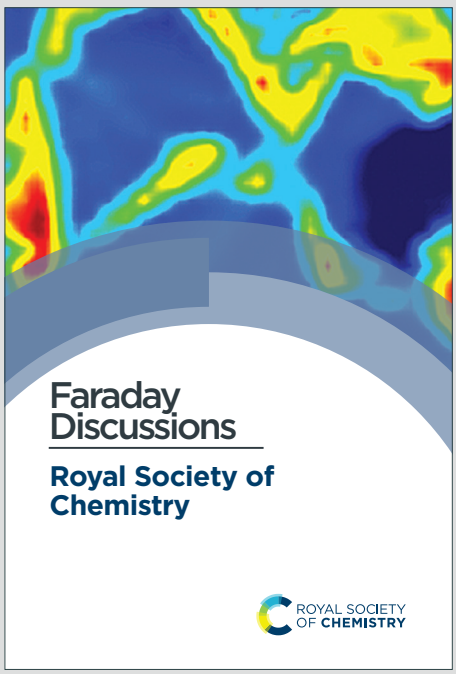
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PERSPECTIVE

Mechanistic Non-Adiabatic Chemistry: Everything you always Wanted to Know About but Were Afraid to Ask

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Abstract

We review the central concepts (e.g. conical intersections) of mechanistic non-adiabatic chemistry as well dynamics methods that can be used where more than one potential surface is involved. With the advent of attochemistry and the fact that one may also see coherences near a conical intersection in photochemistry itself our discussions have a bias towards approaches that allow for a coherent superposition of adiabatic states.

Introduction

When I started to put this together, I realized that it is almost 100 years since the non-crossing rule J. von Neumann and E. Wigner [1] was suggested, thus this article tries to follow, in part, the historical perspective; but with a bias towards those areas where we have had direct experience.

So, what do I want to do? Well, we can't make computations or experiments on every system of interest in photochemistry and other non-adiabatic systems; so, we must distil the basic mechanistic principles from both experiment and theory to guide future scientific work. Further, I use the term non-adiabatic chemistry (rather than photochemistry or excited state chemistry) because the field of excited state chemistry includes not only photochemistry but also attochemistry [2] [3] [4] [5] which originally only referred to cations. So, this perspective outlines some of the mechanistic principles that are intertwined with ideas from theory and computation of excited states and chemical dynamics.

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Can I begin with a quick statement of how I became involved in this field? Almost 60 years ago to the day I started my PhD under Imre Csizmadia. He handed me 3 boxes of punched cards that turned out to be a computer program (**The POLYTOM Code:** Developed at MIT in 1963) written in FORTRAN 2 that did both SCF and CI computations. He also handed me a reference from Bielstein that was a prep for Formaldoxime. He suggested I should make this molecule, measure its UV spectrum, then compute the spectrum and see if they agreed. I never could make the material let alone measure its spectrum. I did manage to implement Roothaan's approximate method [6] for singlet excited states and carried out some computations on the excited states for Formamide that were published in 1968. (One can note that this problem has now been treated fully with quantum dynamics[7] some 50 years later). And so, my personal involvement in this field began. But it was not until some 13 years later that we had some computer codes [8] that made more accurate computations on excited states possible. So, looking for potential applications, I devoured the book of Turro[9] seeking to acquaint myself with the mechanistic aspects of photochemistry. I was also very fortunate to have a preprint of the book of Michl and Bonacic-Koutecky[10]. We, together with Massimo Olivucci and Fernando Bernardi, finally published our first paper on excited state reactivity involving a conical intersection in the 2+2 cycloaddition of two ethylene molecules (see figure 1 for a sketch of the potential surface from Celani et al [11].) in 1990 [12] some 35 years ago. In addition, we even managed some surface hop dynamics some 5 years later [13]. Why did it take so long? Surprisingly it was not just computer hardware development; but rather, the development of multi-reference methods such as CASSCF [14] and gradient methods by Taylor et al [15, 16] that proved to be the bottleneck.

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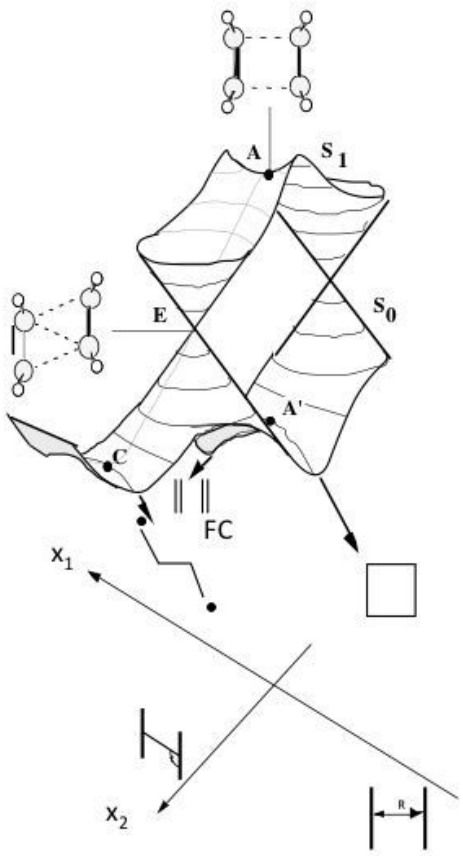


Figure 1. Sketch of the potential energy surface for the 2+2 S_1 cycloaddition of two Ethylene molecules [11]. The point E is the conical intersection and X1 and X2 are the gradient difference and derivative coupling to be discussed later. Adapted from reference 11 with permission from Elsevier, copyright 1995

So, in part of what follows I would like to introduce some of the theoretical ideas that lie under both the theory and experimental aspects of mechanistic non-adiabatic chemistry in general. I will illustrate these ideas with some recent results, mainly from our own work. Many of these ideas have been explored in more detail and at a more pedagogical level elsewhere [17] [18-24] [25]

1) Historical and Conceptual Development

The story begins with the seminal citation for the non-crossing rule which states for a diatomic molecule that the potential surfaces of the same symmetry cannot cross is due to J. von Neumann and E. Wigner [1]. That idea was further generalized by Longuet-

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Higgins [26] and by Teller [27]. However, these ideas only began to move into the world of chemistry due to the work of Michl [28]. We wrote a magazine article in 1996 with Michl that tried to unite the traditional mechanistic ideas of photochemistry (https://scholarworks.bgsu.edu/spectrum/vol9/iss4/1) with the chemical physics associated with surface crossings. We also tried to focus on the chemical aspects in an early review [24]. So we begin, briefly, with the basic aspects: Born Oppenheimer, excited state reaction mechanisms, conical intersections, non-adiabatic dynamics and the chemical nature of excited states.

Born-Oppenheimer approximation: The most important principle of mechanistic photochemistry arises when Born-Oppenheimer approximation begins to break down at conical intersections and even in the region of vertical excitation. This breakdown at conical intersections [20, 29-34] is where electronic and nuclear motion become coupled; hence we are in the realm on non-adiabatic chemistry.

Mechanism in chemistry is usually discussed in terms of minima, intermediates and transition states. However, in non-adiabatic photochemistry (from now on just photochemistry or non-adiabatic chemistry), an elementary mechanism must have at least three segments i) relaxation on an (excited) adiabatic state followed by ii) non-adiabatic dynamics at a conical intersection and iii) relaxation on a ground adiabatic state. Remarkably, it now possible to start photochemical dynamics with a coherent superposition of adiabatic electronic states created in a laser experiment [2, 35-37]. Here we abandon the Born-Oppenheimer approximation from the outset not just at the conical intersection. Hence the conjecture (Attochemistry) “Is Controlling Electrons the Future of Photochemistry” [38]”. So, we are left with the overriding mechanistic ideas of non-adiabatic chemistry: “What are the electrons really doing in molecules i) at the vertical excitation geometry and ii) at a conical intersection” and iii) and in a coherent superposition of adiabatic states, We begin with ii).

Conical intersections have been known since the 1930s [1, 27, 39]. Zimmerman [40] Michl[28] and Ruedenberg [41] were among the first to suggest that internal conversion occurring at a conical intersection was the key feature to enable understanding photochemical mechanisms. Modern theoretical developments began to occur once the necessary theoretical methods [42-45], [46] [47, 48] were developed that enabled the location of minimum energy (points on) conical intersections (MECI). The location of

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many such MECI at low energy has demonstrated (statistically) that such features are an essential part of photochemistry. The historical development of the subject has been summarized elegantly by Michl, in the preface to a collective volume on conical intersections [29]. Organic reactivity has been reviewed by Olivucci et al [49] in this same volume. We have continued this discussion in the second volume of this series [20] where we have focussed on the extended nature of the conical intersection seam.

adiabatic nuclear dynamics: The reaction path idea is still an essential aspect of ground state chemistry. However, in photochemistry the reaction path is only a zeroth order description and non-adiabatic nuclear dynamics must be considered. [50] [51] [19]. Further, the starting point for excited state chemistry is not merely the geometry of the vertical excitation point, but rather a distribution of such geometries that depends on the nature of the ground state zero-point vibrational envelope (for a recent example see the work of Vacher et al [52]). Dynamics computations show that the transition from the excited state surface to the ground state is not localized and the nature of the transition is determined by the phase mixing of ground and exited states [26]. Thus, one needs to consider several "flavours" of non-adiabatic dynamics (e.g. quantum treatment of nuclear motion vs. semi-classical approaches)

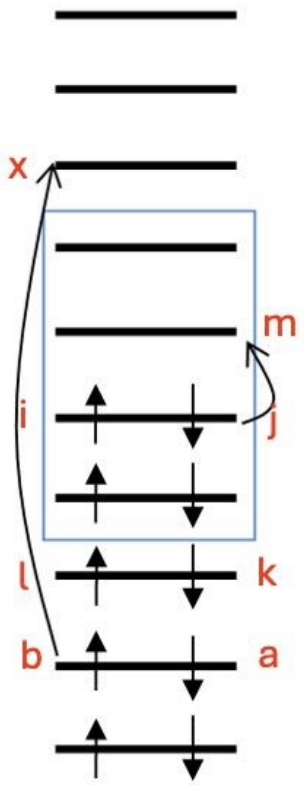
Finally, practical aspects of excited state chemistry must involve the molecular "environment": the solvent, a protein or both. For a recent review see Olivucci et al [17]

The Chemical Nature of Electronic Excited States Excited states can be thought about as electronic isomers of the ground state (i.e. the bonds are in a different place). For example, one can see a change in spin coupling from ground state Kekulé Benzene to excited state Dewar Benzene in the S_0 and S_2 states of Benzene or by creating a zwitterionic state (e.g. the lowest excited state of butadiene. The valence bond method VB, discussed extensively in the book by McWeeny and Sutcliffe[53] as well as in the classic books of Eyring[54] and Coulson [55].

In designing electronic structure computational protocols or methods one needs to understand the nature and the role of electron correlation in the electronic states involved. For example, we were able to show recently that one may get reasonable accuracy using the RASSCF method [56]. In this method one can focus on the concept of semi-internal correlation[57] rather than a more complete computation of electron correlation. A semi-internal excitation involves a single excitation (b->x) from inactive

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to virtual coupled with a single excitation (j->m) within the active space (see Scheme 1 below). In scheme 1 ab are inactive orbitals/electrons, ijkl are active orbitals (the CASSCF active space) and x *y z* are unoccupied orbitals. A semi-internal excitation involves excitation from a configuration where one has an active orbital j and replaced by another active orbital m coupled with an excitation from an inactive orbital b to an inactive orbital x. When orbitals are optimized in a muti-reference approach (e.g. CASSCF) [14] the single excitations vanish on the average. However, this averaging is over all internal excitations of the type j->m. The excitation shown in scheme 1 is formally a double excitation and the weight of the single excitation depends on j and *m*. The contribution will be different if j is tight or diffuse but CASSCF provides only one compromise (average) orbital. As a result, one must include this type of excitation explicitly (in RASSCF) and the average cannot be used.



Scheme 1: A RASSCF semi-internal excited configuration. The blue box encircles the active orbitals. Orbitals a and b have the same spatial part but different spin see reference. [56]

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2)Four important concepts in excited state electronic structure: i) Excited State Variational principle, ii) Gradients and Second derivatives, iii) the Derivative Coupling and iv)Conical Intersections

2-i Variational Principal for Excited States: The **CI** eigenvalue problem, equation 1, is an essential feature of all excited state methods.

$$HU = U\varepsilon \quad \varepsilon_1 \le \varepsilon_2 \le \varepsilon_3 \le \ldots \le \varepsilon_K \tag{1a}$$

$$H = \{H_{\lambda\mu}\} \quad H_{\lambda\mu} = <\Phi_\lambda | \hat{H} | \Phi_\mu> \tag{1b}$$

$$U = \begin{pmatrix} U_{11} & \cdots & \cdots & U_{K1} \\ \vdots & \ddots & & \vdots \\ U_{1\lambda} & & \ddots & U_{K\lambda} \\ U_{1\mu} & \cdots & \cdots & U_{K\mu} \end{pmatrix} \quad \varepsilon = \begin{pmatrix} \varepsilon_1 & & \\ & \ddots & \\ & & \varepsilon_k \end{pmatrix} \tag{1c}$$

In equation 1b, the Φ_λ are the expansion functions, say determinants (or configuration state functions), built from the orbitals (usually molecular orbitals). The K^{th} column of U contains the individual eigenvectors $\{c_\lambda^K\}$ $\lambda = 1.....$ in with energy ε_κ .

Equation 1 describes excited states correctly *only true if the configurations are built from the same set of orbitals*. [58] [59]. Thus, in order to optimize the orbitals, one needs to average the density matrices of the states (so-called state averaging). Secondly, the space spanned by equation 1c needs to be "complete". If there is a state missing (intruder state) then one cannot guarantee a variational upper bound.

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2-ii Gradients E_{R_I} and second derivatives $E_{R_I R_J}$ [15] are an essential part of any ground or excited state approach to chemical reactivity. These are necessary for molecular structure determination, for reaction path computation and for dynamics. In non-adiabatic dynamics one also needs the derivative couplings $\langle \psi_S | \frac{\partial}{\partial R_\alpha} \psi_{S'} \rangle$ that mix states S and S' along the geometric change R_α

For multi-reference methods, such as those used for excited states, Taylor et al [15, 16] have given a general approach, which we follow here. In any excited state problem, there are 3 sets of variables **X** Y and **C.** (From a practical point of view one can sometimes ignore some contributions (e.g. **X** and **C**) in computing the gradient because the orbitals and CI coefficients are optimized). The variables **X** Y and **C are :**

1) $\mathbf{X}$ is the orthogonal rotation of the orbitals among themselves as one displaces the geometry. The derivative is $\mathbf{X}_{R_I}$ with respect to the nuclear co-ordinate R_I

2) $\mathbf{C}$ the orthogonal rotation of the CI eigenvectors among themselves as one displaces the geometry with the derivative $\mathbf{C}_{\mathbf{R_I}}$ with respect to the nuclear co-ordinate and

3) Y the re-orthogonalization of the orbitals as one displaces the geometry with the derivative $\mathbf{S}_{R_I}$.

With a quadratic expansion of the energy, one has

$$E(R) = E^0 + \mathbf{G}^0 \cdot (R - R^0) + \frac{1}{2}(R - R^0)^\dagger \cdot H^0 \cdot (R - R^0) \qquad (2a)$$

In this equation $\mathbf{G}^0$ is the vector of first derivatives of the energy with respect to nuclear displacements *R*, while H^0 is the hessian matrix of second derivatives.

The gradient then involves $\mathbf{E}^C$, the gradient of the energy with respect to the rotation of the CI eigenvectors, $\mathbf{E}^X$ the gradient of the energy with respect to the rotation of the

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orbitals and $\mathbf{E}^{Y}$ the gradient of the energy with respect to the re-orthogonalization of the orbitals. The leading term in the gradient E^{R_I} is the gradient of the energy due to the change in the molecular Hamiltonian with nuclear geometry (The Hellmann-Feynman term). The gradient is thus given compactly as.

$$E_{R_I} = E^{R_I} + \mathbf{E}^{C}\mathbf{C}_{R_I} + \mathbf{E}^{X}\mathbf{X}_{R_I} - \frac{1}{2}\mathbf{E}^{Y}\mathbf{S}_{R_I} \qquad (2b)$$

In state-specific CASSCF [60], the terms $\mathbf{E}^{C}$ and $\mathbf{E}^{X}$ vanish because both the orbitals and CI coefficients are optimized. If the orbitals and CI coefficients are not optimized, then one must evaluate the $\mathbf{C}_{R_I} and \mathbf{X}_{R_I}$ by computing the coupled perturbed equations for each nuclear c-ordinate. These equations generate the derivative of the MO and CI coefficients C_{R_I} X_{R_I} Cases where this occurs are in State Averaged CASSCF and in the computation of non-adiabatic effects. Thus in State Averaged CASSCF, the orbitals are not optimized for the state of interest (i.e. the single specific state we have selected to "follow"). Thus we must include derivatives of the orbital rotations.

The second derivatives have the general form given in equation 2c, where the notation is the same as in equation 2b, e.g. $\mathbf{E}^{CR_J}$ is the mixed second derivative with respect to CI vector rotation and nuclear displacement. Quantities such as $\mathbf{X}_{R_I}$ must be obtained from the coupled perturbed CASSCF equations, which have to be solved for each nuclear displacement.

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$$E_{R_I R_J} = E^{R_I R_J} + \mathbf{E}^{C}\mathbf{C}_{R_I R_J} + \mathbf{E}^{CR_I}\mathbf{C}_{R_J} + \mathbf{E}^{CR_J}\mathbf{C}_{R_I} + \mathbf{E}^{CC}\mathbf{C}_{R_I}\mathbf{C}_{R_J} + \mathbf{E}^{CX}\mathbf{C}_{R_I}\mathbf{X}_{R_J} - \frac{1}{2}\mathbf{E}^{CY}\mathbf{C}_{R_I}\mathbf{S}_{R_J}$$
$$+\mathbf{E}^{X}\mathbf{X}_{R_I R_J} + \mathbf{E}^{XR_I}\mathbf{X}_{R_J} + \mathbf{E}^{XR_J}\mathbf{X}_{R_I} + \mathbf{E}^{XX}\mathbf{X}_{R_I}\mathbf{X}_{R_J} + \mathbf{E}^{XC}\mathbf{X}_{R_I}\mathbf{C}_{R_J} - \frac{1}{2}\mathbf{E}^{XY}\mathbf{X}_{R_I}\mathbf{S}_{R_J} - \frac{1}{2}\mathbf{E}^{YR_I}\mathbf{S}_{R_J} \qquad (2c)$$
$$-\frac{1}{2}\mathbf{E}^{YR_J}\mathbf{S}_{R_I} + \frac{1}{2}\mathbf{E}^{Y}\mathbf{S}_{R_I}\mathbf{S}_{R_J} - \frac{1}{2}\mathbf{E}^{Y}\mathbf{S}_{R_I R_J} + \frac{1}{4}\mathbf{E}^{YY}\mathbf{S}_{R_I}\mathbf{S}_{R_J} - \frac{1}{2}\mathbf{E}^{YC}\mathbf{S}_{R_I}\mathbf{C}_{R_J} - \frac{1}{2}\mathbf{E}^{YX}\mathbf{S}_{R_I}\mathbf{X}_{R_J}$$

Again, in special cases (CASSCF) some of these terms may go to zero. But it is the computation of gradients and hessians that is the major cost of doing molecular dynamics, as we shall discuss shortly. While the computation of orbital-CI hessians of the form $\mathbf{E}^{XC}$ etc. involves only matrix multiplication, the computation of the coupled perturbed equations are required for terms such as $\mathbf{X}_{R_I}$ and this dominates the computation time.

2-iii Derivative coupling Finally, different electronic states ψ_S and $\psi_{S'}$ are coupled due to nuclear motion by the derivative coupling operator, the non-adiabatic coupling (equation 6) which occurs in the full nuclear-electronic Hamiltonian

$$\hat{F}_{ss',\alpha} = \left\langle \psi_s \left| \frac{\partial}{\partial R_\alpha} \psi_{s'} \right\rangle \right. \quad . \qquad (3a)$$

Equation 3a can also be written as

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$$\hat{F}_{ss',\alpha} = \frac{1}{V_{s'} - V_s} \langle \psi_s | \frac{\partial H}{\partial R_\alpha} | \psi_{s'} \rangle \quad . \tag{3b}$$

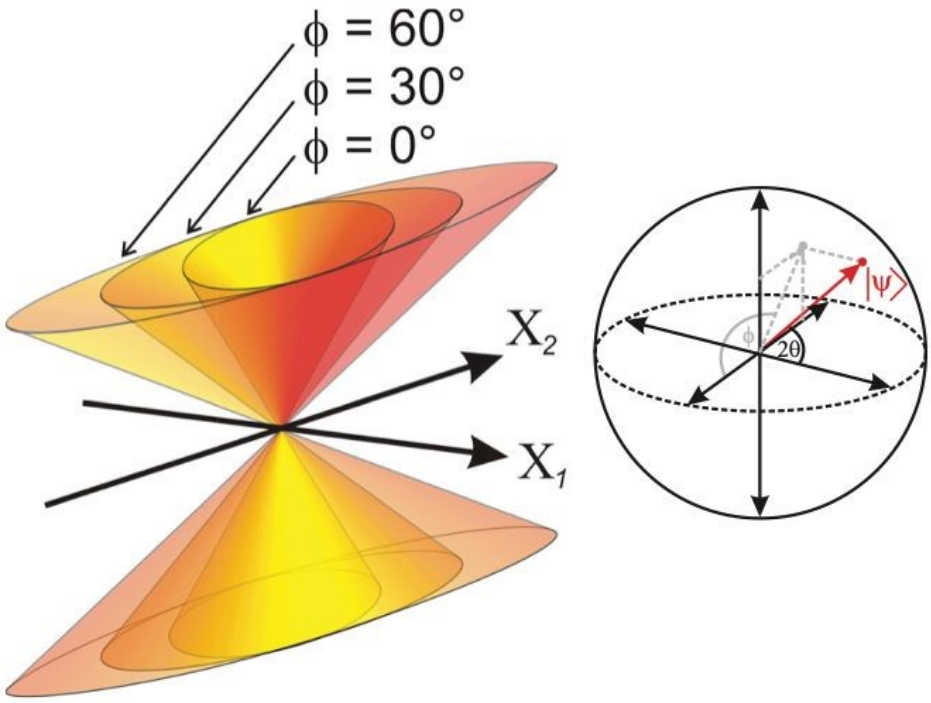
where $V_{S'}$ and V_S are the energies of the two electronic states.

We shall refer to $\langle \psi_s | \frac{\partial H}{\partial R_\alpha} | \psi_{s'} \rangle$ as the interstate coupling vector. It is an off-diagonal gradient and can be evaluated in a similar fashion to equation 3a. [60].

As we shall see, the derivative coupling enters the theory in 3 ways, i)it defines the branching space of a conical intersection (next subsection), ii)it is the direction in which momentum is added in the surface hop method and iii)it is a component of the gradient in a wavefunction that is a superposition the adiabatic chemistry (e.g attochemistry)

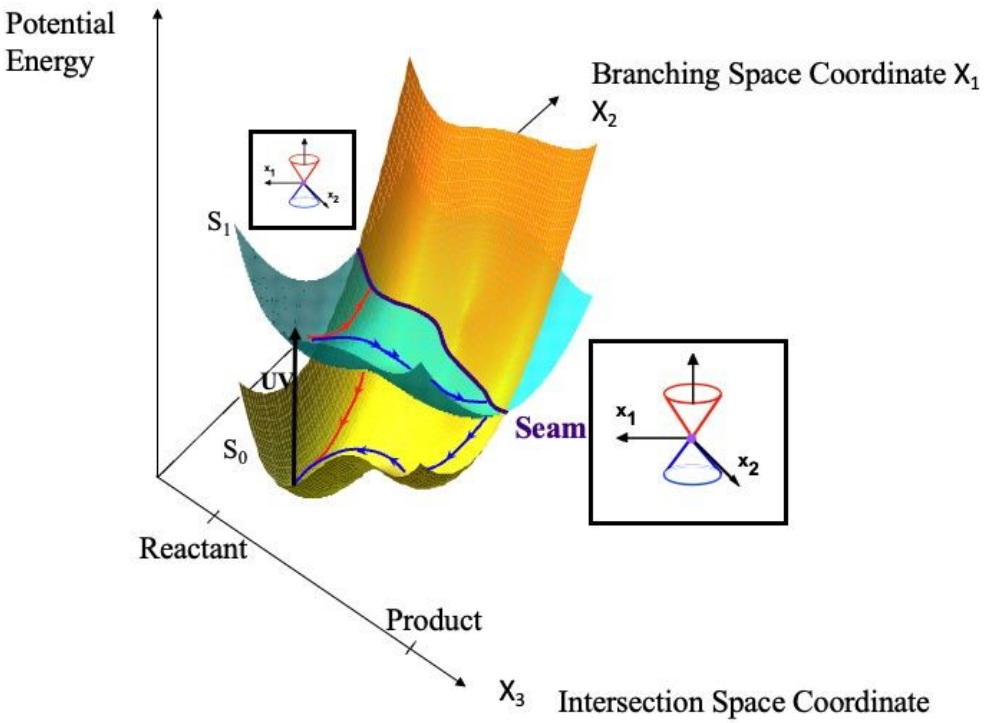
2-iv Conical Intersections. We now give a brief introduction to conical intersections [49] [20, 30, 61]. There are 3 central ideas: i) the phase of the wavefunction, ii) the branching space and intersection space, and iii) the location of a minimum energy conical intersection. Figure 2a and 2b will now be used to discuss these ideas.

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(a)

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b)

Figure 2 Conical intersection Theory a) The **phase idea** [26], the mixing of two diabatic electronic states A (red) and B (yellow) are indicated by shading. If one takes any point on the upper surface and performs a rotation by 180^o followed by a reflection in the X_1X_2 plane, that point is mapped into a point on the lower sheet (i.e. the shading/colour is the same) The different sheets indicated by ϕ correspond to different complex phases as shown on the Bloch Sphere insey. Adapted from Meisener et al reference 62 with permission [J. Meisner, M. Vacher, M. J. Bearpark and M. A. Robb, J. Chem. Theory Comput. 11 (7), 3115-3122 (2015). Copyright [2015] American Chemical Society. Published under a [CC BY / CC BY-NC] license.

b) A cartoon showing **the conical intersection hyperline** X_3 (3N-8 dimensional where N is the number of atom in the molecular system and 3N-6 is the usual number of geometrical degrees of freedom) The system remains degenerate as one traverses the co-ordinate X_3, but the energy and the shape of the double cone must change in X_1 X_2, (adapted from Paterson et al [63] with permission from the Royal Society of Chemistry.)

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First, we discuss the wavefunction formed as a superposition of two diabatic states A (red) and B(yellow) , equation 4a, at a conical intersection [26].

$$\chi = +\cos\left(\frac{\theta}{2}\right)e^{i\phi_A}\psi_A + \sin\left(\frac{\theta}{2}\right)e^{i\phi_B}\psi_B$$
$$\chi' = -\sin\left(\frac{\theta}{2}\right)e^{i\phi_A}\psi_A + \cos\frac{\theta}{2}e^{i\phi_B}\psi_B \quad (4a)$$

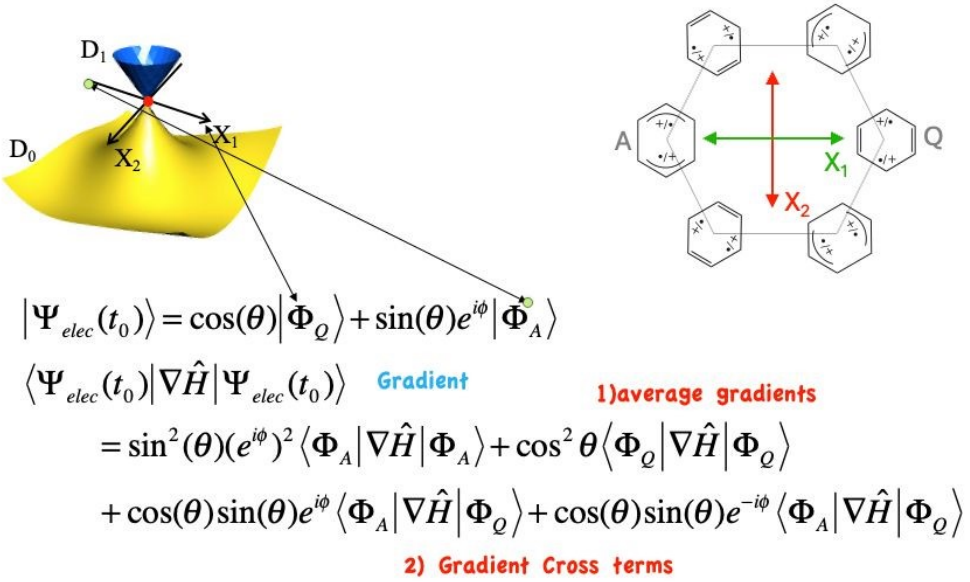
Associated with each of the surfaces at a conical intersection is a wavefunction χ which is a linear combination eq 4a of the two diabatic electronic states: ψ_A and ψ_B. The mixing angle in the X_1 X_2 plane is $\left(\frac{\theta}{2}\right)$ and $e^{i\phi_A}$ is the phase of A. The electronic diabatic states here can just be chosen as some convenient linear combination of the two degenerate eigenstates at the apex of the cone, e.g. two different electronic character or "bonding states" of the system. In figure 2a and in the following we use $\phi = \phi_B - \phi_A$

The space of the degeneracy lifting co-ordinates (branching space X_1 X_2) is shown in the middle of the figure 2a. In Figure 2a, we show the red/yellow shading pattern, indicating the nature of the wavefunctions corresponding to weights corresponding to the mixing angle $\left(\frac{\theta}{2}\right)$ (eq 4a) of the two electronic (diabatic states) states: A (red) and B (yellow). The essential idea is that if one takes a point A on the upper surface, which has electronic structure C_A A + C_B B, (where C_A is given by $\cos\left(\frac{\theta}{2}\right)e^{i\phi_A}$ etc) then the corresponding point on the lower surface, related by 180° rotation plus refection in the X_1X_2 plane has the same electronic structure. Similarly, the point on the upper surface related by a 180° rotation is C_A A - C_B B (e.g pure yellow to pure red). Thus, the red/yellow shading pattern indicates the electronic structure or combinations of diabatic states as a function of the position on the double cone. The Longuet-Higgins phase theorem [26] states that if one does a circuit of the conical intersection structure, remaining on the same upper sheet the wavefunction becomes -C_A A - C_B B. It follows from this that the geometry, in the X_1X_2 plane, is in 1:1 correspondence with the combination of A and B indicated by the red-yellow shading pattern. Thus, we have the important generality that the path in the branching space is related to the Longuet-

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Higgins phase [26] and thus to the change in the electronic character of chemical bonding.

Note that in figure 2a we have generalized the Longuet-Higgins phase idea in equation 4a, to include complex mixing[62]. In figure 3 we give an example using the benzene radical cation that helps one to understand how reactivity is controlled at a conical intersection.



(a)

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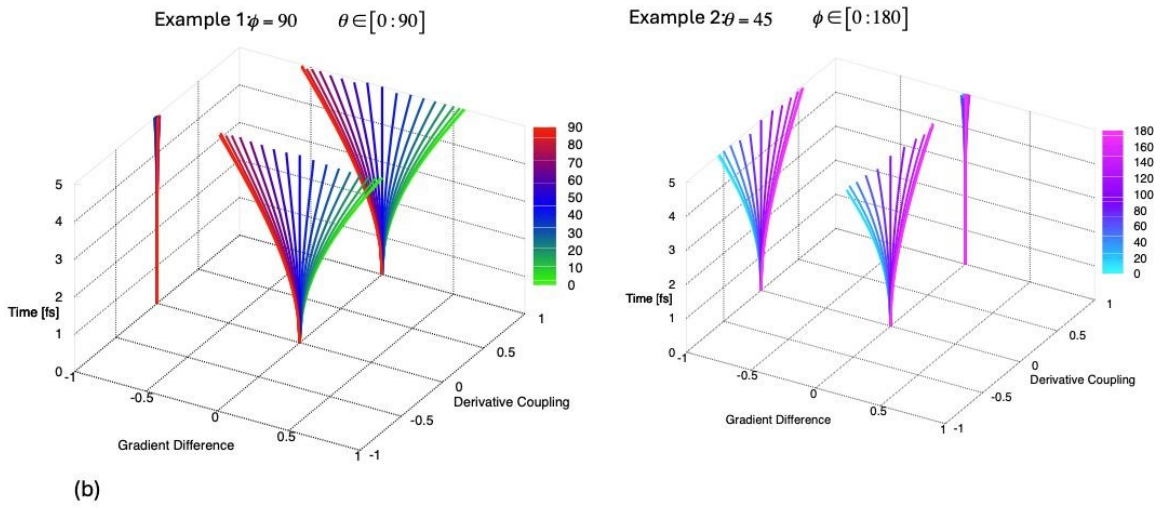


Figure 3 Illustration of the complex phase for benzene radical cation adapted from Meisner et a [62] (a) conical intersection branching space showing the Benzene radical cation VB structures in the branching plane on the left. The expressions for the gradient are also shown inset so that one can connect the algebra with the imaging. b) Trajectories stating at the conical intersection with various phases: Example 1 a scan changing the real phase with fixed complex phase, the resulting trajectories lie in the plane containing the derivative coupling. Example 2: a scan of the phase angle along the gradient difference [62] Adapted from reference 62 with permission [J. Meisner, M. Vacher, M. J. Bearpark and M. A. Robb, J. Chem. Theory Comput. 11 (7), 3115-3122 (2015).Copyright [2015] American Chemical Society. Published under a [CC BY / CC BY-NC] license.

We now discuss the example given in figure 3. Note that we have put the relevant equations in the figure itself so that the relationship between the mathematics and the plots is clearer. If figure 3a we show the branching space of the conical intersection and some VB structures as one does a circuit in the X_1 X_2 plane. Then we give the expression for the gradient. Note that there are 2 components of the gradient: the average or intrastate terms and the cross terms. Then in figure 3b we show in the case of Example 1: the case where we change the real mixing keeping the phase fixed

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and Example 2 where we keep the real mixing at 50:50 and change the phase. This we can populate any region of figure 2a

Now we return to the branching space (figure 2b) from a more chemical point of view. The two coordinates X_1X_2 play a central role in radiationless decay and photochemistry (here a photochemical reaction path can be seen, locally, as a radiationless decay process ultimately leading to a bonding state). In a thermal reactivity problem, we are normally interested in the energy and the reaction path or, locally at the transition state, in *one* coordinate corresponding the so called "transition vector" which give the negative direction of curvature at the saddle point. In a photochemical problem, where the reaction path passes through a conical intersection, we are interested in the energy and *two* coordinates X_1 and X_2. At a conical intersection, the two directions X_1 and X_2 are associated with gradients and transition gradients as shown in equations 4 a and 4b.

$$x_1^{(i\gamma)} = \frac{\partial\left(E_B - E_A\right)}{\partial\xi_{i\gamma}} \qquad (4a)$$

$$x_2^{(i\gamma)} = \frac{\partial\left\langle\Psi_A\left|\hat{H}\right|\Psi_B\right\rangle}{\partial\xi_{i\gamma}} \qquad (4b)$$

In equation 4a and 4b , the states *A* and *B* are the two electronic states: ground and excited states, associated with the conical intersection, $\xi_{i\gamma}$ is the γ*-th* mass-weighted Cartesian co-ordinate of the *i-th* atom. The index *i* labels the *N* atoms and γ the Cartesians components, *x, y* and *z*.

The co-ordinate X_3 is representative of the intersection space. Movement along this co-ordinate changes the energy and the “shape” of the conical intersection surfaces, but the states remain degenerate. This idea is illustrated in figure 2b. It is almost obvious that one can compute the gradient in the space spanned by X_3 (i.e. orthogonal

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to X_1 and X_2.) and minimize the energy [43]. Further, one can compute the hessian in this space [64] [45] and distinguish minima and transition states in the intersection space (i.e. unlike the transition state on a single potential energy surface the transition vector in the intersection space refers to a coordinate that lowers the energy on the "seam" where the states remain degenerate; not a coordinate expected to be a geometry change for an excited molecule).

3)Important Concepts in Nuclear Dynamics Methods for Excited State Computations.

Combining electronic structure methods with classical and quantum dynamics[19].

This subject is both very broad and is undergoing very rapid development. The following discussion is strongly motivated by our own experience in this field. A rather exhaustive discussion that is practically oriented can be found in the article by Prij et al [65], or the reviews of Ibele [66] or Barbatti et al [67]

Of course, if one has gradients and second derivatives of the potential energy with respect to the nuclear coordinates available, then classical dynamics is straightforward. However, for excited state chemistry the dynamics trajectory may begin on an excited state but finish on the ground state. So, one has the issue of how to perform dynamics computation at the point of crossing between two electronic states. There are 2 approaches that use adiabatic surfaces or superpositions of adiabatic surfaces: i) Surface hop [68]: where one may just change from using the gradient of the excited state to using the gradient of the ground state as one passes through the surface crossing (surface hopping), or ii) Quantum Ehrenfest [69, 70]: (or Exact Factorization[71-73] where one may use an electronic structure approach that allows passage through the surface crossing continuously. For both approaches one needs a solution of the electronic time-dependent Schrödinger equation (TDSE) i.e. the time-dependent weights of the states. The only important difference is that in surface hopping one uses the solution of the TDSE to decide when to change the gradient from the excited state gradient to the ground state gradient. However, as we shall show, the Ehrenfest approach, uses the gradient of the TDSE as one passes through the surface crossing. The other possibility is to use diabatic states in the context of the quantum dynamics, for a recent exposition the reader is referred to the

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work of Richings et al[74]. The Quantum Ehrenfest uses all the same methodology (in the quantics code [75]) except that there is only 1 quasi-diabatic state.

The classical equations for nuclear motion in quantum chemistry were first elaborated by Helgaker [76]. In our discussion here, we start with the time Dependent Schrodinger equation TDSE. The ultimate goal is to approach non-adiabatic nuclear dynamics by solving the time-dependent Schrödinger equation 5 equation for the motion of the nuclei Q motion instead of the classical equations which come as a special case.

$$i\hbar\frac{\partial\Psi(Q,t)}{\partial t}=\hat{H}\Psi(Q,t) \qquad (5)$$

But irrespective of whether the nuclei are propagated classically or quantum mechanically, the motion of the nuclei is driven by the gradients and second derivatives of the relevant potential energy surfaces.

The two most used approaches to nuclear dynamics are shown in figure 4. Surface hopping is shown in figure 4a, and quantum dynamics is shown in figure 4b. It is instructive to show how the two approaches are related.

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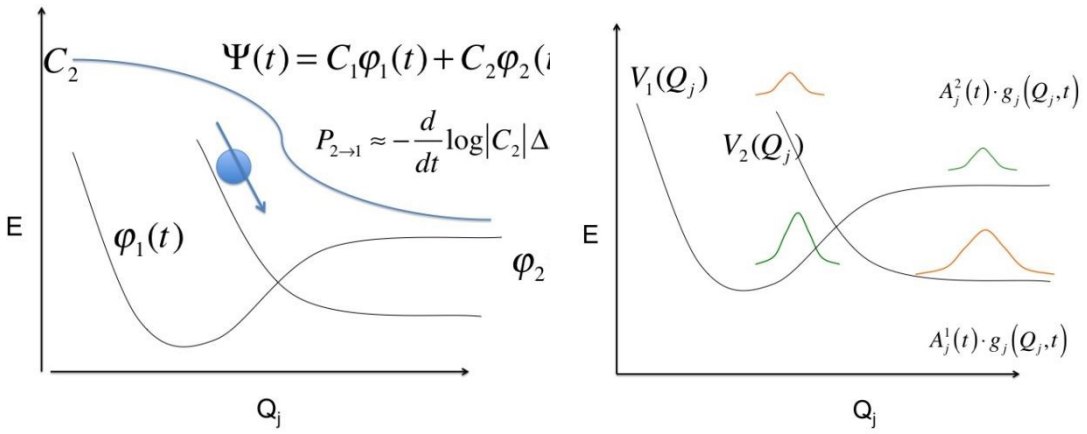


Figure 4 a) **Surface Hopping: Schematic:** [77] [78] representation of a trajectory on a potential surface undergoing a non-adiabatic transition at the surface crossing. In the region of the surface crossing, the electronic states $\varphi_1(t), \varphi_2(t)$ mix under the influence of the derivative coupling. The probability of changing from one surface to another depends on the weight of the coefficient C_2: when C_2 increases sufficiently, the states mix at the crossing. For a review, see the perspective article by Tully [79] b) **Quantum Dynamics:** Multiple trajectories Q_j as a function of time. A Gaussian wavepacket $g_j(Q,t)$ is "floated" (i.e. the centre of the Gaussian that lies on the trajectory) on each trajectory. These wavepackets mix to form the nuclear wavefunction. Adapted from reference 79 with permission from American Chemical Society, copyright 2010.

In trajectories, within the surface hopping (figure 4a) approach, the time evolution of the system is modelled by a 'swarm of trajectories' that follow classical paths. The solution of the TDSE for ***electronic motion*** is given in equation 6a. When a surface crossing is encountered, the surface hop is controlled by $P_{2\to1}$ (equation 6b) where the

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coefficients C_1 and C_2 (equation 6a) are computed by propagating a solution to the time dependent Schrödinger equation 6c in the space of the CI eigenstates.

$$\Psi(t) = C_1\varphi_1(t) + C_2\varphi_2(t) \tag{6a}$$

$$P_{2\to 1} \approx -\frac{d}{dt}\log|C_2|\Delta t \tag{6b}$$

$$i\hbar\dot{c}_i = c_i V_i - i\hbar\sum_j \dot{\mathbf{R}}\cdot\mathbf{F}_{ij}c_j \tag{6c}$$

In equation 6c, V_i is the diagonal element of the Hamiltonian expressed in the eigenvector basis $\varphi_1(t)$ and $\varphi_2(t)$ and $\dot{R}$ is the nuclear velocity.

The quantity F_{ij} is the derivative coupling eq 3b and so we have

$$\dot{R}\cdot F_{ij} = \dot{R}\langle\psi_i|\nabla|\psi_j\rangle = \dot{R}\langle\psi_i\frac{\partial H}{\partial R}\psi_j\rangle/(E_i - E_j) \tag{6d}$$

Now let us consider the **quantum approach to nuclear motion** (figure 4b). The nuclear wavefunction is now given in equation 6e, where A is an expansion coefficient and $g_j(\mathbf{q},t)$ is a Gaussian wavepacket[19]. Thus, the trajectory is replaced by a

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Gaussian wavepacket $g_j(\mathbf{q},t)$ and the expansion coefficients are obtained from a CI-like eigenvalue problem in the space of these wavepackets.

$$\Psi(\mathbf{q},t)=\sum_s\sum_j A_j^{(s)}(t)g_j(\mathbf{q},t) \tag{6e}$$

Each wavepacket is associated with an electronic state s (the electronic wavepacket). (Usually we drop the superscript s on $\sum_j A_j^{(s)}$ in the single set approximation, where the coefficients are the same for both states).

The Ehrenfest formulation, a single set approach. for the electronic wavefunction uses an electronic state vector, which we denote as $X(t_n)$ where t_n is the time-step, which is taken to be a solution of the electronic time dependent Schrodinger equation 6f in a space of configuration state functions (e.g. subsets of Slater determinants that are spin-eigenfunctions) [80]. As we shall see this formulation can be used in the surface hop or Quantum Ehrenfest [69, 70]: (or Exact Factorization[71-73].

The Ehrenfest electronic state vector is given as

$$X(t_n)=\exp\left(-\frac{i}{\hbar}H_e(t_n)\right)X(t_{n-1}) \tag{6f}$$

where $H_e(t_n)$ is the time-independent electronic Hamiltonian at time t_n. If we re-write equation 6f in the eigenstate basis, we have equation 6g.

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$$X(t_n) = U(t_n)\exp\left(-\frac{i}{\hbar}D_e(t_n)\right)U^{\dagger}(t_n)\cdot X(t_{n-1}) \qquad (6g)$$

$\mathbf{U}(t_n)$ is the matrix containing the eigenvectors of $H_e(t_n)$ arranged as columns. $\mathbf{D}_e(t_n)$ is the matrix representation of the electronic Hamiltonian in the basis of the eigenstates: it thus contains the eigenvalues V_i on the diagonal and is zero elsewhere. We now expand this as a Taylor series[80] to give

$$\mathbf{D}_e(t_n) = \mathbf{D}_e(t_{n-1}) + \frac{d\mathbf{D}_e(t_{n-1})}{dt}\cdot(t_n - t_{n-1}) \qquad (6h)$$

The electronic Hamiltonian is time-independent (no external electric field) but it changes with time if the nuclei are allowed to move. Hence, we have the following relation (if it obeys the Hellmann-Feynman theorem):

$$\frac{d\mathbf{D}_e}{dt} = \nabla_R \mathbf{D}_e \cdot \dot{R} = \langle\tilde{\phi}_k | \nabla_{R_l}(\mathcal{H}_e) | \tilde{\phi}_l\rangle \cdot \dot{R} \qquad (6i)$$

If we compare equation 6i with second term in equation 6c , we can conclude that equations used to propagate the two level wavefunction given by equation 6a are equivalent to the electron dynamics equations used to propagate the electronic wavefunction in the Ehrenfest method [69]. In the Ehrenfest method, the potential energy is associated with the time-dependent state $X(t_n)$. The obvious generalization of surface hop method is thus the Ehrenfest method [69] where the nuclei move on the potential surface associated with $X(t_n)$. The downside is that neither the orbitals nor the expansion coefficients are optimized (rather they are solutions of the TDSE), so one must use the general expressions for gradients and hessians given above.

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For the quantum representation of nuclear motion there is a configuration interaction (CI) CI-like representation Hamiltonian $\widehat{\mathscr{H}}_e$ ($H_{jl} = \langle g_j|H|g_l\rangle$) with matrix elements shown in equations 6j and 6k.

$$H_{jl} = \left\langle g_j \left| \left\langle \phi \left| \widehat{\mathscr{H}}_e \right| \phi \right\rangle \right| g_l \right\rangle - \sum_\alpha \frac{\hbar^2}{2M_\alpha} \left\langle g_j \left| \nabla^2_{R_\alpha} \right| g_l \right\rangle \quad (6j)$$

where

$$H_e(\mathrm{R}) = H_e^l + \mathrm{G}^l \cdot (\mathrm{R} - \mathrm{R}^l) + \frac{1}{2}(\mathrm{R} - \mathrm{R}^l)^\dagger \cdot M^l \cdot (\mathrm{R} - \mathrm{R}^l) \quad (6k)$$

The nuclear wavefunction is, in turn, expanded in a set of gwps (gaussian wave packets) as shown in equation 6l.

$$\Phi(t) = \sum_j \sum_s C_j(t)\ g_j(t) \quad (6l)$$

The Dirac–Frenkel variational principle [81] is then used to provide a set of equations for the time propagation of the expansion coefficients and parameters of the gwp (e.g. position and momentum) [82] To calculate the required matrix elements, we use a quadratic approximation (equation 6k) for the hamiltonian in equation 6j, so there is a gradient $\mathbf{G}^l$ and hessian $\mathbf{M}^\mathbf{l}$ matrix for each gwp g_l which evolve over a time-dependent potential surface. Thus the Ehrenfrest trajectory evolves on a time-dependent potential surface The coefficient vectors of equation 6 can be analyzed using a population analysis [78].

The essential point is that the matrix elements in these equations involve an expansion in moments of the Gaussians as well as the gradients and hessians shown in equation 2c. The vector giving the evolution of the Gaussian parameters can be split into a classical part and a purely quantum [74] term. If the quantum term is omitted, then the nuclei evolve along classical trajectories.

When the nuclei are propagated quantum mechanically (using say Gaussian wavepackets), the Ehrenfest method goes under many names, such as “exact factorization” [73], or Quantum Ehrenfest (QuEh) [83] [70] depending on the implementation. In the surface hop method, one uses the time dependent Schoedinger

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equation for electronic motion (equation 6a) only to decide on a surface hop probability. In contrast, in the second approach, one evaluates the gradient of the Ehrenfest wavefunction in equations 2c [70]. An intermediate approach [74] replaces the surface hop with a pair of diabatic states.

To try to summarise the central concepts: In excited state dynamics one needs to describe the non-adiabatic event at a surface crossing. For the electronic part the wavefunction and gradient can be developed as a single state approach where the state is chosen consistent with the surface hop idea (equation 6b and 6c). Alternatively, the electronic part can be represented as an Ehrenfest state (ie a solution of the time-dependent Schrodinger equation for electrons equation 6f and 6g. For the nuclei, one needs both gradient and hessian. The nuclei can in turn be propagated by the classical equation or quantum mechanically[19]. Alternatively, one can use diabatic states [74]

To conclude this section, we should also mention the other ideas that arise from the solution of equation 6f and 6g; namely, electron dynamics. This is most easily illustrated with a generalized 2 level solution of the time dependent Schrodinger equation given in equation 6m and 6n.

$$\Psi(t) = z_1(t)e^{-iE_1(t)t}\phi_1(t) + z_2(t)e^{-iE_2(t)t}\phi_2(t) \tag{6m}$$

$$\begin{aligned}|\Psi(t)|^2 = &|z_1(t)|^2|\phi_1(t)|^2 + |z_2(t)|^2|\phi_2(t)|^2 \\ &+ 2\,\mathrm{Re}\left(z_1(t)^* z_2(t) e^{i(E_1(t)-E_2(t))t}\phi_1(t)^*\phi_2(t)\right)\end{aligned} \tag{6n}$$

From equation 6 n i it is clear that one will see oscillations with a period given in equation 6 o.

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$$T = \frac{h}{E_2 - E_1} \qquad (6o)$$

Thus, one will see oscillations in the density if two eigenstates are both populated and the larger the energy difference is, the shorter the period of the oscillations. Cederbaum has referred to these oscillations as charge migration[84] . Of course, these charge migration oscillations can affect the dynamics by perturbing the nuclei at turning points [85]. Thus it is clear that the surface hop method does not allow for some of the subtleties of this type of non-adiabatic dynamics at the surface crossing except in an averaged way.

4) Requirements of Electronic structure methods

We leave this section to the last because it is only with the benefit of the previous subsections that we can establish what is required of the electronic structure methods that we must consider.

First and foremost, it is clear that one needs to be able to evaluate gradients and second derivatives. The most straightforward approach evaluates these gradients and second derivatives *analytically* (i.e. via equations 5b and 5c). However, it becoming clear that great progress has been made towards computing these quantities numerically for general correlated wavefunctions (eg CASPT2 [86]).

If one is going to use the analytic gradient/hessian approach, then some sort of variational method is useful (e.g. the CASSCF or RASSCF approach see for example [87]. In the RASSCF approach one may selectively include the semi-internal correlation

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Thus, the choice of electronic structure method remains an open question still. On the one hand methods like CASPT2 are almost automatic (only the active space remains open); however, the gradient computation is an issue. Other perturbation based methods such ADC method [88] are also automatic but these start from the ground state.

In contrast, multi-reference methods can be adapted to other dynamics approaches such as Ehrenfest [70] whereas with methods like CASPT2 one focuses on adiabatic states.

4) Symmetry and **gradient at a surface crossing or created by coherent superposition. (i.e. Essentially creating the conditions of a conical intersection with a superposition)**

Often the dynamics can be rationalized in terms of symmetry rules. Here we discuss this as a generalization of the ideas presented in our discussion on conical intersections. The gradient of an adiabatic state must always be totally symmetric. However, for a coherent superposition the situation is different. (This subsection returns to some of the ideas first mentioned in the discussion of figure 3). The gradient (or force) that drives the nonadiabatic dynamics of a coherent superposition has 2 types of components: intrastate and interstate. The latter (off-diagonal gradients that arise from the mixing) are the derivative couplings and have the form $<\psi_I|\partial/\partial Q_i^{\alpha_i}\widehat{H}_e|\psi_{II}>$ where the I and II are two adiabatic states and $\partial/\partial Q_i^{\alpha_i}$ is the gradient operator for each normal mode i with symmetry α_i. As just stated, the gradient of the intrastate terms is only non-zero along normal modes belonging to totally symmetric irreducible representations for the interstate terms, the mixing/superposition of 2 states I and II will be “allowed”, with an off-diagonal gradient component along $Q_i^{\alpha_i}$, only if $\alpha^I \otimes \alpha^{Q_i^{\alpha_i}} \otimes \alpha^{II} = A_{1g}$ (A_{1g} is the totally symmetric representation in the D_{2h} symmetry point group) and α is an irreducible representation label). Thus, for a coherent superposition we can expect to see initial motion along non-totally symmetric coordinates. Of course, in the surface hop method, the momentum redirection also occurs along this direction.

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Finally, it is instructive to connect this idea with Figure 2a to give the gradient

$$\begin{aligned}\vec{\nabla}\langle x|\hat{H}_e|x\rangle &= \cos^2\left(\frac{\theta}{2}\right)(\psi_A|\vec{\nabla}\hat{H}_e|(\psi_A\rangle \\ &+\sin^2\left(\frac{\theta}{2}\right)\langle\psi_B|\vec{\nabla}\hat{H}_e|\psi_B\rangle \qquad (7)\\ &+\sin(\theta)\cos(\phi)(\psi_A|\vec{\nabla}\hat{H}_e|\psi B)\end{aligned}$$

We have discussed this generalization for the benzene radical cation[62] at a conical intersection. See figure 3.

5) Two examples

We now discuss two examples to illustrate a computational approach to non-adiabatic chemistry that uses the Ehrenfest method for the electronic structure part. Thus, our objective is to illustrate the use of a wavefunction that is a superposition of adiabatic states combined with the quantum treatment of the nuclear motion (e.g. Quantum Ehrenfest [70]). From the outset, we are interested in the case where the derivative coupling is large enough one must consider the possibility that wavefunction could be a superposition. This occurs in the catchment region of a conical intersection and in the state observed following excitation by a suitable laser pulse (attochemistry). In what follows we choose two examples, pyrazine that illustrates the creation of a coherent superposition during passage through a conical intersection[89], and the ethylene radical cation [90] that illustrates how the CH stretching vibrations can be controlled by a coherent superposition

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i) Pyrazine S_2->S_1 Conical Intersection [89] (An example of symmetry considerations)

The S_2-S_1 decay of Pyrazine, is a classic problem where the FC region lies in the catchment area of the conical intersection. We set the scene with figure 5 where we show a cartoon of the S_2 S_1 conical intersection of pyrazine that has the form shown in figure 2a. Because the dynamics at the FC lies within the conical intersection, subsequent passage through the conical intersection catchment region can generate a coherent superposition of the adiabatic states [91] before the surface crossing itself can be reached. In this case, one is in the realm of attochemistry and methods like surface hop have limited validity because they cannot describe the dynamics of such a coherent superposition[92]. However, in pyrazine the coherent superposition is partly hidden because the derivative coupling is non-totally symmetric. Thus, there are two equivalent paths to the conical intersection (that we will discuss in figure 6).

We have discussed this problem exhaustively recently [89]. Here we would like to focus our discussion of role of symmetry and to illustrate the ideas with a presentation of the nuclear density along the gradient difference co-ordinate which is antisymmetric in this problem.

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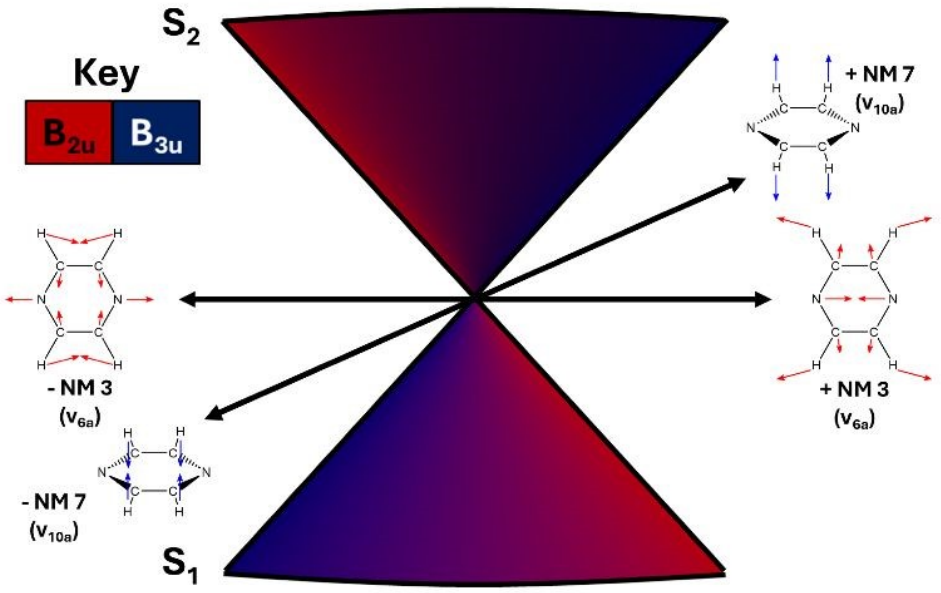


Figure 5 (Moore et al [89]) Two idealised potential surfaces near the conical intersection (CI) between the two adiabatic states S_1 and S_2: the adiabatic states. The colour on the surfaces gives the diabatic components: the diabatic $^1B_{2u}$ ($\pi\pi^*$) state is red and the diabatic $^1B_{3u}$ ($n\pi^*$) state is blue. These diabatic states are the adiabatic states at time zero and the strength of red vs blue gives the diabatic composition at any position (as in figure 2a). Note that to specify the state at any point, 2 indices are required: i) S_1 or S_2 and ii) the diabatic composition. The axes denote the branching space for the conical intersection. Here NM (normal mode) 7 (v_{10a}) is the derivative coupling vector and NM 3 (v_{6a}) is the (simplified) gradient difference vector. Adapted from reference 89 with permission from Elsevier, copyright 2026

In figure 6 we sketch a 2 normal mode model (mainly the gradient difference X_1 (in fig 2, corresponding to nm 3 and derivative coupling X_2 (nm7) in the QuEh dynamics computation (see the full paper [89] for the results with more normal modes and various degrees of accuracy). In figure 6 we give a schematic representation of QuEh trajectories started in opposite directions involving NM 3 and 7. They must be identical by symmetry.

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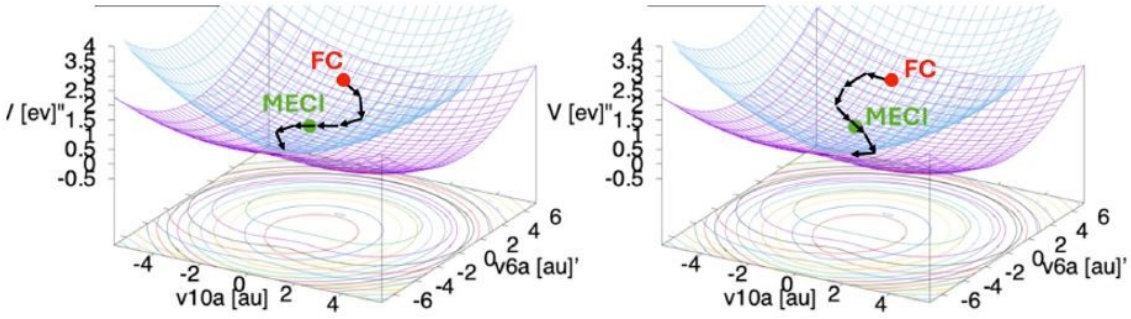


Fig 6 Schematic trajectories of GWPs sent along the + and – v_{10a} directions on a model potential surface, where the axes are the v_{10a} and v_{6a} modes. Adapted from reference 89 with permission from Elsevier, copyright 2026

In figure 7 we plot some numeric data from corresponding the QuEh simulations [89]. The simulations involve Ehrenfest propagation of the electronic states and the QUANTICS [75] direct dynamics for the nuclear motion. The Qu-Eh dynamics simulations were propagated for 50 fs in general, beginning from the pure S_2 state at the FC geometry which has been optimised using DFT-B3LYP/6-31G* level of theory.

A quantitative measure of the coherent superposition of two states is provided by the coherence. For a qualitative approximation for the upper bound of the coherence, M_{coh}, we use the product of the adiabatic state populations, which approximates the off-diagonal values of the electronic state density matrix. [93]

$$M_{coh} \leq 2P^{(s1)}P^{(s2)}. \quad (8)$$

Returning to the numerical results, notice that in figure 7a, the average displacement in nm 7 (the antisymmetric derivative coupling) is zero because the forward and reverse directions are the same. In figure 7b we see a sharp S_2/S_1 decay at 10 fs, and in figure 7c we see that the coherence (black line is approximately zero). However, if we look at the nuclear density for nm 7, figure 7d, it is bi-modal and symmetric (within numerical precision) about zero. Thus, symmetry just hides such detail on the average.

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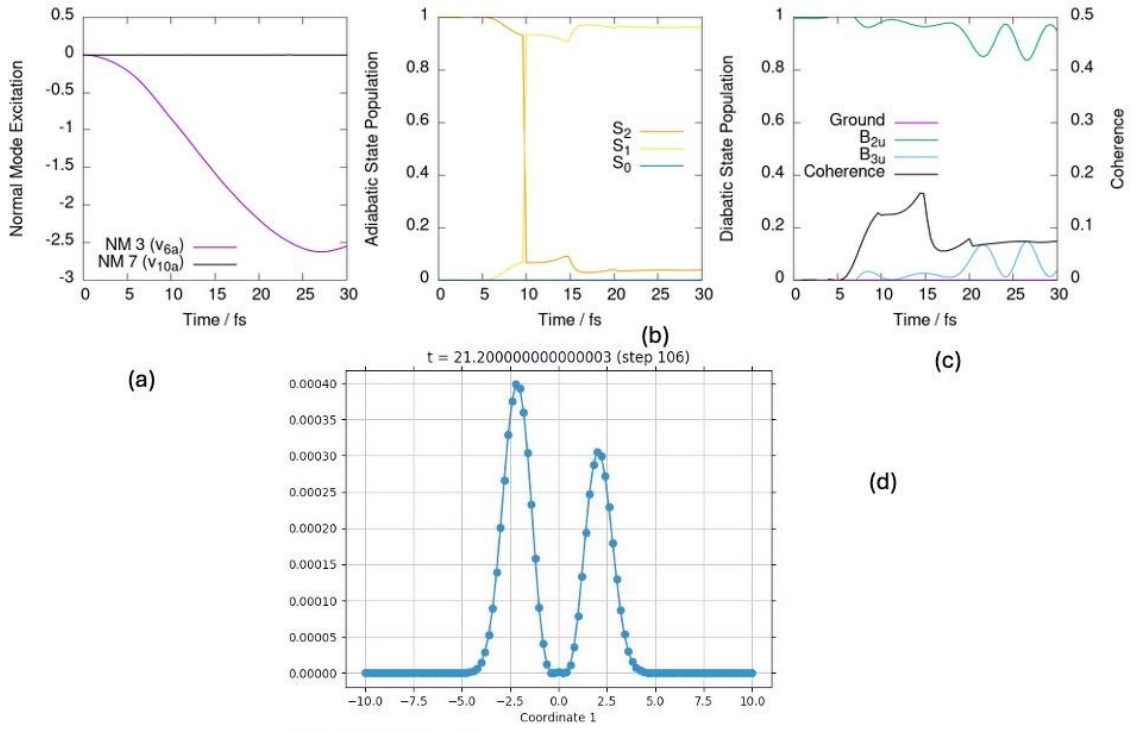


Figure 7 GGP-averaged results for Qu-Eh simulations of pyrazine beginning from the pure S_2 state at the FC geometry, using a 2-mode set with SA(3)-CASSCF. Part d shows the bi-modal nuclear density along nm7 at 21 fs. (Adapted in part from [89] (a) normal mode excitations, (b) adiabatic state populations, (c) diabatic state populations, and approximate coherence values over time, Adapted from reference 89 with permission from Elsevier, copyright 2026

In figure 8 we show the same simulation with a 3:97 S_1:S_2 state mixture of states which breaks the electronic state symmetry slightly. Note that in figure 8d, we still see a bimodal distribution; but because we have mixed the states the centre of the distribution is displaced from 0. Finally, in fig 8a b and c, we see the effect of the coherent superposition that is not cancelled by symmetry. In particular, in figure 8b we see an extended region (5-25 fs) with a superposition of S_2 and S_1. This is accompanied by B_{2u} B_{3u} electron dynamics where the populations oscillate with the opposite phase, and the coherence is approximately 1.

Thus, for the $^1B_{2u}$ ($\pi\pi^*$) $^1B_{3u}$ ($n\pi^*$) conical intersection one has a coherent superposition and electron dynamics. This effect is hidden because of symmetry. However, a small S_2/S_1 initial mixing reveals the coherence.

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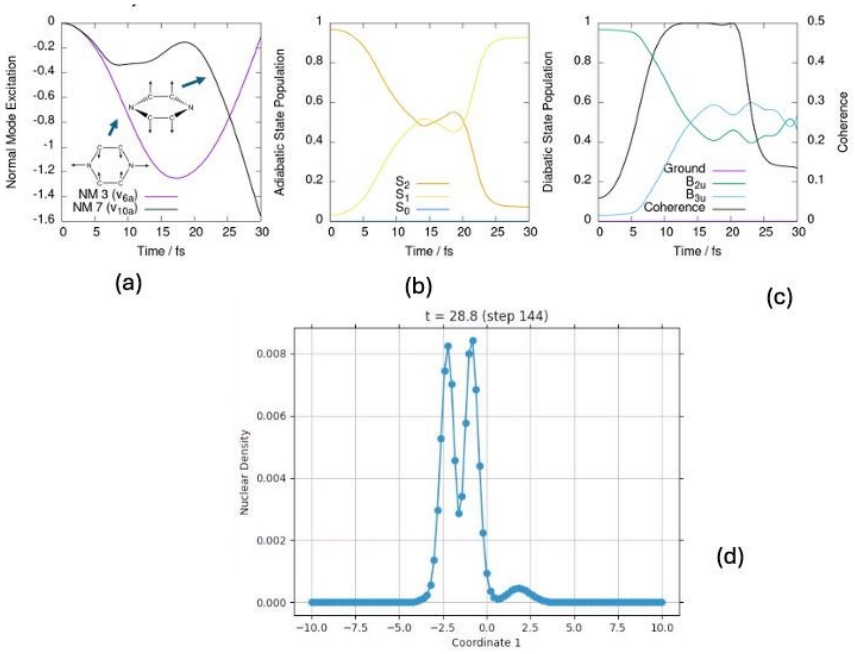


FIG. 8: GGP-averaged from Qu-Eh simulations of pyrazine beginning with a 3:97 S_1:S_2 state mixture at the FC geometry. Fig (a-c) as in fig 7 but with 3:97 S_1:S_2 state mixture. Part d the nuclear density as in fig 7. Adapted from reference 89 with permission from Elsevier, copyright 2026

ii) Role of the Derivative Coupling in Ethylene Cation dynamics [90]

Here [90] we would like to show how creating a coherent superposition of the cation states of Ethylene can be used to control the stretching vibrations in the Ethylene Cation. This is a very simple demonstration of the theory of attosecond control.

One of the properties of attosecond laser experiments is that the high energy photon can lead to photoionization from the whole of the laser energy bandwidth, leading to potential ionization/excitation of multiple electronic states in a coherent manner. The electronic wavepacket created from a coherent superposition of states exhibits properties that are different from those of the constituent states. These properties arise (as discussed previously) from the interstate gradients $<\psi_I|\partial/\partial Q_i^{\alpha}\,i\widehat{H}_e|\psi_{II}>$ where the I

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and II are two adiabatic states and $\partial / \partial Q_i^{\alpha_i}$ is the gradient operator for each normal mode i with symmetry α_i .

The ethylene cation has been extensively studied from both an experimental and theoretical approaches [94-99] [100-102] [103, 104] [4, 105, 106].

The five lowest cation states are D_0:X, π^+,B_{3u}, D_1: A, $\sigma(C-H)^+$, B_{3g}, D_2: B,$\sigma(C-C)^+$,A_g, D_3:C , $\sigma(C-H)^+$,B_{2u}, and D_4: D, π^{*+*}, B_{1u}. (in what follows we shall use X, A, B, etc. to label the states). Here, we shall discuss the nuclear dynamics that occurs if one were to create a coherent superposition of all 5 low-energy states of the ethylene cation $C_2H_4^+$. In the experiments of Lucchini et al. [105], the same 5 states were excited with a broad energy laser pulse but there is an open question as to whether a coherent electronic wavepacket has been created under these experimental conditions. Upon excitation to higher cationic states (D_1 and above), the molecules have been shown to subsequently fragment leading to a H- or H_2-loss with the specific fragment observed dependent on the photon energy used for ionization[94, 105]. Various decay channels are mediated by a conical intersection through either a pyramidalization or isomerization structure see for example Vacher et al. [106]. We now consider the case of coherent excitation.

In figure 9 we show the orbitals corresponding to the singly ionized cation states as direct products with symmetry restricted by the relationship $\alpha^I \otimes \alpha^{Q_i^{\alpha_i}} \otimes \alpha^{II} = A_{1g}$ where I and II correspond to two cationic states. Thus, for example in the last line of the figure 9 states B (Ag) and C(B_{2u}) corresponds to the direct product B_{2u} which is the symmetry of nm 12.

The dynamics was propagated for 20fs with the QuEh method implemented in QUANTICS [75] and interfaced with a development version of the Gaussian quantum chemistry software [107] where the electronic motion is represented using a complete active space configuration interaction (CAS-CI) formulation for the Ehrenfest method with a 6-31g* basis set. The active space consists of 11 electrons in 7 orbitals (the two carbon π orbitals, the four carbon-hydrogen σ bond orbitals and the carbon-carbon σ bond orbital). The dynamics is performed in reduced dimension in NM coordinates

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defined as mass and frequency scaled NM vector from a ground state S_0 Franck-Condon point frequency calculation at 6-31g*/B3LYP level of theory. The reduced dimension comprises 6 NMs out of the full 12 and includes the torsional motion (NM4), the symmetric carbon-carbon bond stretching (NM8), and all 4 NMs related to the carbon-hydrogen bond vibrations (NM9, 10, 11 and 12). The initial nuclear wavefunction is represented as a linear combination of 13 GWPs in a "full shell" sampling in momentum space using a local harmonic approximation along the defined NM coordinate. The "full shell" has 2n+1 GWPs with n corresponding to the number of nuclear degrees of freedom.

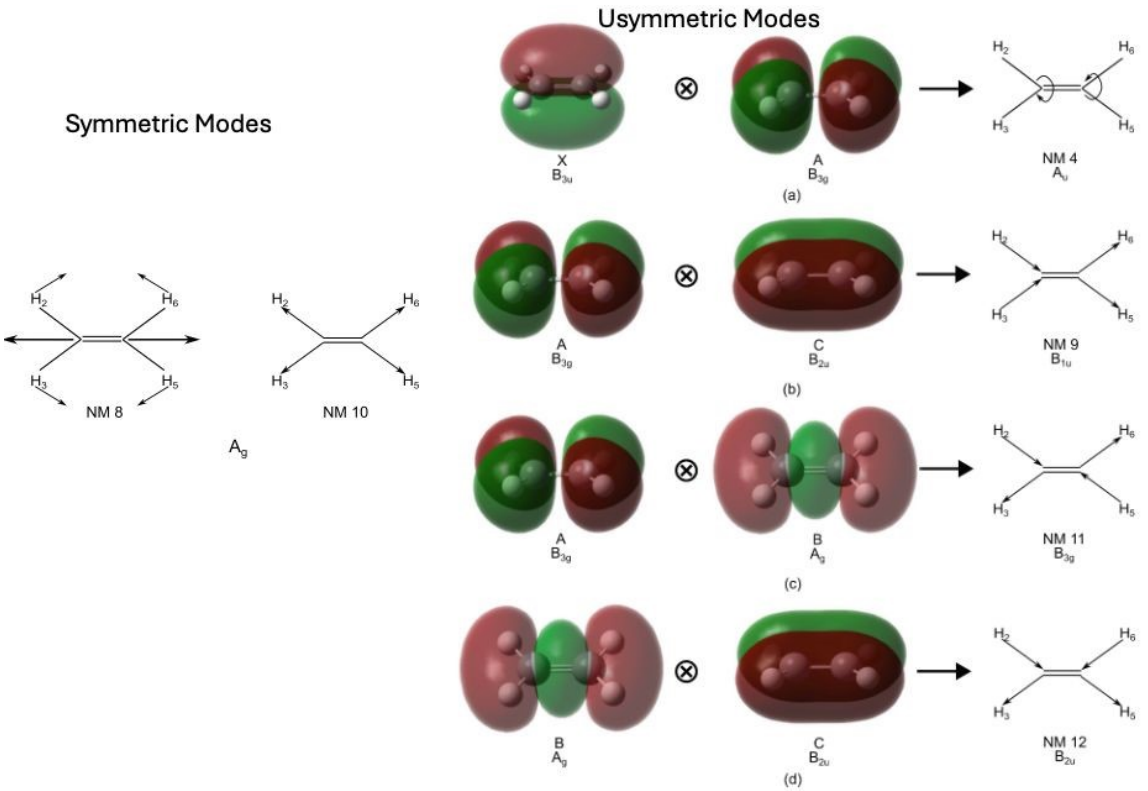


Figure 9 Symmetric (left side) and non-totally Symmetric (right side) Normal Modes of the Ethylene Cation together with the orbitals from which a hole is created in the cation. Satisfying direct product $\alpha^I \otimes \alpha^{Q_i^{a_i}} \otimes \alpha^{II} = A_{1g}$ yields the normal mode shown

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the extreme right column where I is the first electronic state and II is the second electronic state (see Tran et al [90]). Thus, a coherent superposition of states B and C has symmetry B_{2u} corresponding to NM 12. Adapted from reference 90 with permission from Wiley, copyright 2025

The results are collected in figure 10 for a superposition of A and C and for a superposition of all 5 states. Figure 10a illustrates the main ideas. A superposition of A and C produces a gradient from the interstate term along nm 9 (from figure 9). One can see that nm 9 is activated along with totally symmetric modes 8 and 10. Finally in figure 10b, a superposition of the 5 states one sees that all the non-totally symmetric modes predicted in Figure 9 are activated .

Thus, the principle of "designer" attochemistry is clear by choosing states with a known interstate coupling one can predict the qualitative nature of the dynamics. We have recently confirmed this in a study on glycine [108].

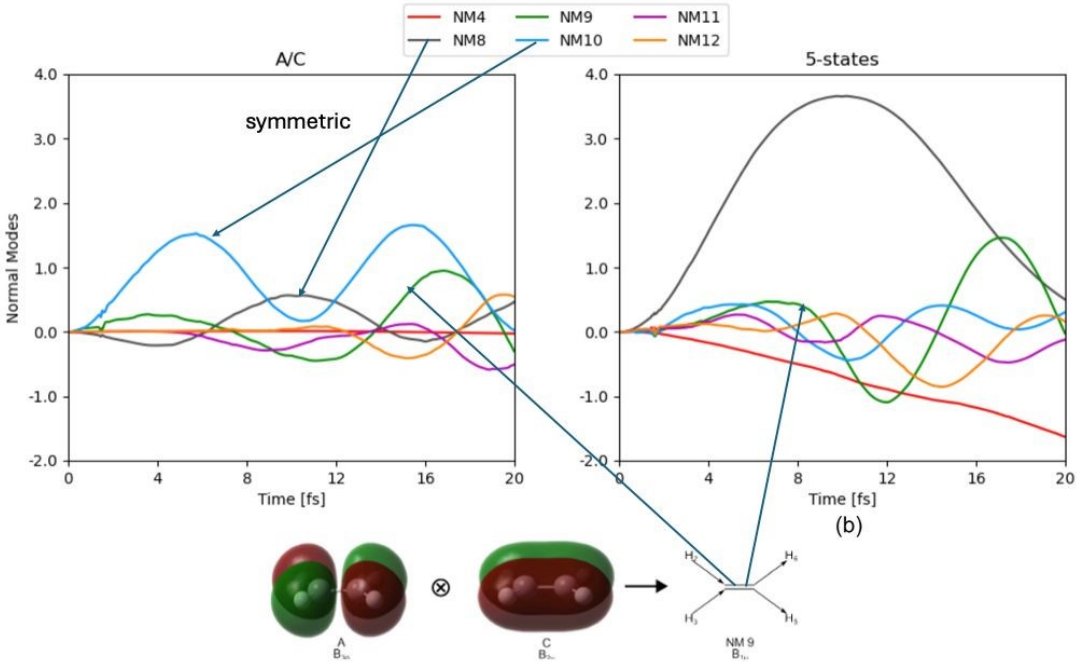


Figure 10 a) Expectation value of the normal modes for the nuclear dynamics of a) a 2 state superposition (A and C) and b) for 5 state superposition. The development of normal mode 9 as a consequence of the A/C superposition is highlighted in a. (see Tran et al [90]). Adapted from reference 90 with permission from Wiley, copyright 2025

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Conclusions

Firstly, I should apologize that I have omitted AI from the above discussion. We did develop a Valence Bond /Force field hybrid [109] some time ago. The Valence bond parameters were fitted against a sample of molecules. But one could never have generated a large enough sample to be accurate enough. But are there lessons for the future here? The parameterisation of MMVB was physically motivated. Perhaps new approaches to fitting / 'learning', need such physical insight from the outset.

So in the proceeding I have tried to outline the mechanistic concepts (e.g. conical intersection) associated with non-adiabatic chemistry. Perhaps the 2 examples I have given suggest the future. The pyrazine example suggests that one might use dynamics to study a complete photochemical reaction. However, the computations are dominated by the electronic structure part. So, one cannot use all the possible normal modes. The ethylene cation example shows that one can control the initial vibrations that get populated so designer attochemistry is possible.

It remains to mention other mechanistic ideas that have proven useful in the past and question their utility in the future. For example, it remains an open question on whether the local “shape” of the potential surface near a conical intersection an important mechanistic idea is. (We have developed algorithms to track the seam of the conical intersection [45, 64, 110]) in contrast to full dynamics run from the Franck Condon point. The answer will depend in part on whether the main flux through the conical intersection involves the derivative coupling, since if it does then one must cope with a superposition of adiabatic states. Further, as we have shown, the interstate coupling in a coherent superposition is a gradient that is parallel to the derivative coupling at a conical intersection. So, by creating a coherent superposition is one creating a conical intersection? However, having made this remark, it clear that one cannot run full non-adiabatic dynamics routinely. So, it is important to extract mechanistic ideas (such as the details of conical intersections near crossing points in the dynamics simulations).

What about future developments in theory and computation? At the beginning of this article, I noted the 20-year gap between the first quantum chemistry codes being available (early 1960’s) and applications to non-adiabatic chemistry. The main reason was both the idea of orbital optimization and the related issue of analytical gradients

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and hessians that are essential for dynamics and geometries. Whether these items will be easier or more difficult in quantum computing or within AI one cannot know yet.

Finally going back to the title, as a referee pointed out “Bearing in the mind the lecture / article title: it might not be that the audience is afraid to ask, rather *that they don't know what they don't know”*

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Data Availability

All the data in the MS is available in the cited literature and/or from the author himself

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