussed here are summarized, together with experiment, in Figure 4 (96, 163).

![Figure 4](image-url)

**Figure 4** Comparison of various predictions for the level structure of $3s^1E'$ sym-triazine with experiment. From the left are: (a) the adiabatic free-rotor model (Eq. 16), (b) linear Jahn-Teller, and (c) linear plus quadratic Jahn-Teller coupling. *Dashed lines* connect states of (approximately) like vibrational angular momentum.
This essentially two-parameter fit of the entire spectrum is significant:

1. It offers the most direct and dramatic confirmation yet of the classic theory formulated over 25 years ago by Longuet-Higgins and co-workers (62, 79).
2. It decidedly confirms the ideal-Rydberg limit (155) for the interpretation of vibronic coupling in molecular Rydberg states; vibration-Rydberg interactions, if present, are beneath the resolution of the correspondence between theory and experiment.

The adiabatic potentials derivable from this calculation must be regarded as very nearly exact to an energy at least as high as the highest measured eigenvalue. It is interesting to compare the potential in the pseudorotation coordinate around the bottom of the trough with the internal rotor levels built on the first radial oscillator state. As shown in Figure 5, the quadratic barriers to pseudorotation only weakly alter the shape of the potential surface. Despite this, and reasonably close correspondence between linear and linear-plus-quadratic eigenvalues, evident splittings and transfers of intensity show that, in the vibronic hamiltonian, these quadratic terms have a significant effect on the wavefunctions.

With near quantitative correspondence between experimental and experiment...
theoretical intensities, wavefunctions can be derived with reasonable confidence from the present calculations. These are conveniently visualized as nuclear probability densities (58–61). Figures 6 through 8 show plots of nuclear probability densities (for complex vibronic wavefunctions) for the first four levels in the \( j = (\pm 1/2) \mod 3 \) manifold. For the first two states we see that quadratic coupling modulates the nuclear probability densities (which are cylindrically symmetric for linear coupling alone). Nuclear density accumulates over surface depressions or saddle points. The states with the unusual density pattern shown in Figure 8 are a close-lying pair labeled by \( j = 1/2 \) and \( 7/2 \) in the linear limit, which repel by mixing due to quadratic terms.

To summarize, sym-triazine presents unprecedented simplicity in an isolated nonadiabatic system. With its single active mode and large linear

\[ \text{Figure 6} \quad \text{Nuclear probability density for the ground vibronic state of } 3s^1E' \text{ sym-triazine calculated as } |x_+|^2 + |x_-|^2 \text{ (see Eqs. 9 and 11) for coupling parameters corresponding to the theoretical level structure of Figures 4 and 5 and intensities of Figure 3.} \]
stabilization, it is possible to visualize easily the dynamics of its vibronic pseudorotation in the adiabatic limit. From the precise correspondence between high resolution jet spectroscopy and theory, when carried to second order in coupling terms, there emerges a quantitative picture of the role of quadratic effects and the loss of cylindrical symmetry in splitting and mixing vibronic levels.

**Slow-Electron Systems: Nonadiabaticity in the Failure of the Ideal-Rydberg Limit and Related Systems**

**Accidental Resonant Mixing in Molecular Rydberg States**

Rydberg states of symmetric molecules provide a convenient view of the vibronic structure of degenerate ion cores. More universally, Rydberg-molecular core assemblies also constitute a class of systems for which commensurate electronic and nuclear frequencies are readily attainable. Such states are
Figure 8  Nuclear probability densities for excited vibronic states of $3s^1E'$ sym-triazine, labeled in the linear limit by $j = 1/2$ and 7/2, as in Figure 6. Comparison of eigenvalues on going from linear to linear-plus-quadratic coupling suggests strong quadratic mixing of these levels.
very important, dominating the resolved absorption spectrum of most molecules beginning at energies above two-thirds of the first ionization potential. As mentioned above, the novel feature of such states is that one electron has escaped from the molecule and now "sees" it predominantly as a rigid ion or even a point charge. The level spacing for this electron reflects its delocalized, hydrogenic character, and can be represented by the formula

\[ E(n) = -R(n-\delta)^{-2} \]

where \( R \) is the Rydberg constant, \( n \) a principal quantum number, and \( \delta \) the quantum defect, which is correlated with the orbital angular momentum and nearly independent of \( n \) (164). Adherence to this zeroth order picture for the case of a degenerate core reveals the nonadiabatic bound state structure of open-shell molecular ions. Deviations constitute a second important class of nonadiabatic interaction.

Three kinds of nonadiabatic interactions can be envisioned:

1. Levels of the same \( n \) but different \( \delta \) (different series) can be coupled by vibration or, for very high \( n \), by rotation. For vibration, Rydberg-nuclear interactions decrease as \( n^{-3} \), so that significant splitting should be expected only for lower Rydberg states. It is also necessary that appropriate excited vibrational levels of the lower energy series overlap lower levels of the upper state. These two factors tend to confine strong vibrational couplings to levels of intermediate \( n \). For example, consider the \( s \) and \( d \) Rydberg orbitals of benzene (156), \( l(\delta) \), which are \( s(0.76) \), \( d_0(0.05) \), and \( d_1(-0.12) \). At \( n = 3 \), the \( 3s - 3d_0 - 3d_1 \) spacings are 9000 and 2000 cm\(^{-1}\). Only high vibrational overtones have such energies, and these should be only inefficiently scattered by the Rydberg electron, so one might expect the adiabatic approximation to be fairly successful. At the \( n = 5 \) level, however, the spacings are 1900 and 400 cm\(^{-1}\). Fundamental vibrations of the correct symmetry are in this range and readily mix the two hydrogenic states.

2. More generally, strong interaction can occur whenever fundamental vibrational frequencies of proper symmetry-type match the gap between Rydberg states of different principal quantum number \( n \), for example \( ns \leftrightarrow (n-1)d_0 \) as observed in benzene (156).

3. As another form of nonadiabatic coupling in many molecules, the lowest Rydberg states having electronically excited cores (excited ionic states) lie overlapped with higher Rydberg states converging to the first threshold.

As with 1, examples of 2 and 3 have been observed (156). Such occurrences can help confirm symmetry assignments of highly-excited molecular states.
Of more interest from the present point of view, they also provide direct information on the mixing of fast internuclear and slow electronic oscillations.

The first molecule to be considered from this viewpoint was H$_2$, by Berry & Nielsen (165). These authors gave a general theoretical formulation in the adiabatic representation in which they constructed electronic wavefunctions and potential energy surfaces, derived the corresponding vibrational states, and finally evaluated the matrix elements of the kinetic energy operator that couples the Born-Oppenheimer states. This procedure, in principle, yields exact energy levels (exclusive of rotation). It is, however, an exhaustive theoretical treatment that is difficult to reproduce for more complex molecules. Among the important results is the identification of zones of strong mixing (166). As discussed in the next subsection, the systematics of these zones can be understood in a very natural way.

It is instructive to look at the interactions between Rydberg electrons and core vibrations from a dynamic point of view. Consider the picture in which a short-pulsed radiation field prepares a coherent state consisting of a particular Rydberg orbital and core-vibration. For a two-state interaction this state would begin to mix with one consisting of the other Rydberg orbital and core vibration pair. The Rydberg electron in effect inelastically scatters off the core. In a strictly two-state picture this mixing leads to a simple pattern of quantum beats, and a higher resolution, longer time experiment would reveal the two mixed eigenstates of the interaction separated by the beat frequency. Weaker interactions dephase these beats and produce an apparent broadening of the individual eigenstates of the two-state interaction. Dynamically the relaxation becomes more complex, with the resulting states not well described in terms of any zeroth-order separation into ion normal modes and hydrogenic orbitals. Rather, in time-dependent language, the system evolves to a vibronically mixed (randomized) core in which complicated, large amplitude nuclear motion strongly couples the possible final electronic states.

In recent nonlinear absorption experiments on ultracold molecules, Whetten et al (156) observed several pronounced examples of this type of nonadiabatic interaction in benzene. These include at least one of each of the three types of interaction described above, including apparent coupling between the core-excited 3s Rydberg state converging to the second IP, and neighboring (zeroth-order) 4d$_1$ and 5d$_1$ states on the ground state core. In dynamical language this latter case provides an example of core-electronic inelastic scattering of the Rydberg electron.

An equally dramatic example is found in the high angular momentum states of H$_2$ (167, 168). In the 5g orbitals of H$_2$, molecular rotation is sufficiently fast compared to evolution among the electronic states that the
latter uncouple from the axis, producing a smaller splitting on each rotational state of the ion core. These were detected by the 5g–4f infrared emission, and explained by an angular momentum coupling model. [High angular momentum states of benzene have also been observed (156, 157), but it does not appear that this inversion of term spacings occurs, since the rotational spacing in benzene is much smaller.] This is an example of an inverse adiabatic situation where it is now the vibrational spacings that are largest. Such a situation is highly counterintuitive, but is to be expected for many systems, particularly those involving electronic fine structure (in photodissociation, for example). Starting from this point of view is essential to understand the term splittings in the Rydberg spectrum of benzene, where, as discussed above, it is best to construct electronic levels on a vibrational state of the ion; the opposite approach leads to qualitatively incorrect expectations (155). In these cases it is essential to avoid associating a distinct adiabatic surface with each electronic term.

More generally, the occurrences of regions of strong mixing are readily predicted in terms of known level spacings (vibrations and rotations of the ion, Rydberg electronic spacings) (169). Furthermore, the information is highly redundant because the wavefunctions producing the zeroth-order pattern of levels are assumed known. Thus, for example, the knowledge of the strength of interaction coupling the v_{16} vibration of benzene to the 5f and 5d hydrogen-like electronic orbitals predicts the strength of this interaction for all other n (156). The correct means of taking this knowledge into account is via the multichannel quantum defect theory (MQDT) (166, 170). This results in an enormous simplification of the description of these interactions. It is based on the electron-ion scattering problem, facilitated by use of the asymptotically correct Coulomb potential, so posed as to allow the experimental data to solve the configuration interaction and nonadiabatic problem at the same time, yielding directly the nonadiabatic interaction matrix elements with minimal assumptions.

Application to molecules has been concerned primarily with NO and H₂, especially in the latter case with regard to rotational channels of interaction, but is readily extended in principle (171, 171a, 172). Very difficult regions of the spectra of these molecules have yielded to this approach, which also offers the simple scattering interpretation of nonadiabatic dynamics discussed above.

RADIATIONLESS DECAY AND AUTOIONIZATION An understanding of the nonadiabatic interaction of weakly bound electrons with vibration and rotation is extremely important in the decay and ionization properties of molecular systems. To see this, let us consider again the interaction in which an electron is scattered into a lower-lying orbital via excitation of a core-vibration. Imagine, as above, preparation of the coherent state consisting of
the zeroth-order $nl$ orbital; vibrational interaction mixes it with another state $(n-1)l'$, which in effect serves as a doorway to a more dense set of overtones associated with lower Rydberg states. At some stage an essentially continuous manifold of lower levels takes over, and one has a Lorentzian linewidth corresponding to exponential decay.

The Rydberg states of benzene (156–158) taken at rotational temperatures near 0 K provide an example of precisely this coupling hierarchy. Pairwise mixings have been discussed above. Moreover, where several states of proper symmetry nearly coincide, one has higher-order mixings. Finally the homogeneous linewidth of each identifiable band reflects strong coupling to the quasicontinuum structure beneath. This latter aspect is confirmed by direct time-resolved experiments using femtosecond laser pulse-probe techniques carried out by Wiesenfeld & Greene (173). A bandwidth of 100 cm$^{-1}$ excites a superposition, which decays exponentially, as probed by time-resolved ionization. Significantly, for both benzene and toluene, the agreement between dynamical (173) and spectroscopic measurements (156, 157, 174) is quite good, thus giving credence to the idea that the final irreversible decay product is a set of states with energy in large amplitude vibrations, states that cannot be ionized by a visible laser. Thus the width of the homogeneous line is that corresponding to the net process by which the electron spirals inward, transferring energy to the core.

The widths or decay times measure the strength of interaction between the background states and the pure electronic excitation, and as might be expected this coupling strength decreases rapidly with $n$. This idea can be carried to an extreme to predict that Rydberg states of very high $nl$ numbers have extreme stability; they are effectively metastable because of the rarity of a collision between the Rydberg electron and the ion core. With very low transition frequencies, radiative lifetimes are also very long. Some evidence for this behavior has been gathered by Freund (175). Multiphoton excitation with circularly polarized light could well offer an effective spectroscopic means to produce these states.

Similar arguments apply to the phenomenon of autoionization, but these are resonances in which the reverse flow (energy from vibrotation to electronic) occurs. For the case of diatomics this manifestly nonadiabatic process has been studied within the MQDT formalism (176), but no explicitly time-dependent experiments have yet been attempted.

**NEGATIVE IONS** In principle a similar treatment could apply to negative ion states, but all the nice features of the Coulomb potential applicable above are not in force here. Space limitations preclude consideration of the highly interesting topic of resonant scattering here. Nonetheless, a point regarding autodetachment is worthy of mention.

The recent experimental observation of electron-dipole bound states
gives a picture of autodetachment that is evidently related to rotational predissociation (177, 178). One can view these states in terms of the electron cycling about the positive end of the dipole, so weakly attached as to have only one bound state for most if not all angular momentum states of the core. With the detached neutral molecule as a core, resonances above threshold are analogous to the case of a Rydberg state excited above the adiabatic IP. Here the core gives up very little rotational energy to detach an electron, yet the resonances are fairly long-lived.

CLASSICAL AND SEMICLASSICAL APPROACHES TO NONADIABATIC PHENOMENA

As is apparent from the preceding discussion, the interaction between theory and experiment has played an important role in developing an understanding of vibronic states of molecules in which a doubly-degenerate electronic state is coupled to one or a very small number of active modes. For such systems a full quantum variational treatment of the vibronic Hamiltonian is feasible, so that model parameters can be determined to provide the best fit to experimental data (e.g. sym-triazine). The size of the associated secular determinant, however, grows extremely rapidly with the number of active modes, and there are no useful decoupling approximations that can be applied. Hence, the limits of current quantum-mechanical technology are reached very quickly for problems involving only a modest number of modes. Although procedures such as the Lanczos algorithm (179) or the related Recursive-Residue method (180) have great potential for solving very large eigenvalue problems, and although a statistical approach may be appropriate for describing vibronic level structure in highly-excited dense manifolds (113, 114), the situation described above points to the desirability as an alternative of a semiclassical (asymptotically valid as $\hbar \to 0$) theory of vibronic level spectra. Such a theory would ideally provide both a quantitative treatment of vibronic spectra in the multimode case and a conceptual framework for obtaining qualitative insight into manifestations of vibronic coupling; it would therefore be an extension to multisurface phenomena of the various semiclassical approaches that have been successfully applied to single surface scattering and bound state problems.

A semiclassical theory of multimode vibronic phenomena as just described is not available at present. Despite an enormous amount of work on the generalization of semiclassical methods to treat nonadiabatic processes occurring in collisions, the general problem involving multiple ($>2$) interacting surfaces, strong and delocalized nonadiabatic couplings,
and many nuclear degrees of freedom remains essentially unsolved. It is our purpose here to review a small body of work that is in our view likely to provide a foundation for future theoretical treatments of problems relevant to the recent experimental advances described in previous sections. Thus, we consider some recent classical and semiclassical approaches to radiationless transitions and bound states in Jahn-Teller systems. Most of the work we describe is within the framework of the "classical electron model" of Miller, Meyer & McCurdy; this model is therefore described in some detail.

In order to place this work in a proper complete context, it would be necessary to give a thorough discussion of all the major lines of development in the semiclassical theory of nonadiabatic phenomena (a huge literature). We stop short of this, presenting instead a few pertinent references. Reviews of many aspects of the subject can be found in Miller (181), Lam & George (33), Tully (17), Child (30–32), Nikitin (28), Nikitin & Zülicke (29), Kleyn, Los & Gislason (39), Rebentrost (36), Ranfagni et al (182), Crothers (34), Ovchinnikov & Ovchinnikova (15), Heller & Brown (183), Nakamura (184).

Background

A central issue in the theory of nonadiabatic processes is the extent to which "classical path" descriptions are meaningful or useful. That is, to what extent can the heavy-particle (nuclear) degrees of freedom be taken to undergo classical motion in an effective potential determined in some fashion by the quantal dynamics of the coupled electronic degrees of freedom? A path-integral formulation (181, 185–187) of the nonadiabatic scattering amplitude enables a formal answer to be given to this question: The exact (semiclassical) effective "potential" is of necessity nonlocal in time and must be determined iteratively. This result clearly implies insuperable practical difficulties unless other, perhaps uncontrollable, approximations are introduced. Further work in this direction has led to the widely used Miller-George (188) and Tully-Preston ("surface-hopping") (189, 190) approaches, whereas the self-consistent matrix propagation method of Freed & Laing (191–193), further developed by Herman & Freed (194), is closer to the original path-integral approach.

At a simpler level, the classical motion of the nuclei can be taken to be determined self-consistently through interaction with the electronic subsystem. The nuclei then provide, through vibronic coupling terms in the complete molecular Hamiltonian, an effective, time-dependent electronic Hamiltonian, which induces transitions in the manifold of electronic states of interest. The time-dependence of the electronic state in turn gives rise to a time-dependent, effective (Ehrenfest) potential for the nuclei through the
expectation value of the nuclear-coordinate dependent molecular hamiltonian in the instantaneous electronic state. A specific example of this self-consistent coupling is treated in the next section.

Considerable effort has been devoted to assessing the validity of classical path methods in general (195, 196). For a system with a single nuclear degree of freedom and a localized crossing of two adiabatic curves, it is necessary that (a) the form (i.e. slope) of the potentials be similar in the region of the crossing, and (b) the nuclear kinetic energy be large compared to differences in the two potential surfaces in the interaction region. In addition, the usual conditions for semiclassical treatment of nuclear motion should hold. Despite such stringent requirements, the self-consistent coupling approach underlies a substantial amount of work in the area. See, for example: Ehrenfest equations (200–202); first-order self-consistent Eikonal method (197–199); Dynamical Hellman–Feynman theorem (203); time-dependent Hartree–Fock theory (204, 205); dynamical vibration-electronic coupling (206). In particular, the classical electron model of Miller, Meyer & McCurdy (207–211) has the self-consistent formulation as its starting point.

Nevertheless, severe conceptual difficulties and inconsistencies are inherent in such a mixing (albeit self-consistent) of classical and quantal dynamics. For example, in a system that is asymptotically in a superposition of two electronic states, the nuclei execute some averaged dynamics, as opposed to motion determined by one or the other adiabatic surface, as might be expected on physical grounds. The classical electron picture is intended to surmount such problems, and to facilitate treatment of resonant processes in electronic-vibrational and electronic-rotational energy transfer (212).

Review of the Classical Electron Picture

The classical electron model of Miller, Meyer & McCurdy, which is an attempt to overcome some of the difficulties of mixed classical/quantal dynamics, works in the following way [we do not discuss the related but apparently less general Spin Matrix Mapping (210) and Classical Pseudopotential (208) approaches]: For a system in which there are \( N \) coupled electronic states of interest, the electronic hamiltonian can be represented as an \( N \times N \) matrix whose elements depend on the nuclear coordinates \( \{Q_a\} \):

\[
H_{kk'}(Q) \quad k, k' = 1, \ldots, N.
\]

A diabatic electronic representation is used for simplicity, but it is also possible to formulate the theory in the adiabatic basis (209). If the nuclear coordinates \( Q(t) \) are taken to be given functions of time, the time-dependent
Schrödinger equation for the electronic wavefunction gives rise to a set of coupled equations for \( \{a_k(t)\} \), the coefficients in the diabatic basis:

\[
 ih \dot{a}_k = \sum_{k'} H_{kk'}(Q(t))a_{k'}.
\]

A key step is now the change of variables [of a type originally due to Dirac (213)]:

\[
 a_k \equiv n_k^{1/2}e^{i\theta_k},
\]

giving the polar decomposition of the complex coefficients \( \{a_k\} \) into (real) amplitudes \( \{n_k\} \) and phases \( \{\theta_k\} \). Note:

\[
 0 < n_k < 1, \quad \sum_k n_k = 1.
\]

Defining the "hamiltonian"

\[
 h(n, \theta; Q) = \sum_{kk'} a_k^*H_{kk'}a_{k'}
\]

\[
 = \sum_{kk'} n_k^{1/2}n_k^{1/2}H_{kk}e^{-i(\theta_k - \theta_{k'})}
\]

as the expectation value of \( H \) in the electronic state, the remarkable result is obtained that the quantum mechanical set of coupled equations is entirely equivalent to "hamilton's equations" for the canonically conjugate pairs \( (n_k, \theta_k) \):

\[
 \dot{n}_k = -\frac{\partial h}{\partial \theta_k}, \quad \dot{\theta} = \frac{\partial h}{\partial n_k} \quad k = 1, \ldots, N.
\]

[This equivalency obtains because mappings of type, Eq. 22, for arbitrary matrix operators transform commutators into Poisson brackets (209).] Adding the classical nuclear kinetic energy then gives a completely classical, time-independent hamiltonian \( \mathcal{H} \) that determines the self-consistently coupled nuclear/electronic time evolution through the classical equations of motion for the nuclear degrees of freedom, together with Eq. 24:

\[
 \mathcal{H}(P, Q, n, \theta) = \sum \frac{P^2_\alpha}{2m_\alpha} + h(n, \theta; Q)
\]

\[
 P_\alpha = -\frac{\partial \mathcal{H}}{\partial Q_\alpha}, \quad \dot{Q}_\alpha = \frac{\partial \mathcal{H}}{\partial P_\alpha}.
\]

This time evolution preserves both total energy and electronic probability \( \sum n_k \).

For the limit of a single-surface problem, \( |n_1| = 1 \) and Eq. 26 simply reduce to the classical nuclear equations of motion for the potential surface
$V(Q) \equiv h(n_1, \theta_1 ; Q)$. In the general two-state case, the classical electron hamiltonian is

$$\mathcal{H} = \sum_a \frac{P_a^2}{2m_a} + (1 - n)H_{11} + nH_{22} + 2[n(1-n)]^{1/2}H_{12} \cos \theta,$$

where a canonical transformation has been made to new variables $n' = n_1 + n_2 = 1, n = n_2, \theta' = \theta_1, \theta = \theta_2 - \theta_1$, so that only the relative phase $\theta$ appears. For the simplest two-state linear $E \times \varepsilon$ Jahn-Teller problem (cf previous section), the classical analog hamiltonian in the diabatic representation is:

$$\mathcal{H} = \frac{p_p^2}{2} + \frac{p_\phi^2}{2p^2} + p^2/2 + k_\rho \cos (\theta - \phi)[n(1-n)]^{1/2}.$$

At this point all that has been achieved is an elegant reformation of the Ehrenfest force classical path equations. The major innovation in the work of Miller, Meyer & McCurdy is the realization that the classical analog hamiltonian can be used within the context of the classical S-matrix or quasiclassical trajectory approaches to determine nonadiabatic transition amplitudes, provided the following “Langer modification” is made:

$$n_i \rightarrow n_i + 1/2,$$

which together with a change in the form of $\mathcal{H}$ that maintains equality between the semiclassical electronic eigenvalues and adiabatic potential surface energies. The substitution of Eq. 29 ensures that there is a nontrivial dependence of the final electronic action upon the initial electronic phase. [For a justification of the Langer modification, see the discussion by Herman & Currier (209a).] The resulting modified hamiltonian for a general two-state system is:

$$\mathcal{H}' = \sum \frac{P_a^2}{2m_a} + (1 - n)H_{11} + nH_{22} + 2[(n + 1/2)(3/2 - n)]^{1/2}H_{12} \cos \theta.$$

Applications of the general two-state classical analog hamiltonians, Eqs. 27 and 30, and the linear Jahn-Teller hamiltonian, Eq. 28, in particular, are reviewed in the next section.

**Applications of Classical Electron and Related Models**

**NONADIABATIC PROCESSES IN COLLISIONS** The classical electron (Ehrenfest with Langer modification) and related classical pseudopotential and spin matrix mapping methods have been applied by Miller and co-workers to a variety of electronically nonadiabatic collision processes: quenching of an
excited fine-structure state of the fluorine atom $F^*(2P_{1/2})$ by collision with $H^+$ or Xe (208); quenching of $F^*(2P_{1/2})$ by collision with $H_2$ (E-R energy transfer) (210); quenching of $Br^*(2P_{1/2})$ by collision with $H_2(v = 0)$ (E-V transfer), for collinear (214) and three-dimensional (215) systems; and charge transfer in Na + I collisions (216).

In all cases where corresponding close-coupled quantum calculations are available for comparison, there is encouraging agreement between the exact results and quasiclassical trajectory calculations of cross sections and transition probabilities. In particular, resonant features are correctly described using the classical analog methods. There is clearly tremendous scope for application of these techniques to nonadiabatic processes already tackled using the popular trajectory surface-hopping method (189, 190), and for quantization of the theory using the classical S-matrix formalism.

BOUND STATES In line with the emphasis laid in preceding sections of this review on nonadiabatic effects in molecular bound states, we proceed to consider now in some detail the few applications made to date of the classical electron picture to these problems. Such an approach is potentially very fruitful, and much remains to be done in this area.

**Ultrafast nonradiative decay via conical intersections** In a pioneering quantum-mechanical calculation, Köppel (107) modeled the ultrafast internal conversion between $\tilde{A} \rightarrow \tilde{X}$ states of $C_2H^+$. The model system was taken to be two near-degenerate states in the diabatic representation coupled by a single nontotally symmetric mode, together with two totally symmetric modes. Such a system has a multidimensional conical intersection, since the totally symmetric modes "tune" the electronic energies. The time-dependent probability of being in the upper (diabatic) state (summed over all vibrational states) after sudden excitation from the neutral molecule ground vibrational state was computed by direct integration of the time-dependent Schrödinger equation.

The key result to emerge from this calculation is the extremely short time scale ($\sim 10^{-14}$ s) characterizing the radiationless decay. The necessity for coupling of the electronic states via more than one vibrational mode, hence the existence of a conical intersection, is borne out by a single mode calculation having revealed no rapid internal conversion. The disposition of energy among vibrational modes in the electronic \rightarrow vibrational energy transfer from the ground vibrational state of the upper diabatic electronic state was also calculated.

It is natural to consider the applicability of the classical electron model to this type of problem. In fact, Meyer (217) has recently investigated the same system as Köppel by using an Ehrenfest classical analog Hamiltonian, set up in the way outlined above. Using the classical histogram method for
assigning electronic states, and taking the initial state used in (107) to correspond to an ensemble of trajectories, remarkably good agreement between classical and quantum mechanical probabilities is obtained for the three-mode problem. Reasonable but “less beautiful” agreement is obtained for model two- and one-mode systems. This is in accord with the general principle that classical calculations are most reliable when some averaging (in this case, over vibrational states) occurs.

The enormous potential of the classical electron model in this context is apparent when it is realized that anharmonic modes or several additional vibrational degrees of freedom are easily included, while quantum mechanically such systems remain intractable. Meyer’s calculations show that mode anharmonicity has little effect on the short-time ($t < 40$ fs) decrease of the probability of remaining in the upper state. Quenching of regular oscillations of $P(t)$ occurs, however, at longer times. Increasing the number of modes to ten, for example, has very little effect on the time-dependent probability (a ten-mode quantal calculation is of course well beyond present-day capabilities). Finally, a recent comparison (110) of exact quantum and classical analog results for the time-dependent photon emission rate from a two-level two-mode system shows reasonable overall agreement with quantum calculations.

The classical electron model thus represents a computationally convenient and tractable approach to multimode vibronic bound state problems, and considerable development along these lines can be expected in the future. One advantage of a completely classical formulation of the vibronic problem is that examination of trajectories can provide insight into complicated vibronic dynamics. In the next subsection we describe some recent calculations in which the classical electron picture is used to study bound states of linear JT systems.

Bound states of linear Jahn-Teller systems. We now briefly survey the results of our investigations of the classical analog hamiltonian for the linear $E \times \epsilon$ Jahn-Teller bound state problem; details are given elsewhere (J. W. Zwanziger et al., submitted for publication). The hamiltonian Eq. 28 is that for a multidimensional nonlinear classical dynamical system. In line with much of the recent research in this area (218), we emphasize the qualitative appearance of trajectories, Poincaré surface of section plots, and the possibility of both quasiperiodic and chaotic motions. The relation between quantum and classical integrability for a two-state (“electronic”) system interacting with a boson (“vibrational”) mode has been studied using several approximations to the exact dynamics (219), including the self-consistent coupling formulation.

Judd (48, 220) has recently described Jahn-Teller trajectories for several systems. It should be noted that Judd’s work goes only as far as the
determination of nuclear trajectories on particular adiabatic potential sheets, so that treatment of the self-consistently coupled dynamics described by Eq. 28 represents a considerable extension of this approach.

The Hamiltonian Eq. 28 leads to six coupled equations for the variables \((p_r, p, p_\phi, n, \theta)\). Initial values of the pair \((n, \theta)\) can be chosen to correspond to starting on either adiabatic sheet, or diabatic state, etc. (Note that we deal here only with the Langer unmodified Hamiltonian Eq. 28.) The complexity of the problem can be reduced by noting that \(\mathcal{H}\) is a 1.1 resonance Hamiltonian, since the angles \(\theta\) and \(\phi\) appear only in the combination \((\theta - \phi)\). Transforming to new canonical variables \((P_\rho, \rho, I_1, \phi_1, I_2, \phi_2)\) we obtain a Hamiltonian \(\tilde{\mathcal{H}}\) independent of \(\phi_1\), so that \(I_1\) is a constant of the motion:

\[
\tilde{\mathcal{H}} = \frac{p_\rho^2}{2} + \frac{\rho^2}{2} + \frac{1}{2\rho^2} [I_2 + I_1/2]^2 \\
+ k\rho [(-I_2 + I_1/2)(1 + I_2 - I_1/2)]^{1/2} \cos \phi_2.
\]

We therefore have effectively a two degree-of-freedom problem, and so can use the standard surface-of-section method to characterize the dynamics.

Typical surfaces of section for a low energy trajectory (corresponding to the lowest quantum state of this system, \(k = 2.0\) and \(j = 1/2\)) are shown in Figures 9 and 10. The \((P_\rho, \rho)\) section, Figure 9, shows straightforward radial

![Figure 9](image-url)  

*Figure 9*  
Surface of section for a low energy trajectory for Hamiltonian Eq. 31, with \(k = 2.0\), \(j = 1/2\), \(I_1 = 1.0\), \(E = -1.446\). The variables \((P_\rho, \rho)\) are plotted at constant \(\phi_2 = \pi\).
librational motion for the most part, except for a prominent high order resonance visible as a chain of eight islands. The \((I_2, \phi_2)\) section, Figure 10, shows relatively small fluctuations of the phase around a value of \(\phi_2\) near \(\pi\), together with a central resonant zone corresponding to the island chain in Figure 9. In the limit of large \(k\) and low energy, which is the realm of "deep states" with negligible nonadiabatic coupling, the phase \(\phi_2\) has the constant value \(\pi\). Constancy of \(\phi_2\) implies perfect correlation between electronic and vibrational degrees of freedom. Nonadiabaticity is then manifest in the classical electron picture in deviations of \(\phi_2\) from the value \(\pi\), such deviations corresponding to a loss of correlation between electronic and nuclear variables.

Examination of nuclear configuration space projections of classical analog Jahn-Teller trajectories provides additional insight into the effects of nonadiabaticity on nuclear dynamics within this model. In Figures 11 we show two low-energy trajectories. One is obtained by solving the coupled equations of motion for Hamiltonian Eq. 28; the other corresponds to motion at the same energy on the lower adiabatic potential surface [where the latter includes the Born-Huang correction \(1/8\rho^2\) \((76, 105)\)]. The two trajectories are remarkably similar! For motion on the lower, cylindrically symmetric adiabatic surface, the nuclear angular momentum is a conserved

![](image)

*Figure 10* \((I_2, \phi_2)\) surface of section at constant \(\rho\) for the trajectory of Figure 9.
Figure 11. Comparison of adiabatic and nonadiabatic dynamics in the linear $E \times z$ system. On the left is the nuclear configuration space projection of a trajectory of the fully coupled classical analog Hamiltonian (Eq. 31). On the right is a trajectory for nuclear motion on the lower adiabatic sheet, with Born-Huang correction.
quantity, whereas for the low energy exact trajectory it is very nearly so. Increasing the energy reveals the effects of nonadiabaticity: In the slightly higher energy trajectory shown on the left in Figure 12, the nuclear radial turning points are beginning to develop a slight asymmetry, while on the right, at higher energy still, the projection of the nuclear motion develops loops and cusps, indicative of a nonadiabatic exchange of angular momentum with the electronic degrees of freedom. At very high energies, we obtain for some initial conditions irregular-looking trajectories that can only be described as “chaotic.”

We have provided a brief overview of studies of nonadiabatic bound states using the classical electron model. There is clearly much more to be learned about vibronic interactions using this approach. Particularly intriguing is the possibility of calculating bound-state energies or energy differences using some semiclassical quantization of the classical analog hamiltonian, i.e. via a “requantization” of the original problem (221).

**Other Semiclassical Approaches**

In the preceding subsection we stress the potential utility of the classical electron picture as a basis for a semiclassical description of nonadiabatic bound states. Another natural framework for such a theory is the multichannel generalization of the WKB method (222). We therefore briefly review some recent progress in this direction.

The general theory of multichannel WKB approaches to molecular scattering phenomena has been reviewed by Eu (223). Herman has recently investigated uniform multichannel semiclassical wavefunctions for nonadiabatic scattering, for both one- (224) and multi-dimensional (225, 226) systems, and has also provided a helpful discussion and comparison of previous approaches to nonadiabatic scattering (225). Herman’s approach seems particularly promising, and is complementary to the classical electron method discussed above.

In the past few years some work has been done on the multichannel WKB quantization of vibronic bound states. Voronin et al (227) and O’Brien (228) have considered the high energy limit of the linear $E \times e$ Jahn-Teller problem, where the conical intersection represents a negligible perturbation of essentially harmonic motion on either adiabatic surface. In this limit, good agreement is obtained (228) with the appropriate asymptotic energy level expressions of Longuet-Higgins et al (79); in fact, impressive agreement with variational energy levels extends over a wide parameter range (227). At the other extreme, Karkach & Osherov have investigated the semiclassical quantization of deep states in a quadratic $E \times e$ Jahn-Teller system (100). In this case the nonadiabatic coupling terms were ignored, and a uniform quantization of the angular nuclear
Figure 12: Effects of nonadiabaticity on nuclear motion in the classical analog Hamiltonian. The trajectory on the left is beginning to show asymmetry at radial turning points. The trajectory on the right has loops and cusps, indicating exchange of angular momentum between electronic and nuclear degrees of freedom.
motion carried out after an adiabatic separation of the radial motion. A notable feature of this calculation is the imposition of nonperiodic boundary conditions on the semiclassical angular wavefunction, thus reflecting the requirement of a change of sign of the nuclear wavefunction upon traversing a loop in nuclear configuration space enclosing a conical intersection (72, 80–85). The general problem of uniform quantization in a multiwell potential with nonperiodic boundary conditions has recently been discussed in some detail by Connor et al (229).

A semiclassical theory for scattering resonances in the upper sheet of a two-dimensional conical intersection has been developed by Osherov and co-workers (230, 231), and a semiclassical treatment of the absorption lineshape for an optical transition to a doubly degenerate electronic state is given in (232) (cf also 233). The multichannel WKB (or its generalization to EBK) approach to bound states for general matrix hamiltonians has been discussed in the context of the Dirac electron (234) and quark dynamics (235).

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