Generalized Electronic Diabatic Theory and Chemical Topology: Conformational Changes as a Transition in Electronic State

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Abstract

**Motivation.** We present a simple conceptual scheme whereby changes in molecular quantum state appear as Franck–Condon–like transitions driven by geometrical rearrangements of a background of positive charges. The model is based upon two basic ingredients that combine notions from quantum– and classical mechanics. First, we construct a complete set of diabatic electronic wave functions, each of which is associated with a labeled three–dimensional chemical graph. Secondly, we represent any electronic quantum state for the molecular system as a superposition of these functions such that the coefficients for the linear combination depend on the geometry of the set of positive charges. In contrast to the standard Born–Oppenheimer approach, only the quantum state depends on the location of these positive charges (and not the basis for the Hilbert space used to describe any transition).

**Results.** The ideas are illustrated using a simple trans→cis transition.

**Conclusions.** The procedure can be applied in general to expose the fundamental electronic processes that accompany real–space motion in more complicated molecular dynamics processes.

**Keywords.** Diabatic states; conformational transitions; Franck–Condon; vertical tunneling.

Abbreviations and notations

GEDA, generalized electronic diabatic approximation TS, transition state

1 INTRODUCTION

Professor Trinajstić has pioneered the use of chemical graph theory as a tool to rationalize qualitative trends in some molecular properties [1,2]. In this conceptual framework, any property that can be related to the topology of the chemical graph should remain invariant over a range of deformations that exclude bond breaking and bond formation. This chemically–intuitive notion stands in contrast, however, with the manner in which calculations are performed when using the

# Dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday.
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Born–Oppenheimer (BO) approximation. In the latter scheme, the electronic wave function changes as one move the nodes of the chemical graph (commonly identified with the nuclei); in fact, the approach can produce a description where the graph edges would appear to be formed or broken in a continuous manner. This antinomy is eliminated if molecular states are described using a basis set of electronic wave functions that are independent from the “external potential” generated by an arbitrary spatial distribution of positive charges [3]. Using this approach, chemical graphs can recover their powerful role as labels for distinct chemical species. In this paper, we develop further these ideas in an attempt to describe conformational changes between chemical species as a quantum process.

In molecular quantum mechanics, the standard procedure is to specify first the spatial coordinates of the nuclear species involved, and then to calculate energy levels and electronic wave functions. But an inverse point of view is also theoretically possible and conceptually attractive: one can prescribe an electronic structure (e.g., an all–electron density function) and then determine the “nuclear configuration” consistent with it. Note that such an approach would be more consistent with the picture of a molecule revealed by available experimental techniques: one does not see fixed nuclei in space but rather assigns a continuum of reasonable locations to a background of positive charges that would account for scattering by the electron density or nuclear spin interactions. In solid state physics, a similar approach has been employed to design atomic lattice configurations with desired electronic or optical properties [4]. Using this point of view, one of us has proposed the hypothesis that it is the stationary electronic wave function that determines the stationary geometry of the set of external positive charges [5]. These wave functions depend only on electron coordinates and can be labeled by the stationary geometry of the positive–charge background; yet, these electronic functions do not change if the positive charges are moved around. We refer to these as diabatic functions. It should be noted that a number of competing definitions for diabatic functions exist in the literature (see Refs. [6] and [7] for a discussion). For example, approximate diabatic states can be extracted from the diagonalization of the molecular electronic hamiltonian (in the standard BO approximation), and they have been used to study atom–atom and atom–molecule collision [8-11]. (See also details in Pacher et al. [12].) Despite the alternative approaches, a commonly desired property is that diabatic functions be associated with a single electronic configuration, instead of interpolating between different configurations as it is the usual case with adiabatic functions. The electronic functions used in this work are diabatic in this sense: they represent the states of an isolated molecular system. Each of the present diabatic functions will be associated with a single chemical species, regardless of the geometry of the background of positive charges. To avoid confusion, we shall use the term generalized electronic diabatic (GED) approach when referring to our method.

Within the present GED approach, a molecular system with an electronic ground state need only be characterized by two entities: (a) a quantum one, in the form of a wave function in Hilbert space.
that depends on electron coordinates \( \{ q_i \} \), \( \Psi(q_1, \ldots, q_n) \), and \((b)\) a classical one, in the form of a three–
dimensional array \( \xi \) for a background of \( m \) positive charges, \( \xi \in \mathbb{R}^3 \). The standard molecular model
appears as the limit case where the nuclei are taken as classical (not quantum) massive point
charges.

Conceptually, we proceed as follows. First, we define a fixed–point electronic hamiltonian,
\( H_e(q, \xi^0) \), with \( \xi^0 \) the stationary ground–state geometry for the positive–charge background. (Each
diabatic state will be characterized, in general, by a distinct attractor, denoted by \( \xi^k \) for the \( k \)–state.)
From this hamiltonian, we derive the complete set of diabatic functions. Chemical graphs and
topological properties arise from these latter functions. A key notion in the GED approach is that
any \( \xi^k \) attractor can be used to define a fixed–point hamiltonian \( H_e(q, \xi^k) \), from where the same
spectrum of diabatic eigenstates emerges. General electronic states can then be represented as linear
superpositions in the basis of diabatic states, and their quantum evolution followed as a function of
the positive–charge configuration \( \xi \). (We assume that the system is subject to external conditions
that permit changing the background, as would be done in atomic–force microscopy. We would
then calculate the effects of such changes on the electronic quantum states). The central notion in
the present approach is that the stationary configuration of the “external background” reflects a
quantum electronic property, not the other way round, as it would be in the BO scheme.

In developing these ideas, our goal is not to do away with the standard quantum–chemical
computations but rather to build an approach where chemists can think of reaction processes in
terms of quantum states and chemical topology. We believe that, by using chemical graphs related
to diabatic quantum states, it might be possible to get simple insights on chemical behavior, while
making quantum chemistry consistent with the tenets of time–dependent quantum mechanics. In
doing so, we would have taken chemical graph theory a step further along the road initiated by
Trinajstić and his co–workers [1].

### 2 THE DIABATIC ELECTRONIC BASIS SET

Within the present conceptual framework, we visualize a molecular system as it was done, for
example, in the original formulation of density functional theory: a system of \( n \) electrons
embedding a background of \( m \) “external” positive charges. Without a major loss of generality, we
focus on the case where the background neutralizes the total electronic charge. This system will be
modeled by a set of electronic quantum states, to be determined as described below. The set should
include the quantum states required to recover all the relevant physical processes that are accessible
to the system, including the formation of both neutral and ionized chemical species. The latter
would be handled by specific asymptotic states. In describing this molecular model, we adopt both a
classical and quantum viewpoint: the electrons provide the quantum system, whereas the
background of positive charges is treated classically. Even though we invoke a natural separability
between electrons and nuclei, the GED approach differs from the BO approximation in several ways. First, note that we treat classically the background of \( m \) positive charges, not the nuclear particles. The background is a set of point charges that one can, formally, manipulate externally; it has no information on nuclear masses. Secondly, this charge background affects only the potential energy of an isolated molecule and not the function describing its electronic state. There is also a difference in the way we handle the coordinate system. The original BO theory is based on an internal hamiltonian where nuclei and electrons appear as particles evolving with respect to a body–fixed moving coordinate frame, with origin at the center of mass of the nuclei. In the GED approach, in contrast, molecules are described entirely with complete sets of diabatic functions. The geometry of the positive–charge background is characterized using a single inertial frame throughout (i.e., the coordinate frame does not accelerate or rotate with the molecule).

The “external potential” is defined by two vectors, denoted by \( \mathbf{Z} = (Z_1, \ldots, Z_m) \) and \( \xi = (\xi_1, \ldots, \xi_m) \), corresponding to the value and physical location of the \( m \) positive charges. (Charges are measures in units of \( e \), the absolute value of the electron charge.) We assume that the position of these charges can be changed at will by some mechanism external to the system. This assumption is consistent with the ability for single–atom and single–molecule manipulation achieved in modern techniques. As a result, even without considering particles masses, the background of positive charges is an object intrinsically different from that of the electrons. It is thus reasonable to adopt a quantum/classical model to deal with the set of negative/positive charges. Note, however, that the fundamental reason for the separation between the two charge sets is different from that used in the common molecular models based on the BO approximation. We make no starting assumption on whether nuclei are heavier or “slower” than electrons, nor do we impose any particular relation between nuclear motion and the electronic state. The two models could nevertheless be related in particular cases by identifying \textit{a posteriori} a proper mapping between electronic states.

Let \( |\Psi\rangle \) denote an abstract quantum state for an \( n \)–electron system embedding the background of \( m \) positive, “classical” test point charges in configuration \( \xi \). This state is considered to be completely represented by a function \( \Psi(q_1, \ldots, q_n) \), defined in a \( 3n \)–dimensional configurational space with vectors \( \mathbf{q} = (q_1, \ldots, q_n) \); the spin component is treated separately. The complete hamiltonian for such an electronic system is:

\[
H_d(q, \xi) = K_e(q) + V_C(q, \xi),
\]

where \( K_e(q) \) is the electronic kinetic energy operator and \( V_C(q, \xi) \) is the complete Coulomb interaction, \textit{including the self–repulsion of the positive background}. (Note that this term is often left out in the standard BO electronic hamiltonian.) As mentioned before, we consider a cartesian inertial frame; no particular test charge is privileged as being an origin (see Ref. [13]). Nevertheless, the Coulomb operator is invariant under rotations or translations of the laboratory frame.
Let us assume that the system has an electronic ground state, represented by the function \( \Psi_0(q_1, \ldots, q_n) \). The hamiltonian (1) will then have an expectation value \( U_0 \):

\[
U_0(\xi) = U(\xi; [\Psi_0]) = \langle \Psi_0(q) | H_c(q, \xi) \Psi_0(q) \rangle_q.
\]

that is a function of \( \xi \) and a functional of \( \Psi_0 \). Note that \( U_0 \) will change if the positive charge background is rearranged as a consequence of the Coulomb operator \( V_C(q, \xi) \) being modified, not because the wave function \( \Psi_0(q) \) is modified. Indeed, since \( \Psi_0(q) \) does not depend on \( \xi \), the change in \( U_0 \) satisfies trivially the Hellmann–Feynman theorem:

\[
\frac{\partial U_0}{\partial \xi} = \langle \Psi_0 | \frac{\partial H_c}{\partial \xi} \Psi_0 \rangle_q \tag{3}
\]

Note that the reason for the validity of the Hellmann–Feynman theorem is not the same used in the standard BO approach, because the adiabatic functions are written as functions of the instantaneous nuclear configuration. For the GED theory, we require that the energy functional (2) be stationary with respect to any displacement with respect to a background configuration denoted by \( \xi^0 \):

\[
\left| \frac{\partial U_0}{\partial \xi} \right|_{\xi^0} = 0 \tag{4}
\]

Now, we define a fixed–point hamiltonian \( H_c(q, \xi^0) \) at the stationary configuration \( \xi^0 \). Since \( \Psi_0 \) is the ground state of the system and \( \xi^0 \) is obtained from \( \Psi_0 \) as in Eqs. (3)–(5), then the electronic operator \( H_c(q, \xi^0) \) is bounded from below. From the homogeneity properties of the Coulomb potential and a fundamental theorem for Schrödinger operators in Hilbert space [14,15], it follows also that the electronic operator \( H_c(q, \xi) \) is essentially self–adjoint, i.e., it has a complete set of (discrete or continuous) eigenfunctions. This property that is in fact independent on the detailed form of \( V_C(q, \xi) \) [14], e.g., the \( \xi \) configuration for the background charges. Given this, we choose construct the complete set of electronic states using the fixed–point operator \( H_c(q, \xi^0) \). By following this approach, the stationary configuration \( \xi^0 \) and the electronic state \( \Psi_0(q) \) are the central entities that define a chemical species and its associated molecular graph.

A complete set of normalized electronic diabatic functions \( \{ \Psi_k \} \) is obtained by applying the variational principle in wave function space to the functional \( U(\xi^0; [\Psi]) \), that is, we impose the condition \( \delta \{ \langle \Psi(q)| H_c(q, \xi^0) \Psi(q) \rangle_q \}, ||\Psi||^2 \} = 0 \). The result is an Euler–Lagrange equation:

\[
H_c(q, \xi^0) \Psi_k(q) = E_k(\xi^0) \Psi_k(q), \tag{5}
\]

where the eigenvalues are functionals of \( \Psi_k \): \( E_k(\xi^0) = U(\xi^0; [\Psi_k]) = U_0(\xi^0) \). The Eqs. (4)–(5) ensure that \( U_0(\xi^0) \) is the global minimum of \( U(\xi^0; [\Psi]) \) both in configurational space (9\( \times 10^2 \)) and in Hilbert space. Note that Eq. (5) is, in principle, iterative: \( \{ \Psi_k \} \) are eigenfunctions of \( H_c(q, \xi^0) \), a operator which is built by knowing the ground state \( \Psi_0 \). In general, these excited states \( \Psi_{k=0} \) may not have
the same stationary positive charge background geometry as the ground state $\xi^0$. We denote these stationary background configurations by $\xi^k$; their associated energies $E_k(\xi^k) = U(\xi^k; [\Psi_k])$ would be lower than $U(\xi^0; [\Psi_k])$. In the present formulation, these stationary points are still related to $\xi^0$: the configurations $\xi^k$ (with $k > 0$) are stationary points of the functionals $U(\xi_k; [\Psi_k])$, which in turn are built with the diabatic eigenfunctions $\Psi_k$ of $H_0(q, \xi^0)$. Finally, it should be noted that the electronic diabatic functions, and their stationary points $\xi^k$, are defined with a single fixed laboratory frame. Without any loss of generality, the complete set $\{\Psi_k\}$ can be taken as orthogonal [14].

We work under an assumption of “universality” for the electronic wave functions [5], i.e., that all electronic states $\Psi_k$ do not depend upon the configuration space $\xi$ and that only the function $\Psi_k$ determines the stationary configuration $\xi^k$. This assumption implies that any fixed–point Hamiltonian $H_0(q, \xi^s)$, with $\xi^s$ the stationary point of the functional $U(\xi; [\Psi_s]) = \langle \Psi_s(q) | H_0(q, \xi) \Psi_s(q) \rangle_q$, produces the same set of diabatic eigenfunctions $\{\Psi_k\}$, including the bound–state function $\Psi_s$ which determines the fixed point for the hamiltonian:

$$H_0(q, \xi^s) \Psi_s(q) = E_s(\xi^s) \Psi_s(q). \quad (6)$$

Note that the eigenfunctions are the same as in Eq. (5), but not the eigenvalue spectrum. As a result of the $\xi$–independence, it is understood that all $U(\xi; [\Psi_s])$ functionals (with $\Psi_s$ a bound state) can only produce one $\{\Psi_k\}$ set, that is, $U$ must be a single–minimum attractor (i.e., a confining function in terms of $\xi$). In the section below, we will use the $\xi$–independence to represent each $\Psi_k$ electronic state, and its corresponding stationary configuration $\xi^k$, with specific chemical graphs.

In closing this section, let us summarize some important differences between the present generalized diabatic functions and other approaches in the literature. First, the present $\{\Psi_s(q)\}$ functions are the only set of eigenfunctions obtained from any fixed–point hamiltonian, $H_0(q, \xi^s)$, defined at a stationary point $\xi^s$; the $\Psi_s(q)$–functions have no parametric dependence on $\xi$. Moreover, the $\{\Psi_s(q)\}$ functions are, by construction, the exact description for the states of an isolated molecules (once we accept the hypothesis for the quantum/classical separability of nuclei and electrons). These GED functions also differ from the type of (quasi–)diabatic functions used in the literature, which are commonly just limiting cases of adiabatic functions whenever adiabatic states are not close to each other [6,7]. The latter quasi–diabatic functions are known to provide poor (although simpler) descriptions for many ground–state properties. In contrast, the present $\{\Psi_s(q)\}$ functions have to provide, by design, the correct vibrational properties once nuclear masses are brought into the description. Basic properties of the Coulomb potential ensure also that a correct description of each attractor $\xi^s$ will emerge from any of a number of approximate methods for solving Schrödinger–like equations such as Eq. (6) [16].
3 CHEMICAL TOPOLOGY AND DIABATIC QUANTUM MECHANICS

We associate a colored graph (i.e., a graph with labeled vertices) to the stationary configuration $\xi^k$ corresponding to the wave function $\Psi_k$. For the sake of simplicity, we will define vertices and edges for the moment in the conventional way of chemical graph theory: vertices correspond to “atoms” and edges to “chemical bonds.” The present approach will thus lead to multigraphs, as more than one edge is possible between connected vertices (corresponding to double and triple bonds). Since we focus in this work on conformational transitions, we assume that all nodes are pathwise–connected on the graph. Moreover, we shall assume that the relevant transformations do not involve the formation of bonds or complete breaking of bonds. Yet, we allow for a reduction in the number of edges between two connected vertices, as long as they remain connected (e.g., transforming a double bond into a single bond is permitted). This condition will allow us to accommodate graphs corresponding to some relevant excited electronic states of a chemical species. In this sense, all $\xi^k$ configurations for our molecular system share the same connectivity pattern at the level of single edges; however, they can be represented by different graphs given two variations: (a) more than one edge occurs between connected vertices, and (b) a $\xi^k$–dependent coloring scheme is introduced for the vertices, as discussed later below.

Let us clarify the topological nature of the present chemical graphs. A chemical graph is, as always, a code for an equivalence class of configurations which transform homeomorphically amongst each other. Here, this corresponds to transformations in $\mathcal{R}^{3m}$ where the test charges preserve their connectivity and coloring. It is easy to see that a $\xi^k$–graph is invariant to any such change in $\mathcal{R}^{3m}$. By construction, the $\xi^k$–graph is determined by a $\xi$–independent electronic state $\Psi_k$ which produces a confining attractor represented by the single–minimum functional $U(\xi; [\Psi_k])$. Accordingly, any rearrangement of the background charges on the isolated system cannot change the diabatic quantum state and therefore leaves the molecule in the same $\xi^k$–graph. Changes in state require an external mediation (e.g., a radiation field); whenever this phenomenon is excluded, the graph topology will be preserved over $\mathcal{R}^{3m}$.

We can cast the above ideas in a more quantitative way. First, let us give the configuration space $\mathcal{R}^{3m}$ a topological structure with the standard (Euclidean) metric $d(\xi, \xi') = ||\xi - \xi'||$. Consider now the system at a state $\Psi_k$ and an arbitrary configuration $\xi$. Let us then deform the vertices of its local graph to a new configuration $\xi^b$; this procedure defines a continuous path in $\mathcal{R}^{3m}$ which we take, for simplicity, as the segment $\xi^{ab}(\lambda) = (1 - \lambda) \xi + \lambda (\xi^b - \xi^a)$, with $0 \leq \lambda \leq 1$. (In all these transformations, we use the same, fixed inertial frame.) The $\xi^{ab}(\lambda)$ path traces a curve $G_d(\xi^{ab}(\lambda))$ on the potential energy hypersurface $U(\lambda; [\Psi_k])$, which is an attractor with a single stationary point $\xi^k$ associated with a unique electronic function $\Psi_k$. We can now introduce a trivial $\Psi_k$–homotopy which makes two paths $\xi^{ab}(\lambda)$ and $\xi^{ab'}(\lambda)$ topologically equivalent by the simple reason that $G_d(\xi^{ab}(\lambda))$ and $G_d(\xi^{ab'}(\lambda))$ can be deformed continuously into each other while remaining on the everywhere–
smooth hypersurface \( U(\xi(\lambda); [\Psi_k]) \). Finally, these paths can be crumpled into the stationary point, \( \xi^{a-k}(1) \), thus making the entire \( \mathcal{M}^3 \) space \( \Psi_k \)-homotopically equivalent to the \( \xi^k \) configuration, and characterizing it by the single \( \Psi_k \)-graph.

We close this section by returning to the issue of graph–coloring, which is essential to characterize completely the diabatic functions \( \{\Psi_k\} \). Our proposal is that the symmetries of the system, understood broadly, can be used for vertex labeling.

Consider the example of the simple \textit{trans}–\textit{cis} transformation in 1,2–difluoroethene, HFC=CHF. Both conformers have the same bond connectivity, therefore the corresponding graphs can only be distinguished by using node coloring. Intuitively, we could profit from the fact that the \textit{trans}–conformer (with \( C_{2h} \) symmetry at its stationary configuration \( \xi^t \)) has a distinct symmetry operation, and thus use the inversion \( i \) to label the \textit{trans}–conformer and the \( C_2 \)–rotation to label the \textit{cis}–conformer (with \( C_{2v} \) symmetry at configuration \( \xi^c \)). If we retain the essential part of the graph \( F-C=C-F \), we can then label the vertices with “±” signs depending on how the atoms transform under the symmetry operations. In this approach, colored graph for the \textit{trans}–conformer would become \( F(+)C(-)C(+)=F(-) \) to indicate how the atoms transform under the inversion \( (i.e., i F(+) = F(-), \text{ etc.}) \), whereas in \textit{cis}–conformer would be \( F(+)=C(+)=C(+)=F(+) \), to indicate how the atoms transform under the rotation \( (i.e., C_2 F(+) = F(+), \text{ etc.}) \). Proceeding this way, the diabatic electronic wave functions for the ground states of the \textit{cis}– and the \textit{trans}–conformers (\( \Psi_c \) and \( \Psi_t \), respectively) are characterized by different graphs. These graphs remain invariant even if we force the nuclear charges in the electronic state \( \Psi_t \) to adopt the configuration \( \xi^c \), and vice versa. (In the latter case, the resulting energy \( U(\xi^c; [\Psi_t]) \) will be much higher than both \( U(\xi^c; [\Psi_c]) \) and \( U(\xi^t; [\Psi_c]) \).) In other words, a continuous transformation between the graphs \( F-C=C-F \) and \( F(+)C(+)=C(+)=F(+) \) is topologically forbidden at both diabatic and adiabatic levels.

The above approach, although conceptually simple, cannot easily be extended to other molecular states and symmetries. For a more general alternative, we must pay closer attention to the actual rearrangement leading from the \textit{trans}– to the \textit{cis}–conformer. As discussed before, transformations in \( \mathcal{M}^3 \) must all be described in the same inertial frame used to derive the diabatic wave functions. This implies that the \( z \)–axis for the \textit{trans}–conformer (conventionally identified with the highest–symmetry rotational \( C_2 \) axis) must remain as the \( z \)–axis for the \textit{cis}–conformer (also coincident with a \( C_2 \) axis). Accordingly, the motion connecting \( \xi^t \) and \( \xi^c \) must be a \textit{disrotatory displacement}, as indicated in Figure 1. This displacement has an important implication on the orbital basis set for diabatic states. In Figure 1, the \( \pi \)–system for the \textit{trans}–conformer is sustained by the \( p_x \)–orbitals of a minimal basis set. In contrast, the \( \pi \)–system for the \textit{cis}–conformer becomes sustained by either the \( p_x \)– or \( p_y \)– or a combination of the two. (Only one case is displayed in Figure 1.) In this description, a deformation of \( \xi^t \) into \( \xi^c \) would be seen as follows. If we start at \( \xi^t \), the \( \Psi_t \) state provides the lowest energy \( U(\xi) \), one where the \( \pi_x \)–orbitals are doubly occupied. These orbitals have lower
energy than the $\pi_x^-$ or $\pi_y^-$ in Eq. (6) computed with either $H_d(q, \xi^t)$ or $H_d(q, \xi^c)$. Yet, as we move towards $\xi^c$, one would eventually obtain a lower $U(\xi)$ value by using the doubly-occupied $\pi_x^-$ or $\pi_y^-$ in Eq. (6) with $H_d(q, \xi^c)$, i.e., by using the $\Psi_c$ wave function for configurations near $\xi^c$. This change in electronic state, however, cannot be triggered by only driving the positive charges; the quantum process must rather be mediated by an external field.

![Diagram](image1.png)

Figure 1. Representation of a trans–to–cis conformational change when using an invariant inertial frame. The inertial frame maintains the $z$–axis aligned with the $C_2$ rotational axes of both the trans and cis conformers. As a result, the motion in real space leading from trans to cis is disrotatory (indicated by the curved arrows on the top diagram). The invariance in $C_2$ causes that different $p$– orbitals are used in building the $\pi$–bonds in the conformers: $p_z$ are used for the trans, and $p_x$ (or equivalently $p_y$) for the cis.
By applying these ideas, we could label distinctly the two conformers with the angular momentum quantum number $m$ for the atomic orbitals $p_m$ used in the double bonds. Thus, the trans–graph becomes $F$–C(0)=C(0)$–F, because of using $p_x = p_0$, and the cis–graph becomes $F$–C($\pm 1$)=C($\pm 1$)$–F$ because of using $p_{\pm 1} \propto p_x \pm i p_y$. Other molecules could be treated similarly by considering the required angular functions.

4 DIABATIC BASIS AND QUANTUM TRANSFORMATIONS

The central tenet of the diabatic theory represented by Eq. (5) (or, in general, Eq. (6)) lays in the invariance of the electronic basis set $\{\Psi_k\}$ with respect to the geometry of the positive–charge background. By using the $\Psi_k$–graphs, this invariance translates into a topological impossibility for transforming one graph into another. Two things do change though when moving the charges in real space $\eta^{3m}$. First, one modifies the potential energy $U(\xi_k|\Psi_k)$ for a diabatic $\Psi_k$ state. Secondly, since an actual quantum state $|\Phi>$ is a linear superposition of the $\{\Psi_k\}$–functions, the former will evolve in Hilbert space if its amplitudes in the basis states change with $\xi$.

Let us consider the simple two–state trans–cis transition introduced previously. An instantaneous quantum state for this system can be represented by a function $\Phi(q)$:

$$\Phi(q) = C_t \Psi_t(q) + C_c \Psi_c(q),$$

in terms of the trans and cis diabatic functions $\Psi_t(q)$ and $\Psi_c(q)$, respectively. Given that the electronic hamiltonian $H_e(q, \xi)$ is diagonal in the $\{\Psi_k\}$–functions, the time evolution of the quantum state $|\Phi>$ (and any change in molecular energy) depends on coupling the molecular system to an external energy source or sink [17].

We can now introduce the potential for the interaction between an electronic system and the standard energy bath, i.e., a radiation field: $V_{e-rad} = \mathbf{A} \cdot \mathbf{p}_e$, where $\mathbf{A}$ is the electromagnetic field vector–operator and $\mathbf{p}_e$ is the total electronic linear momentum operator. Since the positive–charge background is taken to be externally–controlled, we can omit its dynamics for the moment. Accordingly, the total hamiltonian becomes: $H = H_e + V_{e-rad} + H_{rad}$, where $H_{rad}$ is the radiation–only operator. In the standard semi–classical approach for $H_{rad}$, only the first two terms are required when searching for variational solutions for the general quantum–state functions $\Phi$:

$$(H_e(q, \xi) + V_{e-rad}) \Phi(q) = \varepsilon(\xi) \Phi(q).$$

It is important to note the difference between Eq. (8) for the $\Phi$ functions and Eq. (6) for the $\{\Psi_k\}$–functions. The latter (and their associated energies $\{E_k(\xi)\}$) are properties of the isolated molecule and thus independent of $\xi$. In contrast, the $\varepsilon(\xi)$ energies for instantaneous quantum state $\Phi(q)$ reflect how the diabatic states $\{\Psi_k\}$ are coupled at the configuration $\xi$ in the presence of the radiation field; the energies $\varepsilon(\xi)$ are not intrinsic to the molecule but instead describe the molecule in an environment.
Let us now study the transition between \emph{trans}– and \emph{cis}–conformers (Eq. (7)) by using first–order perturbation theory with $V_{e-rad}$ for the transition moments $T$:

$$T_{t\rightarrow c} = \langle \Psi_t | \mathbf{p}_c | \Psi_c \rangle_q .$$

(9)

As in standard electronic spectroscopy, a transition $i\rightarrow j$ is allowed if the transition moment $T_{i\rightarrow j}$ is not zero. We can analyze the element $T_{t\rightarrow c}$ by remembering that all functions and operators in Eq. (9) are written in the same inertial frame. If $\hat{P}$ denotes the parity operator (i.e., $\hat{P} \mathbf{x} = -\mathbf{x}$, etc.), then $\hat{P} \mathbf{p}_c = -\mathbf{p}_c$. Moreover, since both the \emph{cis} and \emph{trans} conformers have closed–shell electronic structure, we have $\hat{P} \Psi_s(q) = \Psi_s(q)$, with $s = t,c$. As a result, we obtain from Eq. (9): $\hat{P} T_{t\rightarrow c} = -T_{t\rightarrow c}$. Yet, $T_{t\rightarrow c}$ and $\hat{P} T_{t\rightarrow c}$ differ only on the axes’ labeling, an artifact that cannot change the physical transition. Accordingly, we conclude that $\hat{P} T_{t\rightarrow c} = -T_{t\rightarrow c} = T_{t\rightarrow c}$, that is $T_{t\rightarrow c} = 0$. In other words, the \emph{trans}–\emph{cis} transition is forbidden, up to first–order perturbation theory.

This result implies that a \emph{transition state} (TS) is required for a general reaction between closed–shell quantum states. We must therefore extend the minimal model needed for general quantum states $\Phi(q)$ to \emph{three} basis functions, by including the TS:

$$\Phi(q; \xi) = C_t(\xi) \Psi_t(q) + C_c(\xi) \Psi_c(q) + C_{TS}(\xi) \Psi_{TS}(q) ,$$

(10)

where we explicitly indicate that the variational solution for fixed $\xi$ produces linear coefficients $\{C_s\}$ that depend on the specific positive–charge configuration. For an allowed transition (i.e., nonzero $T_{TS}$ and $T_{TS,c}$), the electronic function $\Psi_{TS}$ must have opposite parity, $\hat{P} \Psi_{TS}(q) = -\Psi_{TS}(q)$, at least along one axis. Note that $\Psi_{TS}$ will not be among the solutions of Eq. (6) if the latter are prescribed to be closed shell. Obtaining this state, and its \emph{stationary} configuration $\xi^{TS}$, will require an open–shell computation.

The diagonalization of the $\xi$–dependent hamiltonian (8) yields the quantum amplitudes $\{C_s; s = t,c,TS\}$ for each configuration $\xi$. The present model makes it now possible to change quantum states in the electronic Hilbert space by manipulating the background of positive charges. In the next section, we discuss a concrete example by examining the minimal electronic wave functions for ethylene.

5 ETHYLENE BASIS FUNCTIONS

The \emph{trans}–\emph{cis} transition in ethylene (CH$_2$=CH$_2$) is the simplest example of the process depicted in Figure 1. The atomic \emph{p}–orbitals required to describe the molecular $\pi$–orbitals for the \emph{trans}– and \emph{cis}–conformers are also indicated in Figure 1. Let us seek now the basis functions required to describe the transition state minimally. If $(p_{x1}, p_{y1}, p_{z1})$ denote standard 2\emph{p}–orbitals on a carbon atom ($i = 1,2$), then we introduce two new pairs of orbitals for each of the carbon atoms in Figure 1, denoted by $p'$ and $p''$:

$$p'_1 = (p_{x1} + p_{z1})/\sqrt{2} , \quad p''_1 = (-p_{x1} + p_{z1})/\sqrt{2} ,$$

(11a)
\[ p'_2 = \frac{(-p_{x2} + p_{z2})}{\sqrt{2}}, \quad p''_2 = \frac{(p_{x2} + p_{z2})}{\sqrt{2}}. \]  

The \{p', p''\} orbitals are adapted to the disrotatory motions in Figure 1, where rotations by \(+\pi/4\) and \(-\pi/4\) affect the centers “1” and “2”, respectively. These orbitals are independent from the atoms attached to the carbons. In particular, the functions \(p''_1\) and \(p''_2\) play the role of new “\(\pi\)–orbitals” because they represent normal vectors to the local planes defined by three sequentially bonded atoms. Since these orbitals are degenerate, we employ the symmetrized combinations \(\phi_\pm = \frac{1}{\sqrt{2}} (p''_1 \pm p''_2)\). Consequently, the triplet wave function for the diradical becomes (up to a normalization constant):

\[
\Psi(S=1, M_S=+1) = \{\phi_+(1)\phi_-(2) - \phi_-(1)\phi_+(2)\} \alpha(1)\alpha(2), \quad (12a)
\]

\[
\Psi(S=1, M_S=-1) = \{\phi_-(1)\phi_-(2) - \phi_+(1)\phi_+(2)\} \beta(1)\beta(2), \quad (12b)
\]

\[
\Psi(S=1, M_S=0) = \{\phi_+(1)\phi_-(2) - \phi_-(1)\phi_+(2)\} \{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}, \quad (12c)
\]

and the singlet diradical is characterized as:

\[
\Psi_{TS}(S=0, M_S=0) = \{\phi_+(1)\phi_-(2) + \phi_-(1)\phi_+(2)\} \{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}. \quad (13)
\]

These two functions would be obtained in open–shell Hartree–Fock calculations, and they are associated with \(\xi\)–configurations in \(\mathcal{R}^{3m}\) space with minimum \(U(\xi)\) value. In particular, Eq. (13) represents the transition state with symmetry \(C_2\). It is worth insisting on this distinct point: in the present analysis, the relevant “TS” entity is not a saddle point but a minimum. The “TS” emerges therefore as a proper “state” of the system rather than a “transition structure.”

In addition, there is also a closed–shell electronic wave function:

\[
\Psi'(S=0, M_S=0) = \{\phi_+(1)\phi_+(2) + \phi_-(1)\phi_-(2)\} \{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \quad (14)
\]

corresponding to a polarized state. The \(\Psi'\) function would be obtained with a closed–shell Hartree–Fock calculation, and it is associated with a \(\xi\)–configurations that is a type–1 saddle point in \(\mathcal{R}^{3m}\). It is clear that Eq. (13) and (14) represent functions with opposite parity (respectively, \(-1\) and \(+1\)).

A general multi–configurational solution to Eq. (6) will provide all the states required for the analysis of the \textit{trans}–\textit{cis} transition, \textit{i.e.}, the standard closed–shell states and the diradical states. In other types of reactions whose quantum dynamics involves asymptotic fragments, the latter will have to be incorporated into the analysis by correlating them properly to diabatic states derived from the ground state attractor.

### 6 CONFORMATIONAL TRANSITION AS A FRANK–CONDON–LIKE PROCESS

We apply now the previous ideas to the simplified \textit{trans}–\textit{cis} transition depicted in Figure 2. The left–hand–side curve represents the potential energy for the \textit{trans}–conformer, \(U(\theta; [\Psi_t])\), \textit{i.e.}, the ground state solution of Eq. (5). The right–hand–side curve, \(U(\theta; [\Psi_c])\), is a different attractor associated with the \textit{cis}–conformer. These two diabatic curves (associated with closed–shell species)
cross at an energy that is below that of the stationary configuration for the singlet diradical transition state, \( U(\theta; [\Psi_{TS}]) \) (thin line). These three curves are characterized by different \( \Psi_k \)-graphs; the corresponding \( \Psi_k \)-states are basis functions of the electronic Hilbert space and also invariant to changes in geometry of the positive–charge background. The \( \theta \) coordinate relates the conformer geometries (cf. the disrotatory displacement in Figure 1).

\[
\begin{align*}
U(\theta; [\Psi_{TS}]) \\
U(\theta; [\Psi_t]) \\
U(\theta; [\Psi_c])
\end{align*}
\]

\( \theta \)

**Figure 2.** Simple model for the diabatic potential energy curves \( U(\theta; [\Psi_t]) \), \( U(\theta; [\Psi_c]) \), and \( U(\theta; [\Psi_{TS}]) \) corresponding to the trans–, cis–, and transition–states of ethylene, respectively. The \( \theta \)-coordinate corresponds to the disrotatory displacement explained in Figure 1. In the diabatic scheme, each potential energy function is a single–minimum attractor. The curves \( U(\theta; [\Psi_t]) \) and \( U(\theta; [\Psi_c]) \) cross at \( \theta^* = \pi/4 \), measured from the stationary point \( \theta^* \), or \( \theta^* = -\pi/4 \) measured from \( \theta^* \). The points denoted by \( a \), \( b \) and \( c \) represent significantly different energy gaps, such as those reported in Table 1. (See text for further discussion.)

The \( \theta \) coordinate can be used to control the “advance” of the reaction in real space. For the present analysis, it is more convenient to monitor the coefficients \( \{C_s\} \) (Eq. (10)) in terms of the three energy differences: \( \Delta U_{12} = U(\theta; [\Psi_t]) - U(\theta; [\Psi_c]) \), \( \Delta U_{13} = U(\theta; [\Psi_{TS}]) - U(\theta; [\Psi_c]) \), and \( \Delta U_{23} = U(\theta; [\Psi_{TS}]) - U(\theta; [\Psi_t]) \), that are implicit functions of \( \theta \). For example, large positive values for both \( \Delta U_{12} \) and \( \Delta U_{13} \) correspond to \( \theta \) values characteristic of the trans–conformer; similarly, the cis–conformer will appear at \( \theta \) values where both \( \Delta U_{23} \) and \( |\Delta U_{12}| \) are large (with \( \Delta U_{12} \) being negative).

We can understand the role of \( |\Psi_{TS}> \) by exploring how the general function (10) changes as one varies the relative potential energy values and the coupling to the transition state. To this end, we compute the eigenvalues and eigenfunctions of the total hamiltonian (8) in a simple three–level
system $\Psi_1$, $\Psi_2$, and $\Psi_3$ mimicking the $trans$, $cis$, and TS species. First, we note that all diagonal elements of $V_{e-rad}$ are zero, therefore $H_{ij} = (H_{e})_{ii} = U(\theta; [\Psi_i]) = U_i$. The nondiagonal elements can be taken as variable parameters. Furthermore, note that $\Psi_1$ and $\Psi_2$ are orthogonal and have zero transition moment (cf. Eq. (9)). From this and the fact that the Coulombic operator $V_C(q, \xi)$ (Eq. (1)) is symmetric under an inversion of electronic coordinates for all $\xi$, we deduce $H_{12} = 0$. Similarly, we conclude that $(H_2)_{13} = (H_e)_{23} = 0$, thus $H_{13} = V_{13}$ and $H_{23} = V_{23}$, because the $1 \to 3$ and $2 \to 3$ transitions are allowed. For simplicity, we choose here $V_{13} = V_{23}$. Finally, upon factorizing $U_1$, we get the following hamiltonian matrix:

$$
[H_{e} + V_{e-rad}]_{ij} = \begin{pmatrix}
0 & 0 & V_{13} \\
0 & \Delta U_{12} & V_{13} \\
V_{13} & V_{13} & \Delta U_{13}
\end{pmatrix}.
$$

Table 1 shows the coefficients $\{C_{ij}\}$ for the eigenfunction corresponding to the lowest eigenvalue $E$ of Eq. (15) (energies are in arbitrary units). The values chosen for $\Delta U_{12}$ and $\Delta U_{13}$ represent situations resembling the points a, b, and c in Figure 2. Thus, $\Delta U_{12} = 5$ can be taken as point “a” near the $trans$–conformer, while $\Delta U_{12} = 0$ corresponds to point “c” where the diabatic curves cross. In most cases, $U_3$ is kept constant by setting $\Delta U_{13} = \Delta U_{12} = 3$ as $U_1$ and $U_2$ vary. Only the last entry in Table 1 shows a transition state that is closer in energy to the lower–energy conformers. For a pair ($\Delta U_{12}$, $\Delta U_{13}$), we tested various $V_{13}$ values spanning the range from weak to strong inter–state couplings. These values reflect different radiation fields (e.g., lasers) that can be imposed on the molecular system.

Using Table 1 and Figure 2, we can now discuss the mechanism underlying the conformational change $1 \to 2$. First of all, note that the amplitudes of the three states remain constant if we switch off the radiation field ($V_{13} = V_{23} = 0$). In other words, in absence of $V_{e-rad}$, an initial state $|\Psi_i(q)\rangle$ will persist as such regardless of a displacement in the positive–charge background (represented here by $\theta$). Any change in state is quantum–mechanically determined by the matrix elements of $V_{e-rad}$ that couple “reactant” and “product” states to the transition state. Moreover, note that $V_{13}$ and $V_{23}$ are electronic transition integrals that are independent of $\xi$, since both $\Psi_i(q)$ and $V_{e-rad}$ do not depend on the geometry of the positive–charge background. In this sense, the $1 \to 2$ transitions can be regarded as Franck–Condon–like processes.

Let us now focus on the role of the positive–charge background as the driver for the $trans \to cis$ transition. In Table 1, the initial state $\Phi(q; \xi)$ corresponds to large values of $\Delta U_{12}$ and $\Delta U_{13}$; the emerging amplitudes ($|C_1| = 1$ and $|C_2| \approx |C_3| \approx 0$) indicate a state that is essentially $trans$–conformer (point “a” in Figure 2). This situation remains essentially unchanged for all $V_{13}$ coupling strengths and $\Delta U_{12} > 0.05$ (where $|C_2| < 0.07$). The point “b” in Figure 2 will fall in this category. However, as $0 \to 0^*$ (the point where the diabatic potential energy curves cross), the amplitude in $\Psi_2$ increases rapidly up to a maximum value. (In this model, this corresponds to $|C_1| = |C_2|$.) The region where
both cis/trans amplitudes are important appears as a narrow “bottleneck” about \( \theta^* \); its actual size depends on \( V_{13} \) and \( V_{23} \), \textit{i.e.}, the strength of the couplings to the TS. (These couplings depend in turn on the external radiation field.) Note that the amplitude in \( \Psi_3 \) also maximizes at \( \theta = \theta^* \). Yet, Table 1 shows that only a small amplitude \(|C_3|\) in the transition state is necessary for the system to evolve from the trans– to the cis–conformer. (A similar reasoning will apply to the reverse cis\( \rightarrow \) trans transformation.)

Table 1. Change in the wave function for the quantum state of a three–level model of the trans\( \rightarrow \) cis transition. The trans–, cis–, and transition state (TS) species are denoted by the subindices 1, 2, and 3, respectively. In this model, the TS–energy is constant, and thus both \( \Delta U_{12} \) and \( \Delta U_{13} \) decrease along the control coordinate \( \theta \) (cf. Figure 2). The coupling to the transition state is taken as a variable parameter (\( V_{13} = V_{23} \)); these values are representative of weak and strong interactions (0.001 and 0.1, respectively), and depend on the external field. The last columns give the lowest eigenvalue in Eq. (8) and its eigenfunction’s coefficients in Eq. (10). The amplitude in the cis–conformer increases as \( \Delta U_{12} \) decreases (see text).

| \( \Delta U_{12} \) | \( \Delta U_{13} \) | \( V_{13} = V_{23} \) | \( -e \) (lowest) | \( |C_1| \) | \( |C_2| \) | \( |C_3| \) |
|-----------------|-----------------|------------------|----------------|-----------------|-----------------|----------------|
| 5.0000          | 8.0000          | 0.001            | \( 1.25 \times 10^{-7} \) | 1               | \( 2.50 \times 10^{-8} \) | \( 1.25 \times 10^{-4} \) |
|                 |                 | 0.010            | \( 1.25 \times 10^{-5} \) | 1               | \( 2.50 \times 10^{-6} \) | \( 1.25 \times 10^{-3} \) |
|                 |                 | 0.100            | \( 1.25 \times 10^{-3} \) | 1               | \( 2.50 \times 10^{-4} \) | 0.013           |
| 0.1000          | 3.1000          | 0.001            | \( 3.2 \times 10^{-7} \) | 1               | \( 3.23 \times 10^{-6} \) | \( 3.23 \times 10^{-4} \) |
|                 |                 | 0.010            | \( 3.2 \times 10^{-5} \) | 1               | \( 3.23 \times 10^{-4} \) | \( 3.23 \times 10^{-3} \) |
|                 |                 | 0.100            | \( 2.5 \times 10^{-3} \) | 0.999           | 0.032           | 0.033           |
| 0.0500          | 3.0500          | 0.001            | \( 3.3 \times 10^{-7} \) | 1               | \( 6.56 \times 10^{-6} \) | \( 3.28 \times 10^{-4} \) |
|                 |                 | 0.010            | \( 3.3 \times 10^{-5} \) | 1               | \( 6.56 \times 10^{-4} \) | \( 3.28 \times 10^{-3} \) |
|                 |                 | 0.100            | \( 3.5 \times 10^{-3} \) | 0.997           | 0.065           | 0.035           |
| 0.0050          | 3.0050          | 0.001            | \( 3.3 \times 10^{-7} \) | 1               | \( 6.6 \times 10^{-4} \) | \( 3.34 \times 10^{-4} \) |
|                 |                 | 0.010            | \( 3.4 \times 10^{-5} \) | 1               | \( 6.56 \times 10^{-3} \) | \( 3.35 \times 10^{-3} \) |
|                 |                 | 0.100            | \( 4.9 \times 10^{-3} \) | 0.894           | 0.446           | 0.045           |
| 0.0005          | 3.0005          | 0.001            | \( 3.3 \times 10^{-7} \) | 1               | \( 6.66 \times 10^{-4} \) | \( 3.34 \times 10^{-4} \) |
|                 |                 | 0.010            | \( 3.5 \times 10^{-5} \) | 0.998           | 0.066           | 3.55 \times 10^{-3} |
|                 |                 | 0.100            | \( 4.9 \times 10^{-3} \) | 0.732           | 0.679           | 0.047           |
| 0.0000          | 3.0000          | 0.001            | \( 6.7 \times 10^{-7} \) | 0.707           | 0.707           | 4.71 \times 10^{-4} |
|                 |                 | 0.010            | \( 6.7 \times 10^{-5} \) | 0.707           | 0.707           | 4.71 \times 10^{-3} |
|                 |                 | 0.100            | \( 4.9 \times 10^{-3} \) | 0.706           | 0.706           | 0.047           |
| 0.0001          | 1.0000          | 0.010            | \( 1.6 \times 10^{-4} \) | 0.851           | 0.526           | 0.04             |
|                 |                 | 0.100            | \( -0.2 \)          | 0.702           | 0.699           | 0.137           |

We can now define an “effective” potential energy, \( \epsilon_{\text{c,c}}(\theta) \), associated with the trans/cis subspace, upon the assumption that only \(|\Psi_4(q)\rangle\) and \(|\Psi_5(q)\rangle\) are accessible when using the frequencies supplied to the system by the external radiation bath:

\[
\epsilon_{\text{c,c}}(\theta) = |C_1|^2 <\Psi_4(q)|H(q,\xi)\Psi_4(q)> + |C_2|^2 <\Psi_5(q)|H(q,\xi)\Psi_5(q)> . \tag{16}
\]

Note that in our simulation, the transition state operates only in the Hilbert space; there is no actual “excitation” to \(|\Psi_5(q)\rangle\), since energy appears to be supplied only until the crossing at \( \theta^* \). Let us now suppose that we move the background of positive charges adiabatically, using the control coordinate \( \theta \). In the neighborhood of the attractor for the trans–conformer (\( \theta = \theta^* \)), the energy \( \epsilon_{\text{c,c}}(\theta) \) follows the diabatic potential energy function \( U(\theta; |\Psi_i|) \) because \(|C_2| \approx 0 \). The fact that
|C_3| > 0 implies that $e_{t,c}(\theta)$ becomes a lower bound to $U(\theta; [\Psi_c])$ when $\theta$ approaches the bottleneck from below (i.e., $0^+\theta^*$). Loosely speaking, the TS appears to “push down” the energy of the system. After the bottleneck ($0^+\theta^*$), $e_{t,c}(\theta)$ decreases until it overlaps the diabatic potential energy curve $U(\theta; [\Psi_c])$ for the cis–conformer. Since the external driving of the $\theta$ coordinate is truly adiabatic in the mechanical sense, the trans→cis transition can appear in the resulting description as a thermodynamically reversible process where one fully recovers the work done on the system. Moreover, $e_{t,c}(\theta)$ allows us to recover also the familiar double–well energy profile for the chemical process with a maximum at $\theta^*$. Note, however, that this profile does not appear as an adiabatic eigenvalue function of $\xi$ but instead as an effective potential projected to the subspace defined by the diabatic functions for reactant and products.

We can also discuss other aspects of the model by using the experimental concept of pump–probe [18]. Imagine that we prepare an initial trans–state $|\Psi_t\rangle$, but we study the system with a probe specific to the electronic cis–state $|\Psi_c\rangle$. If we do work by pumping energy on the system but the latter does not reach an existing bottleneck threshold, then there will be no induced change in electronic state. Let us suppose now that energy is pumped so that we reach the bottleneck region with a level just below the diabatic energy crossing. If we now probe the signal intensity of the cis–conformer, the latter will increase proportionally to $|C_2|^2$ from 0 up to a value just below 0.5 under the influence of the transition state. The emerging behavior of the pump/probe experiment can be described as a “tunneling effect,” but one that takes place vertically along the energy axis, instead of horizontally (as it would be along a conventional “reaction coordinate” $\theta$ in the BO approach).

We close this section by highlighting the different behavior of a single system as opposed to an ensemble. In the case of a single system [19], only a few fundamental properties can be stated if one excludes the details of the positive–charge dynamics. In summary, we know that a change in positive–charge geometry does not alter by itself the electronic state of a single quantum system. Once the required factors are included (i.e., the nonzero off–diagonal matrix elements of $V_{e-rad}$), the $\xi$ geometry of the charge background can be used to control the changes of electronic state in Hilbert space. This is a most important insight that the present model offers, one that is relevant to understanding more complicated chemical processes. For instance, active sites of enzymes have the property to fix the geometry of reacting species [19]. The present approach provides a quantum–mechanical rationale for their kinetic mechanism [20].

The behavior of an ensemble of molecular systems could also be addressed by generalizing the notion of “effective” potential energy of Eq. (16) from that of an expectation value to an average over independent copies of the system. In this case, it would be possible to estimate the frequency of measuring the system in the cis or trans–states, provided that the coefficients are normalized with respect to the number of times these states are detected in the laboratory. By proceeding this way, however, the quantum mechanism for the transition becomes hidden.
7 CONCLUSIONS AND FINAL REMARKS

In this work, we have presented an electronic diabatic approach whereby a molecular system is treated as a model with both quantum and classical features. The classical part is a positive background of $m$ discrete massless point charges in real space; these can be identified with the nuclear charges in a configuration $\xi$. The quantum part corresponds to the configuration space of a system of $n$ electrons. The diabatic basis functions $\{\Psi_i(q)\}$ are derived from a fixed–point electronic hamiltonian, $H_e(q, \xi)$. This ansatz is supplemented with the hypothesis that each electronic diabatic state function $\Psi_i(q)$ for a molecular bound state determines the stationary coordinates $\xi^k$ of a single confining attractor. A colored chemical multigraph is associated with each $\Psi_i(q)$ diabatic basis function and $\xi^k$ attractor; the graph is topologically invariant because $\Psi_i(q)$ is independent from the $\xi$ configuration of the background charges. Quantum states for unbound states (i.e., those correlated with dissociated fragments) can also be incorporated into the present analysis if the asymptotic state along the corresponding coordinate has zero gradients at infinite separation. The shape of the diabatic potential curve along this coordinate will be repulsive.

A general quantum state $|\Phi>)$ for the entire system, including the classical background, is represented as a linear superposition in the diabatic basis. Note that it is the $|\Phi>)$ state that depends parametrically on the $\xi$ configuration; the result can be regarded as a generalized multiconfigurational wave function.

The model allows one to study the interplay between changes in real space coordinates ($\xi$) and changes in the total electronic quantum state ($|\Phi>)$. Real space displacements such as those in molecular motors can now be rationalized as being driven by Franck–Condon–like quantum electronic processes. An illustrative example of such a process appears in our analysis of a trans$\rightarrow$cis conformational change. For a fixed external field, this system exhibits Franck–Condon–like transitions [17]. Given that the electronic ground states are spin closed shell, this transition is forbidden up to first order by parity conservation rules. However, transitions are still possible by a “vertical tunneling” mechanism where one “borrows” intensity from a transition state with singlet diradical electronic structure. (This state can be coupled to the closed–shell states depending on the external radiation field used.) The intensity borrowing can be modulated by an advance coordinate. By means of the vertical–tunneling effect, the electronic properties of the cis–conformer may be “prompted to appear”, so to speak, without a full mechanical shift of away from the trans–conformation. In this sense, the present theory does not require the familiar argument of surmounting an intermediate barrier; the barrier can be seen as an apparent effect resulting from monitoring the potential energy projected only to amplitudes in reactants and products (cf. Eq. (16)). Note that the net result in the GED approach is a sharp transition in the total quantum state, from a reactant–like state to a product–like state. In our case, the transition is mediated by the electromagnetic field. Standard adiabatic or diabatic approaches reach, of course, the same outcome.
in absence of a field, but they do so by conveniently re–mixing the electronic configurations as the nuclear configuration changes. The two methodologies produce a similar final result, but their interpretations are fundamentally different. This above GED interpretation for the electronic transitions can be extended without difficulty to understanding transitions in a statistical sense. Here, the number of events classified on the $k$–reaction channel can be estimated from the amplitude $|C_k|^2$ of the linear superposition in the diabatic basis function $\Psi_k(q)$. The actual relaxation path is thereafter controlled by the way the experiment is designed (e.g., how the positive–charge geometry is modulated externally in real space).

Vertical–tunneling effects can be used for interpreting a number of effects observed, for instance, in experiments measuring the $pH$–dependence of physical observables or the environmental dependence of dissociation constants ($pK_a$). Consider the case of a standard proton exchange, where reactants and products can be characterized by colored graphs where “B” denotes base and “A” denotes acid:

$$X \cdot A \cdot H \rightarrow (X \cdot A^-) \rightarrow (H \cdot B).$$

(17)

Experimentally, these graphs can describe the system at various $pH$ values and the stability of the anion fragment is controlled by the group X. For simplicity, however, we shall denote the corresponding states as $|A \cdot H \rightarrow B>$ and $|A^- \rightarrow H^- \cdot B>$; these are described respectively by the diabatic functions $\Psi_1$ and $\Psi_2$. Figure 3 shows a simple scheme where these states are associated with single–minima attractors, with their interconversion made possible by the presence of a transition state function $\Psi_{TS}$. As before, the geometry of the positive–charge background is modulated externally and described by an “advance” coordinate. In the present case, however, it is more convenient to think of $pH$ as a sort of control coordinate. At low $pH$ values, the positive–charge background is consistent with a continuum of geometries, but it is biased towards the stationary configuration $\xi_1$, denoted by “a” in Figure 3. As the $pH$ increases, the system will be prompted to explore geometries farther from $\xi_1$, e.g., those corresponding to “b” and “c” Figure 3. In this fashion, the “pH coordinate” allows the system to probe different energy gaps with $U(\xi_1(\Psi_2))$ and $U(\xi_1(\Psi_{TS}))$.

In the presence of the proper couplings to the state $|\Psi_{TS}>$, transitions may become possible. If we now probe the final $|A^- \rightarrow H^- \cdot B>$ state, its corresponding amplitude $|C_2|^2$ will be found to increase as we approach the bottleneck region where the two diabatic closed–shell state cross. (At the crossing, the amplitudes should be equal and $pH=pK_a$.) Note, however, that the $pH$ variable is not consistent with a single $\xi$–configuration but rather with a subset of in $\Re^3$. We use then $\langle \langle |C_2|^2 \rangle \rangle_\xi$ to denote the amplitude of the $|A^- \rightarrow H^- \cdot B>$ state averaged over the set of configurations accessible at a given $pH$ value. The expected response of this function is indicated with the inset in Figure 3. The $\langle \langle |C_2|^2 \rangle \rangle_\xi$ function increases as one moves from “a” to “c,” with a typical S–shape. This response is actually seen experimentally, where the chemical shift of the proton serves as probe for
one of the species. An interesting example of this phenomenon can be observed in the pH–dependent cross–modulation of aglycones in dinucleosides by nearest–neighbor interaction of stacked states [21].

Figure 3. The diabatic potential energy model for a generic acid–base system. The function Ψ₁ describes the state |A–H⁺B> with graph “X–A–H⁺(B)”, whereas Ψ₂ stands for the state |A⁻⁻⁻H⁺B> with graph “(X–A⁻⁻⁻)⁺⁻⁻⁻(H⁻B)⁺⁻⁻⁻.” The pH serves as a control. The inset indicates the expected response in the amplitude of the product state, <<C₂|2>, averaged over the ξ-configurations of the positive–charge background that are accessible (or probed) at a given pH. This curve resembles the pH–dependent behavior observed experimentally for the chemical shifts of dinucleoside monophosphates [21]. (See text for further comments.)

The present GED model can be extended in order to study different molecular phenomena [3,22], including time–dependent ones [23]. Our approach allows one to recast as electronic transitions a host of processes previously viewed as ground–state phenomena within the BO model. The use of a diabatic basis set simplifies the physical picture and facilitates the straight use of the quantum–mechanical linear superposition principle. The two central notions that one must employ in all analyses are that: (a) conformational changes are described as Franck–Condon–like electronic processes, and (b) vertical–tunneling effects involve transition states that are parity–adapted excited electronic states. In the presence of proper couplings mediated by an external radiation field (or collisional environment), these excited states determine the interconversion rates of the lower energy states. These effects may be tested in the laboratory with time–resolved pump–probe experiments.
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5 REFERENCES

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