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

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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; Frank–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

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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 $\{\mathbf{q}_i\}$, $\Psi(\mathbf{q}_1,...\mathbf{q}_n)$, and (*b*) a classical one, in the form of a three–dimensional array ξ for a background of *m* positive charges, $\xi \in \Re^3$. 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, $H_e(\mathbf{q}, \xi^0)$, with ξ^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 ξ^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* ξ^k *attractor* can be used as to defined a fixed–point hamiltonian $H_e(\mathbf{q}, \xi^k)$, 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 ξ. (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 $Z = (Z_1,...,Z_m)$ and $\xi = (\xi_1,..., \xi_m)$, 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 *a posteriori* a proper mapping between electronic states.

Let $|\Psi>$ denote an abstract quantum state for an n–electron system embedding the background of m positive, "classical" test point charges in configuration ξ. This state is considered to be completely represented by a function $\Psi(\mathbf{q}_1,..., \mathbf{q}_n)$, defined in a $3n$–dimensional configurational space with vectors $\mathbf{q} = (\mathbf{q}_1,..., \mathbf{q}_n)$; the spin component is treated separately. The *complete* hamiltonian for such an electronic system is:

$$H_e(\mathbf{q}, \xi) = K_e(\mathbf{q}) + V_C(\mathbf{q}, \xi) \,, \tag{1}$$

where $K_e(\mathbf{q})$ is the electronic kinetic energy operator and $V_C(\mathbf{q}, \xi)$ is the complete Coulomb interaction, *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 $\Psi_0(\mathbf{q}_1, ..., \mathbf{q}_n)$. The hamiltonian (1) will then have an expectation value U_0:

$$U_0(\xi) = U(\xi; [\Psi_0]) = < \Psi_0(\mathbf{q}) \mid \mathrm{H_e}(\mathbf{q}, \xi)\, \Psi_0(\mathbf{q}) >_{\boldsymbol{q}}, \tag{2}$$

that is a function of ξ and a functional of Ψ_0. Note that U_0 will change if the positive charge background is rearranged as a consequence of the Coulomb operator $\mathrm{V_C}(\mathbf{q}, \xi)$ being modified, *not* because the wave function $\Psi_0(\mathbf{q})$ is modified. Indeed, since $\Psi_0(\mathbf{q})$ does not depend on ξ, the change in U_0 satisfies trivially the Hellmann–Feyman theorem:

$$\frac{\partial U_0}{\partial \xi} = < \Psi_0 \mid \frac{\partial H_e}{\partial \xi} \Psi_0 >_q \tag{3}$$

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 ξ^0:

$$\left\| \left(\frac{\partial U_0}{\partial \xi}\right)\Big|_{\xi^0} \right\| = 0 \tag{4}$$

Now, we define a *fixed–point* hamiltonian $\mathrm{H_e}(\mathbf{q}, \xi^0)$ at the stationary configuration ξ^0. Since Ψ_0 is the ground state of the system and ξ^0 is obtained from Ψ_0 as in Eqs. (3)–(5), then the electronic operator $\mathrm{H_e}(\mathbf{q}, \xi^0)$ 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 $\mathrm{H_e}(\mathbf{q}, \xi)$ 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 $\mathrm{V_C}(\mathbf{q}, \xi)$ [14], *e.g.*, the ξ configuration for the background charges. Given this, we choose construct the complete set of electronic states using the fixed–point operator $\mathrm{H_e}(\mathbf{q}, \xi^0)$. By following this approach, the stationary configuration ξ^0 and the electronic state $\Psi_0(\mathbf{q})$ 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 $\delta_\Psi\{<\Psi(\mathbf{q})| \mathrm{H_e}(\mathbf{q}, \xi^0)\Psi(\mathbf{q})>_{\boldsymbol{q}}/||\Psi||^2\} = 0$. The result is an Euler–Lagrange equation:

$$\mathrm{H_e}(\mathbf{q}, \xi^0)\, \Psi_k(\mathbf{q}) = \mathrm{E_k}(\xi^0)\, \Psi_k(\mathbf{q}) \ , \tag{5}$$

where the eigenvalues are functionals of Ψ_k: $\mathrm{E_k}(\xi^0) = U(\xi^0;[\Psi_k]\,) = U_k(\xi^0)$. The Eqs. (4)–(5) ensure that $U_0(\xi^0)$ is the global minimum of $U(\xi;[\Psi])$ both in configurational space ($\Re^{3m}$) and in Hilbert space. Note that Eq. (5) is, in principle, iterative: $\{\Psi_k\}$ are eigenfunctions of $\mathrm{H_e}(\mathbf{q}, \xi^0)$, a operator which is built by knowing the ground state Ψ_0. In general, these excited states $\Psi_{k>0}$ may not have the same stationary positive charge background geometry as the ground state ξ^0. We denote these stationary background configurations by ξ^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 ξ^0: the configurations ξ^k (with $k > 0$) are stationary points of the functionals $U(\xi; [\Psi_k])$, which *in turn are built with the diabatic eigenfunctions* Ψ_k of $H_e(\mathbf{q}, \xi^0)$. Finally, it should be noted that the electronic diabatic functions, and their stationary points ξ^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 Ψ_k do not depend upon the configuration space ξ and that only the function Ψ_k determines the stationary configuration ξ^k. This assumption implies that *any* fixed–point Hamiltonian $H_e(\mathbf{q}, \xi^s)$, with ξ^s the stationary point of the functional $U(\xi; [\Psi_s]) = \langle\Psi_s(\mathbf{q}) \,|\, H_e(\mathbf{q}, \xi)\, \Psi_s(\mathbf{q})\rangle_q$, produces the *same set* of diabatic eigenfunctions $\{\Psi_k\}$, including the bound–state function Ψ_s which determines the fixed point for the hamiltonian:

$$H_e(\mathbf{q}, \xi^s)\, \Psi_k(\mathbf{q}) = E_k(\xi^s)\, \Psi_k(\mathbf{q}) \,. \tag{6}$$

Note that the eigenfunctions are the same as in Eq. (5), but not the eigenvalue spectrum. As a result of the ξ–independence, it is understood that all $U(\xi; [\Psi_s])$ functionals (with Ψ_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 ξ). In the section below, we will use the ξ–independence to represent each Ψ_k electronic state, and its corresponding stationary configuration ξ^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 $\{\Psi_k(\mathbf{q})\}$ functions are the only set of eigenfunctions obtained from any fixed–point hamiltonian, $H_e(\mathbf{q}, \xi^s)$, defined at a stationary point ξ^s; the $\Psi_k(\mathbf{q})$–functions have *no* parametric dependence on ξ. Moreover, the $\{\Psi_k(\mathbf{q})\}$ 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 $\{\Psi_k(\mathbf{q})\}$ 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 ξ^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 ξ^k corresponding to the wave function Ψ_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 ξ^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 ξ^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 $\Re^{3m}$ where the test charges preserve their connectivity and coloring. It is easy to see that a ξ^k–graph is invariant to any such change in $\Re^{3m}$. By construction, the ξ^k–graph is determined by a ξ–independent electronic state Ψ_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 ξ^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 $\Re^{3m}$.

We can cast the above ideas in a more quantitative way. First, let us give the configuration space $\Re^{3m}$ a topological structure with the standard (Euclidean) metric $d(\xi,\xi') = ||\xi - \xi'||$. Consider now the system at a state Ψ_k and an arbitrary configuration ξ^a. Let us then deform the vertices of its local graph to a new configuration ξ^b; this procedure defines a continuous path in $\Re^{3m}$ which we take, for simplicity, as the segment $\xi^{a\rightarrow b}(\lambda) = \xi^a + \lambda\,(\xi^b - \xi^a)$, with $0 \leq \lambda \leq 1$. (In all these transformations, we use the same, fixed inertial frame.) The $\xi^{a\rightarrow b}(\lambda)$ path traces a curve $G_k(\xi^{a\rightarrow b}(\lambda))$ on the potential energy hypersurface $U(\xi(\lambda); [\Psi_k])$, which is an attractor with a single stationary point ξ^k associated with a unique electronic function Ψ_k. We can now introduce a trivial Ψ_k–homotopy which makes two paths $\xi^{a\rightarrow b}(\lambda)$ and $\xi^{a'\rightarrow b'}(\lambda)$ topologically equivalent by the simple reason that $G_k(\xi^{a\rightarrow b}(\lambda))$ and $G_k(\xi^{a'\rightarrow b'}(\lambda))$ 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, $\xi^{a\rightarrow k}(1)$, thus making the entire $\Re^{3m}$ space Ψ_k–homotopically equivalent to the ξ^k configuration, and characterizing it by the single Ψ_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 *trans→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 *trans*–conformer (with C_{2h} symmetry at its stationary configuration ξ^t) has a distinct symmetry operation, and thus use the inversion $\hat{\imath}$ to label the *trans*–conformer and the C_2–rotation to label the *cis*–conformer (with C_{2v} symmetry at configuration ξ^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 *trans*–conformer would become F(+)–C(–)=C(+)–F(–) to indicate how the atoms transform under the inversion (*i.e.*, $\hat{\imath}$ F(+) = F(–), etc.), whereas in *cis*–conformer would be F(+)–C(+)=C(+)–F(+), to indicate how the atoms transform under the rotation (*i.e.*, C_2 F(+) = F(+), etc.). Proceeding this way, the diabatic electronic wave functions for the ground states of the *cis*– and the *trans*–conformers (Ψ_c and Ψ_t, respectively) are characterized by different graphs. These graphs remain invariant even if we force the nuclear charges in the electronic state Ψ_t to adopt the configuration ξ^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 $U(\xi^t; [\Psi_t])$.) 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 *trans*– to the *cis*–conformer. As discussed before, transformations in $\Re^{3m}$ must all be described in the same inertial frame used to derive the diabatic wave functions. This implies that the *z*–axis for the *trans*–conformer (conventionally identified with the highest–symmetry rotational C_2 axis) must remain as the *z*–axis for the *cis*–conformer (also coincident with a C_2 axis). Accordingly, the motion connecting ξ^t and ξ^c must be a *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 π–system for the *trans*–conformer is sustained by the p_z–orbitals of a minimal basis set. In contrast, the π–system for the *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 ξ^t into ξ^c would be seen as follows. If we start at ξ^t, the Ψ_t state provides the lowest energy $U(\xi)$, one where the π_z–orbitals are doubly occupied. These orbitals have lower energy than the π_x– or π_y– in Eq. (6) computed with either $H_e(\mathbf{q}, \xi^t)$ or $H_e(\mathbf{q}, \xi^c)$. Yet, as we move towards ξ^c, one would eventually obtain a lower $U(\xi)$ value by using the doubly–occupied π_x– or π_y– in Eq. (6) with $H_e(\mathbf{q}, \xi^c)$, *i.e.*, by using the Ψ_c wave function for configurations near ξ^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.

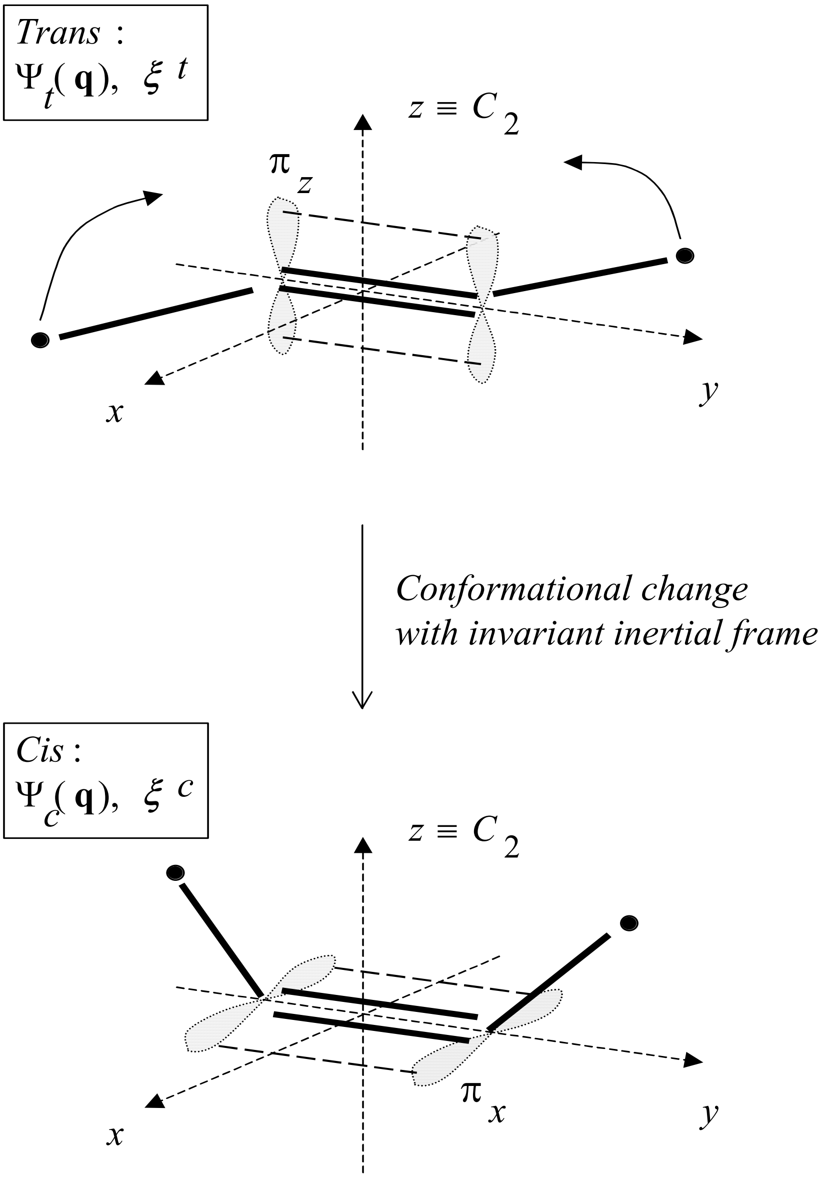

Figure 1. Representation of a *trans*–to–*cis* conformational change when using an invariant inertial frame. The inertial frame maintains the *z*–axis aligned with the C_2 rotational axes of both the *trans* and *cis* conformers. As a result, the motion in real space leading from *trans* to *cis* is 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 π–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 $p_z = p_0$, and the *cis*–graph becomes F–C(±1)=C(±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 Ψ_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 $\Re^{3m}$. First, one modifies the potential energy $U(\xi;[\Psi_k])$ for a diabatic Ψ_k state. Secondly, since an actual quantum state $|\Phi\rangle$ 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 ξ.

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 $\Phi(\mathbf{q})$:

$$\Phi(\mathbf{q}) = C_t\, \Psi_t(\mathbf{q}) + C_c\, \Psi_c(\mathbf{q}) \,, \tag{7}$$

in terms of the *trans* and *cis* diabatic functions $\Psi_t(\mathbf{q})$ and $\Psi_c(\mathbf{q})$, respectively. Given that the electronic hamiltonian $H_e(\mathbf{q}, \xi)$ is diagonal in the $\{\Psi_k\}$–functions, the time evolution of the quantum state $|\Phi\rangle$ (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: $V_{e\text{–}rad} = \mathbf{A}\bullet\mathbf{p}_e$, 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: $H = H_e + V_{e\text{–}rad} + H_{rad}$, 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 Φ:

$$(H_e(\mathbf{q}, \xi) + V_{e\text{–}rad})\, \Phi(\mathbf{q}) = \varepsilon(\xi)\; \Phi(\mathbf{q}) \,. \tag{8}$$

It is important to note the difference between Eq. (8) for the Φ functions and Eq. (6) for the $\{\Psi_k\}$–functions. The latter (and their associated energies $\{E_k(\xi_S)\}$) are properties of the *isolated* molecule and thus independent of ξ. In contrast, the $\varepsilon(\xi)$ energies for instantaneous quantum state $\Phi(\mathbf{q})$ reflect how the diabatic states $\{\Psi_k\}$ are coupled at the configuration ξ *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 *trans*– and *cis*–conformers (Eq. (7)) by using first–order perturbation theory with $V_{e\text{–}rad}$ for the transition moments **T**:

$$\mathbf{T}_{t\to c} = \langle \Psi_t \,|\, \mathbf{p}_e\, \Psi_c \rangle_q \,. \tag{9}$$

As in standard electronic spectroscopy, a transition $i\to j$ is allowed if the transition moment $\mathbf{T}_{i\to j}$ is not zero. We can analyze the element $\mathbf{T}_{t\to c}$ 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.*, $\hat{P}x = -x$, etc.), then $\hat{P}\mathbf{p}_e = -\mathbf{p}_e$. Moreover, since both the *cis* and *trans* conformers have closed–shell electronic structure, we have $\hat{P}\Psi_s(\mathbf{q}) = \Psi_s(\mathbf{q})$, with s = t,c. As a result, we obtain from Eq. (9): $\hat{P}\mathbf{T}_{t\to c} = -\mathbf{T}_{t\to c}$. Yet, $\mathbf{T}_{t\to c}$ and $\hat{P}\mathbf{T}_{t\to c}$ differ only on the axes' labeling, an artifact that cannot change the physical transition. Accordingly, we conclude that $\hat{P}\mathbf{T}_{t\to c} = -\mathbf{T}_{t\to c} = \mathbf{T}_{t\to c}$, that is $\mathbf{T}_{t\to c} = \mathbf{0}$. In other words, the *trans*→*cis* transition is forbidden, up to first–order perturbation theory.

This result implies that a *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 $\Phi(\mathbf{q})$ to *three* basis functions, by including the TS:

$$\Phi(\mathbf{q};\xi) = C_t(\xi)\,\Psi_t(\mathbf{q}) + C_c(\xi)\,\Psi_c(\mathbf{q}) + C_{TS}(\xi)\,\Psi_{TS}(\mathbf{q})\,, \tag{10}$$

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

The diagonalization of the ξ–dependent hamiltonian (8) yields the quantum amplitudes $\{C_s;\, s = t,c,TS\}$ for each configuration ξ. 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 *trans*→*cis* transition in ethylene ($CH_2{=}CH_2$) is the simplest example of the process depicted in Figure 1. The atomic p–orbitals required to describe the molecular π–orbitals for the *trans*– and *cis*–conformers are also indicated in Figure 1. Let us seek now the basis functions required to describe the transition state minimally. If (p_{xi}, p_{yi}, p_{zi}) denote standard 2*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″:

$$p'_1 = (p_{x1} + p_{z1})/\sqrt{2}\,,\quad p''_1 = (-p_{x1} + p_{z1})/\sqrt{2}\quad, \tag{11a}$$

$$p'_2 = (-p_{x2} + p_{z2})/\sqrt{2}\ ,\quad p''_2 = (p_{x2} + p_{z2})/\sqrt{2}\ . \tag{11b}$$

The {p′,p″} orbitals are adapted to the disrotatory motions in Figure 1, where rotations by +π/4 and −π/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 "π–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 $\phi_\pm = p''_1 \pm p''_2$. Consequently, the triplet wave function for the diradical becomes (up to a normalization constant):

$$\Psi(S{=}1,M_S{=}{+}1) = \{\phi_+(1)\phi_-(2) - \phi_-(1)\phi_+(2)\}\ \alpha(1)\alpha(2), \tag{12a}$$

$$\Psi(S{=}1,M_S{=}{-}1) = \{\phi_+(1)\phi_-(2) - \phi_-(1)\phi_+(2)\}\ \beta(1)\beta(2), \tag{12b}$$

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

and the singlet diradical is characterized as:

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

These two functions would be obtained in open–shell Hartree–Fock calculations, and they are associated with ξ–configurations in $\Re^{3m}$ 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:

$$\Psi^+(S{=}0,M_S{=}0) = \{\phi_+(1)\phi_+(2) + \phi_-(1)\phi_-(2)\}\ \{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \tag{14}$$

corresponding to a *polarized state*. The Ψ^+ function would be obtained with a closed–shell Hartree–Fock calculation, and it is associated with a ξ–configurations that is a type–1 *saddle point* in $\Re^{3m}$. 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 *trans→cis* transition, *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 *trans→cis* transition depicted in Figure 2. The left–hand–side curve represents the potential energy for the *trans*–conformer, $U(\theta; [\Psi_t])$, *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 *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 Ψ_k–graphs; the corresponding Ψ_k–states are basis functions of the electronic Hilbert space and also invariant to changes in geometry of the positive–charge background. The θ coordinate relates the conformer geometries (cf. the disrotatory displacement in Figure 1).

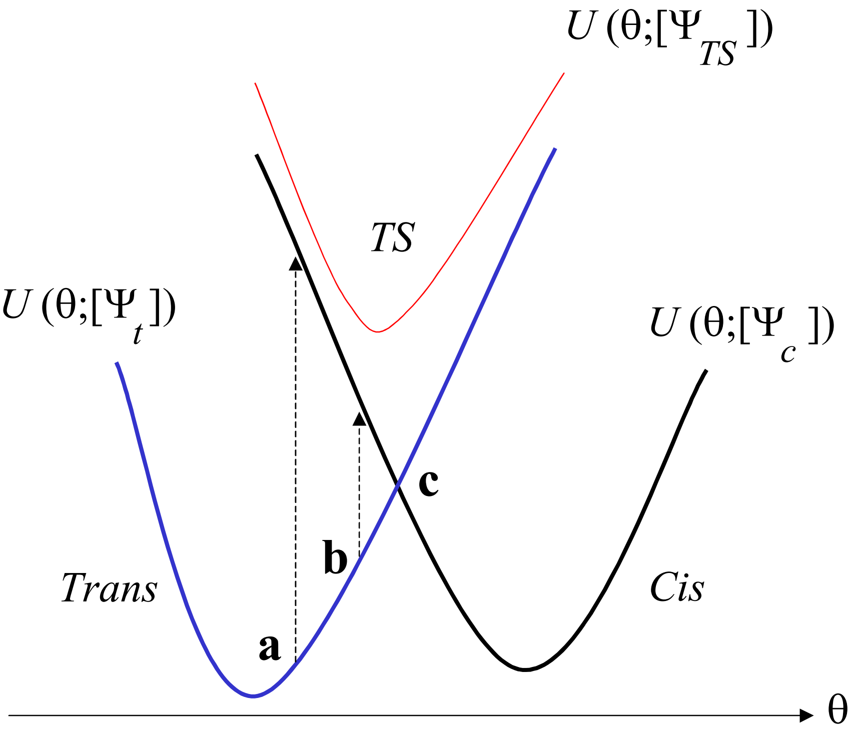

Figure 2. Simple model for the diabatic potential energy curves $U(\theta; [\Psi_t])$, $U(\theta; [\Psi_c])$, and $U(\theta; [\Psi_{TS}])$ corresponding to the *trans*–, *cis*–, and transition–states of ethylene, respectively. The θ–coordinate corresponds to the disrotatory displacement explained in 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 θ^t, or $\theta^* = -\pi/4$ measured from θ^c. 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 θ 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: $\Delta U_{12} = U(\theta; [\Psi_c]) - U(\theta; [\Psi_t])$, $\Delta U_{13} = U(\theta; [\Psi_{TS}]) - U(\theta; [\Psi_t])$, and $\Delta U_{23} = U(\theta; [\Psi_{TS}]) - U(\theta; [\Psi_c])$, that are implicit functions of θ. For example, large positive values for both ΔU_{12} and ΔU_{13} correspond to θ values characteristic of the *trans*–conformer; similarly, the *cis*–conformer will appear at θ values where both ΔU_{23} and $|\Delta U_{12}|$ are large (with ΔU_{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 Ψ_1, Ψ_2, and Ψ_3 mimicking the *trans*, *cis*, and TS species. First, we note that all diagonal elements of $V_{e\text{–}rad}$ are zero, therefore $H_{ii} = (H_e)_{ii} = U(\theta; [\Psi_i]) = U_i$. The nondiagonal elements can be taken as variable parameters. Furthermore, note that Ψ_1 and Ψ_2 are orthogonal and have zero transition moment (cf. Eq. (9)). From this and the fact that the Coulombic operator $V_C(\mathbf{q}, \xi)$ (Eq. (1)) is symmetric under an inversion of electronic coordinates for all ξ, we deduce $H_{12} = 0$. Similarly, we conclude that $(H_e)_{13} = (H_e)_{23} = 0$, thus $H_{13} = V_{13}$ and $H_{23} = V_{23}$, because the 1→3 and 2→3 transitions are allowed. For simplicity, we choose here $V_{13} = V_{23}$. Finally, upon factorizing U_1, we get the following hamiltonian matrix:

$$([H_e+V_{e\text{–}rad}]_{ij}) = \begin{pmatrix} 0 & 0 & V_{13} \\ 0 & \Delta U_{12} & V_{13} \\ V_{13} & V_{13} & \Delta U_{13} \end{pmatrix}. \tag{15}$$

Table 1 shows the coefficients $\{C_s\}$ for the eigenfunction corresponding to the lowest eigenvalue ε of Eq. (15) (energies are in arbitrary units). The values chosen for ΔU_{12} and ΔU_{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 (ΔU_{12}, ΔU_{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→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 $V_{e\text{–}rad}$, an initial state $|\Psi_t(\mathbf{q})\rangle$ will persist as such regardless of a displacement in the positive–charge background (represented here by θ). Any change in state is quantum–mechanically determined by the matrix elements of $V_{e\text{–}rad}$ 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 ξ, since both $\Psi_k(\mathbf{q})$ and $V_{e\text{–}rad}$ do not depend on the geometry of the positive–charge background. In this sense, the 1→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→cis* transition. In Table 1, the initial state $\Phi(\mathbf{q}; \xi)$ corresponds to large values of ΔU_{12} and ΔU_{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 $\theta \to \theta^*$ (the point where the diabatic potential energy curves cross), the amplitude in Ψ_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 θ^*; its actual size depends on V_{13} and V_{23}, *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 Ψ_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*→*trans* transformation.)

Table 1. Change in the wave function for the quantum state of a three–level model of the *trans*→*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 $\Delta U_{1,2}$ and $\Delta U_{1,3}$ decrease along the control coordinate θ (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 $\Delta U_{1,2}$ decreases (see text).

$\Delta U_{1,2}$	$\Delta U_{1,3}$	$V_{13}=V_{23}$	$-\varepsilon$ (lowest)	$\lvert C_1\rvert$	$\lvert C_2\rvert$	$\lvert C_3\rvert$
5.0000	8.0000	0.001	1.25×10^{-7}	1	2.50×10^{-8}	1.25×10^{-4}
		0.010	1.25×10^{-5}	1	2.50×10^{-6}	1.25×10^{-3}
		0.100	1.25×10^{-3}	1	2.50×10^{-4}	0.013
0.1000	3.1000	0.001	3.2×10^{-7}	1	3.23×10^{-6}	3.23×10^{-4}
		0.010	3.2×10^{-5}	1	3.23×10^{-4}	3.23×10^{-3}
		0.100	2.5×10^{-3}	0.999	0.032	0.033
0.0500	3.0500	0.001	3.3×10^{-7}	1	6.56×10^{-6}	3.28×10^{-4}
		0.010	3.3×10^{-5}	1	6.56×10^{-4}	3.28×10^{-3}
		0.100	3.5×10^{-3}	0.997	0.065	0.035
0.0050	3.0050	0.001	3.3×10^{-7}	1	6.56×10^{-5}	3.33×10^{-4}
		0.010	3.4×10^{-5}	1	6.56×10^{-3}	3.35×10^{-3}
		0.100	4.9×10^{-3}	0.894	0.446	0.045
0.0005	3.0005	0.001	3.3×10^{-7}	1	6.66×10^{-4}	3.34×10^{-4}
		0.010	3.5×10^{-5}	0.998	0.066	3.55×10^{-3}
		0.100	4.9×10^{-3}	0.732	0.679	0.047
0.0000	3.0000	0.001	6.7×10^{-7}	0.707	0.707	4.71×10^{-4}
		0.010	6.7×10^{-5}	0.707	0.707	4.71×10^{-3}
		0.100	4.9×10^{-3}	0.706	0.706	0.047
0.0001	1.0000	0.010	1.6×10^{-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, $\varepsilon_{t,c}(\theta)$, associated with the *trans*/*cis* subspace, upon the assumption that only $|\Psi_t(\mathbf{q})>$ and $|\Psi_c(\mathbf{q})>$ are accessible when using the frequencies supplied to the system by the external radiation bath:

$$\varepsilon_{t,c}(\theta) = |C_1|^2 <\Psi_t(\mathbf{q})|H(\mathbf{q},\xi)\Psi_t(\mathbf{q})> + |C_2|^2 <\Psi_c(\mathbf{q})|H(\mathbf{q},\xi)\Psi_c(\mathbf{q})> . \tag{16}$$

Note that in our simulation, the transition state operates only in the Hilbert space; there is no actual “excitation” to $|\Psi_c(\mathbf{q})>$, since energy appears to be supplied only until the crossing at θ^*. Let us now suppose that we move the background of positive charges adiabatically, using the control coordinate θ. In the neighborhood of the attractor for the *trans*–conformer ($\theta\approx\theta^t$), the energy $\varepsilon_{t,c}(\theta)$ follows the diabatic potential energy function $U(\theta; [\Psi_t])$ because $|C_2|\approx0$. The fact that

$|C_3| > 0$ implies that $\varepsilon_{t,c}(\theta)$ becomes *a lower bound* to $U(\theta; [\Psi_t])$ when θ approaches the bottleneck from below (*i.e.*, $\theta \uparrow \theta^*$). Loosely speaking, the TS appears to "push down" the energy of the system. After the bottleneck ($\theta > \theta^*$), $\varepsilon_{t,c}(\theta)$ decreases until it overlaps the diabatic potential energy curve $U(\theta; [\Psi_c])$ for the *cis*–conformer. Since the external driving of the θ 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, $\varepsilon_{t,c}(\theta)$ allows us to recover also the familiar double–well energy profile for the chemical process with a maximum at θ*. Note, however, that this profile does *not* appear as an adiabatic eigenvalue function of ξ 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 $|\Psi_t\rangle$. 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" θ 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 ξ 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 ξ. The quantum part corresponds to the configuration space of a system of *n* electrons. The diabatic basis functions $\{\Psi_s(\mathbf{q})\}$ are derived from a fixed–point electronic hamiltonian, $H_e(\mathbf{q}, \xi^k)$. This ansatz is supplemented with the hypothesis that each electronic diabatic state function $\Psi_k(\mathbf{q})$ for a molecular bound state determines the stationary coordinates ξ^k of a single confining attractor. A colored chemical multigraph is associated with each $\Psi_k(\mathbf{q})$ diabatic basis function and ξ^k attractor; the graph is topologically invariant because $\Psi_k(\mathbf{q})$ is independent from the ξ 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 ξ 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 (ξ) 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→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 $\Psi_k(\mathbf{q})$. 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 *p*H–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:

$$\text{X–A–H}^{\cdots}\text{(:B)} \rightarrow \text{(X–A}^{-}\text{)}^{\cdots}\text{(H–B)}^{+} . \tag{17}$$

Experimentally, these graphs can describe the system at various *p*H values and the stability of the anion fragment is controlled by the group X. For simplicity, however, we shall denote the corresponding states as $|\text{A–H}^{\cdots}\text{B}>$ and $|\text{A}^{-\,\cdots}\,\text{H}^{+}\text{–B}>$; these are described respectively by the diabatic functions Ψ_1 and Ψ_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 Ψ_{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 *p*H as a sort of control coordinate. At low *p*H values, the positive–charge background is consistent with a continuum of ξ geometries, but it is biased towards the stationary configuration ξ_1, denoted by "**a**" in Figure 3. As the *p*H increases, the system will be prompted to explore geometries farther from ξ_1, *e.g.*, those corresponding to "**b**" and "**c**" Figure 3. In this fashion, the "*p*H coordinate" allows the system to probe different energy gaps with $U(\xi;[\Psi_2])$ and $U(\xi;[\Psi_{TS}])$.

In the presence of the proper couplings to the state $|\Psi_{TS}>$, transitions may become possible. If we now probe the final $|\text{A}^{-\,\cdots}\,\text{H}^{+}\text{–B}>$ 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 *p*H variable is *not* consistent with a single ξ–configuration but rather with a subset of in $\Re^{3m}$. We use then $<<|C_2|^2>>_\xi$ to denote the amplitude of the $|\text{A}^{-\,\cdots}\,\text{H}^{+}\text{–B}>$ state averaged over the set of configurations accessible at a given *p*H value. The expected response of this function is indicated with the inset in Figure 3. The $<<|C_2|^2>>_\xi$ 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 *p*H–dependent cross–modulation of aglycones in dinucleosides by nearest–neighbor interaction of stacked states [21].

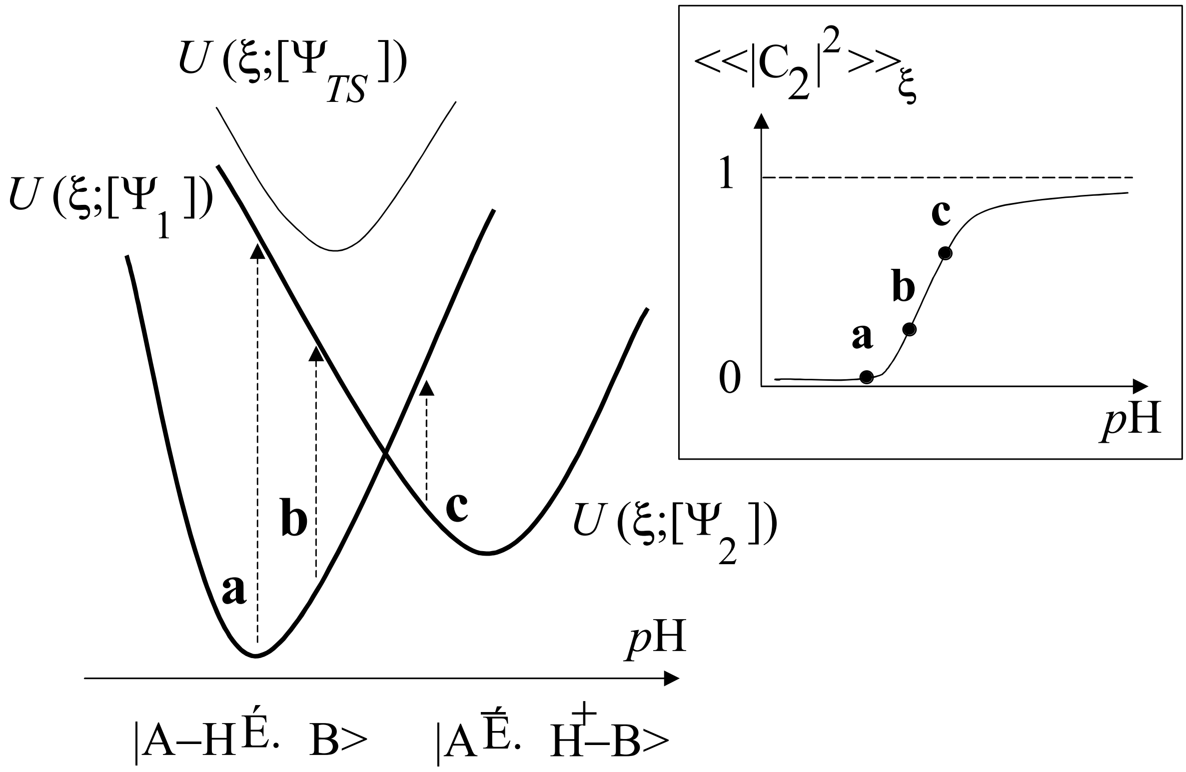

Figure 3. The diabatic potential energy model for a generic acid–base system. The function Ψ_1 describes the state |A–H$\cdots$ B> with graph "X–A–H$\cdots$(:B)", whereas Ψ_2 stands for the state |A$^-$ $\cdots$ H$^+$–B> with graph "(X–A$^-$) $\cdots$ (H–B)$^+$." The *p*H serves as a control. The inset indicates the expected response in the amplitude of the product state, $<<|C_2|^2>>_\xi$, averaged over the ξ–configurations of the positive–charge background that are accessible (or probed) at a given *p*H. This curve resembles the *p*H–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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