Comparison between a generalized electronic diabatic approach and the Born–Oppenheimer separation scheme in inertial frames

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We discuss a generalized electronic diabatic (GED) approach to diagonalize the exact Hamiltonian of an n-electron system which embeds an "external" background of positive charges. This Hamiltonian, denoted by $\mathcal{H}_e(\mathbf{q}, \xi)$, is defined in an inertial frame, and it contains a *quantum* part (the electrons with coordinates $\mathbf{q}$) and a *classical* part (the external charges in a three-dimensional configuration ξ). We derive a GED basis set $\{\psi_k(\mathbf{q})\}$ using an operator $\mathcal{H}_e(\mathbf{q}, \xi^0)$ for a single configuration ξ^0, and then show that these are also eigenfunctions for any other $\mathcal{H}_e(\mathbf{q}, \xi)$; only the ordering of eigenvalues may depend on ξ (i.e., $k = k(\xi)$). The GED functions can also be used to represent the eigenstates of a fully quantum-mechanical system of electrons and nuclei. We discuss briefly the differences between the present procedure and the standard Born–Oppenheimer (BO) technique in the "clamped-nuclei" approximation. As illustration, we show how chemical changes emerge as transitions among diabatic states mediated by an electromagnetic field.

KEY WORDS: diabatic states, electronic transitions, clamped nuclei, transition state

1. Introduction

Scattering experiments on atoms and molecules can be regarded as involving the interplay between two very different spaces: by setting up objects in a *classical* laboratory three-dimensional space (the beams), we study chemical changes represented in a *nonclassical* space (the Hilbert space for the electrons). Modern techniques for manipulating individual atoms and molecules have taken this notion farther by allowing a

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very detailed control of well-defined regions of "real" space that affect the behaviour of a quantum system [1,2]. For instance, scanning tunneling microscopy and atomic force microscopy [3] produce real-space resolved features where it is possible to detect actual motions of molecules and atoms on metal surfaces. With the development of these and other nanotechnologies [4], there is a need for understanding how a quantum subsystem responds in experiments where nuclei can be moved around as if they were classical particles. In this work, we discuss a theoretical framework which is adapted to tackle problems where a fully quantum-mechanical approach might not be needed (e.g., understanding and controlling some phenomena at interfaces).

The Born–Oppenheimer (BO) separation scheme is the standard approach followed to describe approximately the electrons as a quantum subsystem inside a molecule. The method has been instrumental in developing the familiar algorithms used to compute electronic wave functions. Yet, there are questions about the validity of the BO approach (in its various implementations) in a quantum mechanical context [5–8]. For example, this method describes changes in electronic configuration as spontaneous processes occurring on the single potential energy hypersurface of an *isolated* molecule. Instead of being mediated by an exterior electromagnetic field, chemical change involving ground-state species is triggered artificially by *nonadiabatic couplings* which seek to "correct" the BO energy hypersufaces at special points. These and other conceptual problems [8] make it difficult to develop simple models where the classical and quantum aspects are well identified. In this work, we propose a generalized electronic diabatic (GED) approach as an alternative to the BO approximation for the study of an n electrons system embedded in the external field of m positive charges. The latter are treated, in a first approximation, as *classical massless test charges* whose configuration can be changed externally at will.

The paper is organized as follows. In section 2, the GED approach is introduced as a model consisting of an electronic system interacting with m external sources of Coulomb potential (the V-potential) with a ξ-configuration in the laboratory space of m charges (i.e., $\xi \in \Re^{3m}$). The method leads to electronic quantum states that are V-representable using a complete set of diabatic wave functions; we show that this set diagonalizes the electronic Hamiltonian for any ξ-geometry of the external positive charge background. In section 3, we contrast the present GED approach and the standard BO scheme. If an inertial frame is used (instead of a body-fixed rotating frame), we show that the GED approach and the BO approximation with "clamped nuclei" share a spectrum of *diabatic* electronic basis functions, instead of standard wave functions that depend parametrically on nuclear coordinates. In section 4, we show how the quantum-classical approach can be used to study molecular phenomena in the laboratory as processes mediated by an external electromagnetic field.

2.   The generalized electronic diabatic model

In order to describe quantum systems evolving in real space, one needs to define in a consistent way what the quantum aspect of the problem is (i.e., the one described

in Hilbert space) and what its classical aspect is (the one described in laboratory space). A quantum system should always be defined with respect to an inertial reference frame. The requirement comes from the special theory of relativity: conservation of energy, angular and linear momentum derives from inertial frame invariance to time and space translations, as well as frame rotations. The corresponding invariances in Hilbert space are also well known [9,10]. In the context of using the inertial frame, the state of a single isolated charged and massive particle is described by the Dirac equation, which is the relativistic version (i.e., invariant under the Lorentz group) of the Schrödinger equation [11]. From this, we can extract the standard Schrödinger equation as an approximation, and then use it to build the spatial part of the basis functions for a one-particle system in an external (electromagnetic) field. Finally, n-electron quantum states can be represented as direct products of one-particle states, including the spin.

We now introduce an external (time-independent) Coulomb potential acting on the n-electron system, specified by a vector $\mathbf{Z} = (Z_1, \ldots, Z_m)$, where $Z_k|e|$ represents a (massless) positive *test* charge. In addition, the vector $\xi = (\xi_1, \ldots, \xi_m)$ specifies the distribution of these positive charges in the laboratory space $\Re^{3m}$ (i.e., $\xi_k \in \Re^3$ is the position of the kth charge). These two vectors define the *classical part* in the present model (the classical or C-system).

For the electrons (the quantum or Q-system), we consider a transverse electromagnetic field represented by the field vector $\mathbf{A}(\mathbf{x}, t)$, $\mathbf{x} \in \Re^3$, defined with respect to the laboratory frame. This operator is coupled to the linear momentum operator leading to an effective kinetic energy operator $K_e(\mathbf{q}) = 1/2m(\mathbf{p} - e/c\mathbf{A}(\mathbf{x}, t))^2$. The n-electron operator $\mathbf{p}$ is represented with derivatives in the $\mathbf{q}$-coordinates, $\mathbf{q} = (\mathbf{q}_1, \ldots, \mathbf{q}_n) \in \Re^{3n}$, where $\Re^{3n}$ supports the Hilbert space for the electrons. Finally, the Hamiltonian for the Q-system becomes:

$$\mathcal{H}_e(\mathbf{q}, \xi) = K_e(\mathbf{q}) + V_{ee}(\mathbf{q}, \mathbf{q}') + V(\mathbf{q}, \xi), \tag{1}$$

with $V_{ee}(\mathbf{q}, \mathbf{q}')$ the electron–electron repulsion. Note that we arrive at the operator (1) after defining a quantum subsystem in the field of classical charges; equation (1) does not involve the removal of centre of mass translations. In turn, the *external* Coulomb potential contains the classical–quantum (V_{CQ}) and classical–classical (V_{CC}) interactions:

$$V(\mathbf{q}, \xi) = V_{CQ} + V_{CC} = -e^2 \sum_{j,s} \frac{Z_j}{\|\xi_j - \mathbf{q}_s\|} + e^2 \sum_{j<k} \frac{Z_j Z_k}{\|\xi_j - \xi_k\|}, \tag{2}$$

written in units of $4\pi\varepsilon_0 = 1$. For the moment, we leave aside the linear and quadratic coupling terms, $\mathbf{p} \bullet \mathbf{A}$ and $\|\mathbf{A}\|^2$, in $K_e(\mathbf{q})$. These operators are later included to describe the interaction between the external world and the Q-system. (Other operators such as the spin-orbital coupling should also be included at a later stage.)

We focus now on the construction of the electronic basis for the Q-system. These functions will be determined from the quantum Hamiltonian $\mathcal{H}_e(\mathbf{q}, \xi)$, but they must also be subject to the special-relativity transformation. The latter can easily be taken into account by adding phase factors to the electronic states. For a beam experiment, for

example, the inertial frames related to the reactant quantum states appear to move with respect to the laboratory frame. If the inertial frame moves along the unit vector $\mathbf{k}$ with speed $\mathbf{v} = \mathbf{k}v$, then its velocity and kinetic energy will be included in the phase factor: $\exp(im_{\mathrm{e}}[2c^2 + v^2]t/2\hbar)$, where m_{e} is the electron mass at rest [12]. (As usual, quantum calculations are carried out with rest masses.) When using this approach, the classical dynamics of the system will enter via phase factors. Moreover, the classical nature of the external source is incorporated through the Coulomb potential $V(\mathbf{q}, \xi)$. Below, we discuss how to build the remaining quantum-mechanical contribution to the electronic state.

2.1. GED wave functions

For the Q-system, the basic idea [13] is that there exists an attractor for the external sources of Coulomb potential completely defined in terms of a *stationary electronic wave function* $\psi_k(\mathbf{q})$. The attractor for the positive charges corresponds to a minimum of the energy functional $U(\xi; [\psi_k(\mathbf{q})])$ defined as an expectation value over $\mathbf{q}$:

$$U\big(\xi; [\psi_k(\mathbf{q})]\big) = \big\langle \psi_k(\mathbf{q}) \big| \mathcal{H}_{\mathrm{e}}(\mathbf{q}, \xi) \psi_k(\mathbf{q}) \big\rangle. \tag{3}$$

The electronic functions $\{\psi_i(\mathbf{q})\}$ are such that those corresponding to bound states yield *one and only one* minimum energy configuration in real space $\Re^{3m}$, i.e., $U(\xi; [\psi_k(\mathbf{q})])$ is a single-well confining potential. The single minimum for $U(\xi; [\psi_k(\mathbf{q})])$ is denoted by $\xi^k \in \Re^{3m}$. We find two types of ξ^k-attractors: (a) those belonging to molecular bound states, where $\|\xi^k\| < \infty$, and (b) those for subsystems asymptotically-separated along a specific direction in ξ-space, where $\|\xi^k\| \to \infty$. Note that, whereas the potential energy $U(\xi; [\psi(\mathbf{q})])$ changes with ξ, the functions $\{\psi_i(\mathbf{q})\}$ do *not* depend on the geometrical arrangement of the background of positive charges. These functions are *diabatic* in the sense that they preserve *one* electronic configuration for all ξ values.

Let us now consider an n-electron system with vector $\mathbf{Z}$ whose ground-state electronic wave function $\psi_0(\mathbf{q})$ defines a single-minimum attractor, i.e., $\|\nabla_\xi U(\xi; [\psi_0(\mathbf{q})])\| = 0$ only at $\xi = \xi^0$. In addition to this necessary condition, $U(\xi; [\psi_0(\mathbf{q})])$ is also chosen stationary with respect to variations in Hilbert space, $\delta_\psi U(\xi; [\psi_0(\mathbf{q})]) = 0$. The variational principle leads to

$$\big\langle \delta\psi \big| \big[\mathcal{H}_{\mathrm{e}}\big(\mathbf{q}, \xi^0\big) - E_0\big(\xi^0\big) \big] \psi_0(\mathbf{q}) \big\rangle = 0, \tag{4}$$

where $E_0(\xi^0)$ is a Lagrange multiplier ensuring normalization of the wave function. Since $\delta\psi$ is arbitrary, $\psi_0(\mathbf{q})$ satisfies an Euler–Lagrange relation: $\mathcal{H}_{\mathrm{e}}(\mathbf{q}, \xi^0)\psi_0(\mathbf{q}) = E_0(\xi^0)\psi_0(\mathbf{q})$ [14]. In other words, the ground-state wave function can be obtained as a solution of a Schrödinger-like equation with the single-point Hamiltonian $\mathcal{H}_{\mathrm{e}}(\mathbf{q}, \xi^0)$. For an n-fermion system, this electroneutral Hamiltonian is bounded from below and has a nondegenerate spatial eigenfunction $\psi_0(\mathbf{q})$ [15]. Moreover, it follows from the properties of the Coulomb operators that single-point molecular Hamiltonians $\mathcal{H}_{\mathrm{e}}(\mathbf{q}, \xi^k)$

are essentially self-adjoint [16], i.e., $\mathcal{H}_e(\mathbf{q}, \xi^k)$ will have a complete set of eigenfunctions (which can be taken orthogonal):

$$\mathcal{H}_e\big(\mathbf{q}, \xi^k\big)\psi_j(\mathbf{q}) = E_j\big(\xi^k\big)\psi_j(\mathbf{q}). \tag{5}$$

Except for accidental degeneracies, the potential energy values $E_j(\xi^k)$ will be distinct for different ξ^k. These results ensure that there exist a set of eigenfunctions $\{\psi_j(\mathbf{q})\}$ for $\mathcal{H}_e(\mathbf{q}, \xi^0)$. It remains to show that the set $\{\psi_j(\mathbf{q})\}$ diagonalizes the electronic Hamiltonian $\mathcal{H}_e(\mathbf{q}, \xi)$ for all ξ-configuration, i.e., that $\{\psi_j(\mathbf{q})\}$ are *V-representable* diabatic functions.

2.2. *Diagonalization of the electronic molecular Hamiltonian*

In the present conceptual scheme, the most relevant Hamiltonians for the molecular system are the $\mathcal{H}_e(\mathbf{q}, \xi^k)$ operators associated with unique attractors. These attractors (and the associated symmetries they impose on molecular properties) are, in turn, determined by the solutions of equation (5), and not by spatial distribution of the background of positive test charges. We reason as follows. Let $\{\psi_j(\mathbf{q})\}$ be the set of eigenfunctions computed with the single-point Hamiltonian for the lowest energy attractor $\mathcal{H}_e(\mathbf{q}, \xi^0)$. These functions are independent of ξ, but they may not be, in general, eigenfunctions of $\mathcal{H}_e(\mathbf{q}, \xi)$. However, since the set is complete, we can represent any function in the image of $\mathcal{H}_e(\mathbf{q}, \xi)$ as

$$\mathcal{H}_e(\mathbf{q}, \xi)\psi_j(\mathbf{q}) = \sum_k c_{jk}(\xi)\psi_k(\mathbf{q}), \tag{6}$$

where, by definition, $U(\xi; [\psi_j(\mathbf{q})]) = \langle\psi_j(\mathbf{q})|\mathcal{H}_e(\mathbf{q}, \xi)\psi_j(\mathbf{q})\rangle = c_{jj}(\xi)$. Let us now also rewrite the general Hamiltonian as $\mathcal{H}_e(\mathbf{q}, \xi) = \mathcal{H}_e(\mathbf{q}, \xi^0) + \Delta V(\xi^0, \xi, \mathbf{q})$, and consider that $\{\psi_j(\mathbf{q})\}$ are the basis functions for the irreducible representations of the Schrödinger group, with ψ_0 being associated with the totally symmetric representation in $\mathbf{q}$ coordinates. Since the $\{\psi_j(\mathbf{q})\}$ are eigenfunctions of $\mathcal{H}_e(\mathbf{q}, \xi^0)$, the off-diagonal brackets $\langle\psi_s(\mathbf{q})|\mathcal{H}_e(\mathbf{q}, \xi^0)\psi_j(\mathbf{q})\rangle$ will vanish for $s \neq j$. However, the "left-over" operator $\Delta V(\xi^0, \xi, \mathbf{q})$ is also symmetric with respect to electron and ξ-coordinates, and therefore $\langle\psi_s(\mathbf{q})|\Delta V(\xi^0, \xi, \mathbf{q})\psi_j(\mathbf{q})\rangle = 0$ if $s \neq j$. (Note that the shift in ξ in the V_{CC} potential in equation (2) does not affect the electrons.) It follows that

$$\big\langle\psi_s(\mathbf{q})\big|\mathcal{H}_e(\mathbf{q}, \xi)\psi_j(\mathbf{q})\big\rangle = 0, \quad \text{if } s \neq j, \tag{7}$$

i.e., the set $\{\psi_j(\mathbf{q})\}$ diagonalizes the Hamiltonian for all ξ: $\mathcal{H}_e(\mathbf{q}, \xi)\psi_j(\mathbf{q}) = E_j(\xi)\psi_j(\mathbf{q})$. These basis functions are ξ-independent eigenfunctions of all one-point Hamiltonians, including those associated with the ξ^k attractors. Accordingly, each attractor produces the same set of eigenfunctions, although their associated eigenvalues $E_j(\xi^k) = U(\xi^k; [\psi_j(\mathbf{q})])$ may appear in different order. In this latter case, the only apparent dependence of the electronic diabatic functions on the ξ-geometry would be in the j-indices used to label them.

The diabatic functions represent the electronic states of an isolated molecule in the classical-quantum model. The idea is that, in absence of an external electromagnetic

field (e.g., radiation, a solvent, or a colliding molecule), there is no physical mechanism for changing a diabatic $|\psi_j(\mathbf{q})\rangle$-state. Yet, given that the $\{\psi_j(\mathbf{q})\}$ is a complete set, the diabatic functions can be used to describe the electronic state in the presence of a field. In this case, the general quantum states $|\Phi\rangle$ will be solutions of the extended eigenvalue equation:

$$\left(\mathcal{H}_e(\mathbf{q}, \xi) + V_{e\text{-field}}\right)\Phi(\mathbf{q}; \xi) = E(\xi)\Phi(\mathbf{q}; \xi), \tag{8}$$

where the operator for the interaction between the electrons and the external field can be written approximately as $V_{e\text{-field}} \approx -(e/mc)\mathbf{A} \bullet \mathbf{p}$, with $\mathbf{A}$ the field vector and $\mathbf{p}$ the total electronic linear momentum operator. The $|\Phi\rangle$ states are represented as a superposition

$$\Phi(\mathbf{q}; \xi) = \sum_s c_s(\xi)\psi_s(\mathbf{q}) \tag{9}$$

of diabatic functions. The $\{c_s\}$ coefficients, and consequently the state function $\Phi(\mathbf{q}; \xi)$, depend on the spatial arrangement of the classical positive charges *and* the intensity of the electromagnetic field. As a result of the dependence on the field, it is possible that the contribution of various diabatic states to $|\Phi\rangle$ will evolve as the positive charges move in the laboratory space. Given that a diabatic state $|\psi_j\rangle$ represents a state of the isolated molecule (i.e., a chemical species), these ξ-dependent changes correspond to electronic (Franck–Condon-like) transitions in the field [17]. As shown in the next section, the set of diabatic functions can also be used to build the wave function for the complete quantum-mechanical system of nuclei and electrons with and without an external field.

3. Born–Oppenheimer separation scheme in the clamped-nuclei approximation

In the context of the BO method, the electronic Hamiltonian is denoted as $H_e(\mathbf{q}, \mathbf{R})$, where $\mathbf{R}$ is the vector defining the configuration space for m massive point charges (the nuclei). In the present work, we include the Coulomb operator for the nuclear repulsion in $H_e(\mathbf{q}, \mathbf{R})$; note that this term is often omitted in the electronic BO Hamiltonian, but added later to build a potential energy hypersurface. Central to the BO approach is the occurrence of a nuclear equilibrium configuration for the ground state [18], denoted by $\mathbf{R}_0^{BO}$. It is also implicit in the original formulation of the method that one associates a body-fixed rotating system with the Hamiltonian $H_e(\mathbf{q}, \mathbf{R}_0^{BO})$ [19]. The body-fixed frame introduces a constraint in $\mathbf{R}$-space, and, in fact, it makes impossible to use rigorously this space as the domain for the nuclear wave functions. (See [8] for a discussion on the difficulties of electron–nuclear separation in body-fixed frames.) For clarity, we use $\mathbf{R}^{BO}$ (instead of $\mathbf{R}$) to label the nuclear position vector when used in the BO scheme with a frame constraint.

In common practice though, the *clamped-nuclei model* has taken the place of the original BO approach (see [20, appendix 8]); we refer consequently to this approach as the *standard* BO scheme. Here, the nuclear masses are taken to be infinite in order to solve the electronic problem defined by $H_e(\mathbf{q}, \mathbf{R}^{BO})$; this operator is implicitly taken to be defined with respect to an inertial (i.e., a non-rotating) frame [21].

Mathematically, the central assumption of the standard BO method is as follows. An *exact* quantum state $|\Psi\rangle$ for an isolated molecule is given as a function of all quantum particles (electrons and nuclei); this $\Psi(\mathbf{q}, \mathbf{R})$ is an eigenfunction of the total operator $H_{\text{tot}}(\mathbf{q}, \mathbf{R}) = K_{\text{N}}(\mathbf{R}) + H_{\text{e}}(\mathbf{q}, \mathbf{R})$, where $K_{\text{N}}(\mathbf{R})$ is the kinetic energy operator for the nuclei. Using an integration over $\mathbf{q}$-coordinates, this function can be written as a product [22]:

$$\Psi(\mathbf{q}, \mathbf{R}) = f(\mathbf{R})g(\mathbf{q}, \mathbf{R}). \tag{10}$$

Although rigorous, this result is of little use because the functions f and g are not associated with any physical operators. However, the standard BO approach interprets the g-function as an "electronic" function, with a dependence on the nuclear coordinates that is purposely denoted as *parametric* by writing $g(\mathbf{q}, \mathbf{R}) = g_{\text{e}}(\mathbf{q}; \mathbf{R})$. The approximation is completed by computing $g_{\text{e}}(\mathbf{q}; \mathbf{R}) = g_{\text{e},j}(\mathbf{q}; \mathbf{R}^{\text{BO}})$, the jth eigenfunction of the clamped-nuclei Hamiltonian:

$$H_{\text{e}}(\mathbf{q}, \mathbf{R}^{\text{BO}})g_{\text{e},j}(\mathbf{q}; \mathbf{R}^{\text{BO}}) = E_j(\mathbf{R}^{\text{BO}})g_{\text{e},j}(\mathbf{q}; \mathbf{R}^{\text{BO}}). \tag{11}$$

Finally, by considering $E_j(\mathbf{R}^{\text{BO}})$ the jth potential energy hypersurface for the motion of the nuclei, an approximation to $\Psi(\mathbf{q}, \mathbf{R})$ emerges by computing the nuclear wave function as

$$\left[K_{\text{N}}(\mathbf{R}^{\text{BO}}) + E_j(\mathbf{R}^{\text{BO}})\right]f_{sj}(\mathbf{R}^{\text{BO}}) \approx \varepsilon_{sj}^{\text{BO}}f_{sj}(\mathbf{R}^{\text{BO}}). \tag{12}$$

with the additional assumption

$$K_{\text{N}}(\mathbf{R}^{\text{BO}})f_{sj}(\mathbf{R}^{\text{BO}})g_{\text{e},j}(\mathbf{q}; \mathbf{R}^{\text{BO}}) \approx g_{\text{e},j}(\mathbf{q}; \mathbf{R}^{\text{BO}})K_{\text{N}}(\mathbf{R}^{\text{BO}})f_{sj}(\mathbf{R}^{\text{BO}}),$$

i.e., the dependence of $g_{\text{e},j}(\mathbf{q}; \mathbf{R}^{\text{BO}})$ on $\mathbf{R}^{\text{BO}}$ is neglected for infinitely-massive nuclei. For our discussion below, the key aspect of the approximation is to assume that the exact result in equation (10) can be transferred to the structure of the electronic wave function as in equation (11).

3.1. Comparison with the GED approximation

We can now compare this procedure with the one described in section 2, and discuss how the $|\Psi\rangle$ state for the electro-nuclear system can be represented in the GED scheme.

First, we note that the $H_{\text{e}}(\mathbf{q}, \mathbf{R}^{\text{BO}})$ Hamiltonian has no information on nuclear masses; in fact, it resembles the Hamiltonian $H_{\text{e}}(\mathbf{q}, \xi)$ for the classical system of m positive charges. (The operators are still motivated by different conceptual models, given that $H_{\text{e}}(\mathbf{q}, \mathbf{R}^{\text{BO}})$ is extracted from the complete Hamiltonian *after separating the nuclear centre-of-mass*.) When using *the same inertial frame*, $H_{\text{e}}(\mathbf{q}, \mathbf{R}^{\text{BO}})$ and $\mathcal{H}_{\text{e}}(\mathbf{q}, \xi)$ will indeed be identical, and thus two single-point Hamiltonians, e.g., $H_{\text{e}}(\mathbf{q}, \mathbf{R}_0^{\text{BO}})$ and $\mathcal{H}_{\text{e}}(\mathbf{q}, \xi^0)$, must produce the same eigenfunctions $g_{\text{e},j}(\mathbf{q}; \mathbf{R}_0^{\text{BO}}) \equiv \psi_j(\mathbf{q})$. Since the set $\{\psi_j(\mathbf{q})\}$ is valid for all ξ-configurations (thus, all $\mathbf{R}_0^{\text{BO}}$ configurations), we conclude that $\{g_{\text{e},j}(\mathbf{q}; \mathbf{R}_0^{\text{BO}})\}$ and the diabatic set $\{\psi_j(\mathbf{q})\}$ are the same set of eigenfunctions for

all $\mathbf{R}^{\mathrm{BO}}$. In other words, the standard BO scheme in an inertial frame with clamped nuclei does *not* produce functions that are parametrically dependent on the nuclear positions. The only geometrical dependence will appear in the potential energies, given that equations (5), (7) and (11) imply that $E_j(\mathbf{R}^{\mathrm{BO}}) \equiv E_j(\xi) = U(\xi; [\psi_j(\mathbf{q})])$.

This reasoning may appear perplexing because it implies that the electronic wave functions extracted from the BO (so-called adiabatic) approximation does not depend on the nuclear geometry, that is, they should be *diabatic* in the sense used in the present work. Regarding their *apparent* dependence on $\mathbf{R}^{\mathrm{BO}}$, two points must be taken into account:

(a) If one uses the lowest energy attractor $H_{\mathrm{e}}(\mathbf{q}, \mathbf{R}_0^{\mathrm{BO}})$ to label the $\{g_{\mathrm{e},j}(\mathbf{q}; \mathbf{R}_0^{\mathrm{BO}})\}$ functions, this labeling may not necessarily reflect the ordering of eigenvalues at other geometries. Given that the energy curves $E_j(\mathbf{R}^{\mathrm{BO}}) = \langle g_{\mathrm{e},j}(\mathbf{q}; \mathbf{R}_0^{\mathrm{BO}})|H_{\mathrm{e}}(\mathbf{q}, \mathbf{R}^{\mathrm{BO}}) \cdot g_{\mathrm{e},j}(\mathbf{q}; \mathbf{R}_0^{\mathrm{BO}})\rangle$ cross each other at discrete $\mathbf{R}^{\mathrm{BO}}$ values, it is customary to re-label the electronic wave function so as to assign a lower j-index for the $g_{\mathrm{e},j}(\mathbf{q}; \mathbf{R}_0^{\mathrm{BO}})$ function with the lower $E_j(\mathbf{R}^{\mathrm{BO}})$ value. That is, after a *diabatic curve crossing* $E_j(\mathbf{R}^{\mathrm{BO}}) = E_k(\mathbf{R}^{\mathrm{BO}})$, an electronic wave function would have appeared to change *adiabatically* of electronic configuration at $g_{\mathrm{e},j} \rightarrow g_{\mathrm{e},k}$ at $\mathbf{R}^{\mathrm{BO}}$. In this sense, the diabatic functions do depend *implicitly* on the ξ-geometry through the j-indices. To reflect this fact, we can write the functions as $\{\psi_{j(\xi)}(\mathbf{q})\}$. In particular, the electronic *molecular* ground-state function $\psi_{0(\xi^0)}(\mathbf{q})$ describes a different state from the $\psi_{0(\infty)}(\mathbf{q})$ function associated with a dissociated system at an asymptotic attractor $\|\xi\| \rightarrow \infty$. However, a $g_{\mathrm{e},j} \rightarrow g_{\mathrm{e},k}$ switch does not represent a physical process but only a change in the diabatic potential energy function being monitored (e.g., the lowest energy configuration). As discussed in section 4, only an external electromagnetic field provides a mechanism to change the dominant diabatic state as a function of a change in the $\mathbf{R}^{\mathrm{BO}}$-geometry.

(b) There is an artificial, *explicit* dependence on the $\mathbf{R}^{\mathrm{BO}}$-geometry that is introduced by the practical manner in which electronic functions are usually determined. In the familiar computational algorithms, electronic configurations are cast in molecular orbitals. In turn, these are built as linear combinations of atomic orbitals centred at "nuclear" positions, rather than being defined at points fixed with respect to a reference frame. As a result, the basis set actually varies with the geometry (e.g., when studying an asymptotic separation channel leading to $\|\xi\| \rightarrow \infty$). This change in basis set translates into an apparent continuous geometrical drift in the electronic function as the BO approximation numerically connects two different electronic states. The resulting functions are indeed parametrically dependent on the geometry, and they can be denoted by the usual $\psi_j(\mathbf{q}; \mathbf{R}^{\mathrm{BO}})$. Although the resulting dependence on $\mathbf{R}^{\mathrm{BO}}$-geometry is artificial, it is certainly hard to avoid since it is embedded in the standard molecular-orbital methodology. One alternative would be to represent the electronic wave functions using basis functions centred on a fixed grid [23]. A sufficiently fine grid would allow one to represent electronic wave functions with high angular momentum by using very simple s-type functions defined at each grid point.

In summary, the continuous re-optimization of the atomic basis set, in addition to the re-labeling of states after energy crossings, should be regarded as *artifacts* introduced

when trying to fit the BO approach into a concept of bond dissociation. From first principles, the eigenfunctions of the clamped-nuclei electronic Hamiltonian could be taken to be *strictly diabatic*, in the sense used in this work.

3.2. Quantization of the nuclear motion in the GED approximation

While $H_e(\mathbf{q}, \mathbf{R}^{BO})$ and $\mathcal{H}_e(\mathbf{q}, \xi)$ are equivalent in the same inertial frame, there is no reason to mimic the BO approximation when trying to build the electro-nuclear function $\Psi(\mathbf{q}, \xi)$ from the diabatic functions $\{\psi_{j(\xi)}(\mathbf{q})\}$. In particular, it is not necessary to assume that $\Psi(\mathbf{q}, \xi)$ is the product of a *single* electronic function and a *single* nuclear function. In order to approximate the states of the full electro-nuclear quantum system, given by the Hamiltonian $H_{full}(\mathbf{q}, \xi) = K_N(\xi) + \mathcal{H}_e(\mathbf{q}, \xi)$, we reason as follows. First, we consider that the $\{\psi_j(\mathbf{q})\}$-set of GED eigenfunctions is complete, and thus can be used to represent the states of an *n*-electron system. (For the sake of a simpler notation, we return to omitting the ξ-dependence in the j-labels.) Secondly, we take into account that the quantum nuclear dynamics provides a mechanism for coupling the GED states. Accordingly, we assume the *i*th molecular quantum state $|\Psi_i\rangle$ to be represented as a linear superposition (cf. equation (9)):

$$\Psi_i(\mathbf{q}, \xi) = \sum_j B_{ij}(\xi)\psi_j(\mathbf{q}), \tag{13}$$

where the $\{B_{ij}(\xi)\}$ coefficients determine the nuclear dynamics in the absence of an electro-magnetic field. We now use (13) to solve the Schrödinger equation for the entire system. Given that the diabatic functions satisfy $\mathcal{H}_e(\mathbf{q}, \xi)\psi_j(\mathbf{q}) = E_j(\xi)\psi_j(\mathbf{q})$ and $\langle\psi_i|\psi_j\rangle = \delta_{ij}$ for all but isolated ξ-geometries, then $\|\Psi_i(\mathbf{q}, \xi)\|^2 = \sum_j \|B_{ij}(\xi)\|^2 = 1$, and the matrix element $\langle\Psi_i|H_{full}(\mathbf{q}, \xi)\Psi_i\rangle = \mathrm{E}_{full}^{(i)}$ leads to:

$$\sum_j \left\{\langle B_{ij}(\xi)|K_N(\xi)B_{ij}(\xi)\rangle + \langle B_{ij}(\xi)|E_j(\xi)B_{ij}(\xi)\rangle\right\} = E_{full}^{(i)}, \tag{14a}$$

which implies the differential equation for the individual nuclear functions:

$$K_N(\xi)B_{ij}(\xi) + E_j(\xi)B_{ij}(\xi) = E_{full}^{(i)}B_{ij}(\xi). \tag{14b}$$

Masses appear in the differential operator $K_N(\xi)$; whether one uses atomic or nuclear masses is a matter of convenience [24]. According to equations (14), any state for the entire molecular system *may* be a superposition of diabatic electronic states; the requirement is that there be two or more nuclear functions $\{B_{ij}(\xi)\}$ degenerate at $E_{full}^{(i)}$ for different $E_j(\xi)$ diabatic potentials. This condition can be achieved in reactions that are effectively described by symmetric double-well potentials. Thus, superposition is a possibility even for the ground state $E_{full}^{(0)}$, where a highly-localized nuclear function $B_{0j}(\xi)$ would often be expected. Yet in practice, near-degeneracies will be more common for higher-energy levels; in particular, levels in a high-energy continuum will certainly couple a large number of diabatic basis functions. In contrast, degeneracy should

be infrequent in a low-lying state, which would then be approximated as a single prod-uct: $\Psi_{ij}(\mathbf{q}, \xi) \sim B_{ij}(\xi)\psi_j$, in agreement with the so-called "rigged" BO approach [25]. Nevertheless, the fact remains that each $|\Psi_i\rangle$ state of an *isolated* molecular system *can* still contain information on multiple diabatic attractors and dissociation channels when using the GED approach. The coupling between electronic diabatic states will of course be much more extensive in the presence of an external electromagnetic field, as shown below.

When considering a single diabatic molecular attractor, equation (14b) provides a model for the calculation of vibration–rotation spectra. For the coefficient $B_{ij}(\xi)$, the standard procedure would be to define a centre of mass using the coordinates for ξ^j-attractor, and then impose the Eckart conditions for vibro-rotational separation. For oscillations near the attractor, the function $B_{ij}(\xi)$ will approach the ith eigenfunction of a $3m$-dimensional oscillator with a quasi-harmonic well given by the $E_j(\xi)$ diabatic energy function.

The case of a molecular system in the presence of an electromagnetic field can be treated similarly. First, we can represent the states of the purely-electronic system by a function such as $\Phi_k(\mathbf{q}, \xi)$ in equation (9); the linear superposition coefficients $\{c_{kj}(\xi)\}$ will depend on the field vector $\mathbf{A}$. Then, we can represent the states of the complete electro-nuclear quantum system as a linear superposition of $\Phi_k(\mathbf{q}, \xi)$ functions

$$\Psi_i(\mathbf{q}, \xi) = \sum_k a_{ik}(\xi)\Phi_k(\mathbf{q}, \xi) = \sum_k \sum_j a_{ik}(\xi)c_{kj}(\xi)\psi_j(\mathbf{q}), \qquad (15)$$

which reduces to (13) if $B_{ij} = \sum_k a_{ik}c_{kj}$. These coefficients depend on the external field.

Nevertheless, it is not necessary to solve the nuclear dynamics if we only seek to study the interplay of electronic states relevant to a given chemical reaction. In the next section, we show how the GED procedure can be used to monitor the evolution of elec-tronic states in a field of *classical* nuclear charges and in the presence of electromagnetic radiation.

4.   Electronic transitions and chemical processes in the GED approach

A quantum-classical system prepared in a diabatic state $\psi_j(\mathbf{q})$ associated with the ξ^j-attractor cannot spontaneously change of electronic state. If its corresponding di-abatic potential energy curve crosses another at ξ^*, say $E_j(\xi^*) = E_{j+1}(\xi^*)$, one can always re-order the electronic functions so that $\psi_{j(\xi^*-d\xi)}(\mathbf{q}) \rightarrow \psi_{j+1(\xi^*+d\xi)}(\mathbf{q})$ and $\psi_{j+1(\xi^*-d\xi)}(\mathbf{q}) \rightarrow \psi_{j(\xi^*+d\xi)}(\mathbf{q})$. However, there is no physical process associated with this re-labeling. In order to produce a transition, we need an electromagnetic field that couples a manifold of electronic states. In fact, the presence of an external field vector may be able to cause a change in the dominant diabatic function at a geometry *other than* that of the diabatic crossing $E_j(\xi^*) = E_{j+1}(\xi^*)$. Moreover, the transition between two states $\psi_j(\mathbf{q}) \rightarrow \psi_{j+1}(\mathbf{q})$ may require, depending on symmetry considerations, the

presence of a third state $\psi_k(\mathbf{q})$ (an actual *transition state*). In our discussions, we follow the formulation based on equations (8) and (9).

4.1. Two-state model for a dissociative transition

Consider a chemical reaction involving an *initial* diabatic state $\psi_1(\mathbf{q})$ associated with a molecular attractor ξ^1 and a *final* diabatic state $\psi_2(\mathbf{q})$ associated with a asymptotic attractor ξ^2. Let us also assume that the $\psi_1(\mathbf{q})$ and $\psi_2(\mathbf{q})$ have different symmetry with respect to coordinate inversion in the inertial frame. A simple example is found in the dissociation of a diatomic radical, e.g., $H_2^+ \rightarrow H^+ + H(1s)$. Here, $\psi_1(\mathbf{q})$ can be taken as the σ_g molecular ground state. The correct dissociation into H^+ and $H(1s)$ requires the linear combinations of molecular orbitals $\sigma_g + \sigma_u$ and $\sigma_g - \sigma_u$. However, since these two basis functions are not degenerate at the ground-state attractor ξ^1, then we can in practice correlate the σ_u function to the dissociation limit represented by $\psi_2(\mathbf{q})$. (Alternatively, we could consider the exchange reaction with molecular beams, $H^+ + H(1s) \rightarrow H(1s) + H^+$, for which H_2^+ acts as a transition state. This case is omitted here since it requires a 3-state model.) A convenient coordinate to study the reaction is the elongation variable x that measures the deviation in the position of the two positive charges with respect to the attractor ξ^1. In terms of x, $\psi_1(\mathbf{q})$ and $\psi_2(\mathbf{q})$ have different parity and are coupled in the presence of an electromagnetic field. As a result, this reaction can be studied in first approximation by monitoring the behaviour of a quantum state $|\Phi\rangle$ that superimposes only two diabatic states $\psi_1(\mathbf{q})$ and $\psi_2(\mathbf{q})$:

$$\Phi(\mathbf{q}, x) = c_1(x)\psi_1(\mathbf{q}) + c_2(x)\psi_2(\mathbf{q}). \tag{16}$$

Depending on the external field, we can expect that the initial state, specified by $c_1(0) \approx 1$, will transform into the dissociated state $c_2(\infty) \approx 1$; in this case, no transition state is required.

Figure 1 shows typical curves $U_1 = \langle\psi_1(\mathbf{q})|H_e\psi_1(\mathbf{q})\rangle$ and $U_2 = \langle\psi_2(\mathbf{q})|H_e\psi_2(\mathbf{q})\rangle$ for the bound and asymptotic diabatic states, respectively (top diagram, dotted lines). (From now on, we make no distinction between H_e and $\mathcal{H}_e$.) The confining attractor ξ^1 is associated with a potential energy function U_1 that increases monotonically for $x > 0$. In the case of H_2^+, this situation corresponds to an electronic state that remains diabatically as σ_g and therefore does not lead to dissociation. For the present qualitative analysis, we omit the particulars of any diatomic molecule and just consider two curves parametrized as $U_1(x) = 1.25x^2$ and $U_2(x) = 5 + 10e^{-x/2}$, in arbitrary units.

Using the trial function (16), we compute the matrix elements of the Hamiltonian $H_{tot} = H_e(\mathbf{q}, \xi) + V_{e\text{-field}}$ for the interaction between the external field and the electronic subsystem. In first approximation, the interaction potential is represented only as one term: $V_{e\text{-field}} \propto \mathbf{A} \bullet \mathbf{p}$. Symmetry considerations show that $V_{12} = \langle\psi_1(\mathbf{q})|V_{e\text{-field}}\psi_2(\mathbf{q})\rangle$ is not zero; we take the matrix element V_{12} as a parameter proportional to the external field. (Note also that symmetry implies $[H_{tot}]_{12} = V_{12}$ and $[H_{tot}]_{ii} = [H_e]_{ii} = U_i$.)

The diagonalization of the resulting matrix ($[H_{tot}]_{ij}) \in \Re^{2\times2}$ yields a lowest-energy solution $E(x)$:

$$E(x) = U_1 + \frac{1}{2}\left\{\Delta U_{12} - |\Delta U_{12}|\left[1 + 4\left(\frac{V_{12}}{\Delta U_{12}}\right)^2\right]^{1/2}\right\},\qquad(17a)$$

where $\Delta U_{12} = U_2 - U_1$. The corresponding coefficient in the $\psi_2(\mathbf{q})$ function is:

$$|c_2(x)| = \left\{1 + \left(\frac{V_{12}}{[E(x) - U_1]}\right)^2\right\}^{-1/2},\qquad(17b)$$

with the normalization condition $|c_1|^2 + |c_2|^2 = 1$. As $x \to \infty$, equations (17) predict that: (i) the total wave function approaches the asymptotic diabatic state as $|c_2(x)| \to \{1 - (V_{12}/2U_1)^2\}$, and (ii) its corresponding energy is approached from below, $E(x) \to \{U_2 - (V_{12})^2/|\Delta U_{12}|\}$.

Figure 1(a) shows the lowest value for $E(x) = \langle\Phi|H_{tot}\Phi\rangle$ as a function of x (thick line), in the particular case of $V_{12} = 1$. In this model, this value corresponds to a relatively weak coupling between the states. Note that the total energy $E(x)$ interpolates smoothly between the diabatic curves, producing a result that effectively *resembles* an avoided crossing. The contribution of the quantum subsystem to the total energy is given by $\langle\Phi|H_e\Phi\rangle$, which appears in dotted line in figure 1(a); it shows a similar behaviour to that of $\langle\Phi|H_{tot}\Phi\rangle$, but it produces a maximum located over the diabatic crossing $U_2 = U_1$. The analysis is completed in figure 1(b), which shows the evolution in the diabatic basis states. As x increases, there is a sharp transition from $c_1 \approx 1$ to $c_2 \approx 1$; the transition is centred about the diabatic crossing $U_2 = U_1$.

Figure 2 contrasts the latter behaviour with a case where the diabatic states are strongly coupled (e.g., when using a more intense electromagnetic field). In this case, all parameters are the same as those in figure 1, except for $V_{12} = 5$. Again, we observe that the total quantum state evolves from $\Phi \approx \psi_1$ to $\Phi \approx \psi_2$ as x increases, but the change is not very sharp. There is a large region of configurational space where both states contribute strongly to the state $|\Phi\rangle$. Figure 2(a) shows a significant difference in the effective total energy with respect to the case $V_{12} = 1$ in figure 1. The curve for the lowest eigenvalue in the field ($E(x) = \langle\Phi|H_{tot}\Phi\rangle$, in thick line) interpolates between the diabatic curves U_1 and U_2, *but it does not produce a barrier*. The curve $E(x)$ exhibits a flat maximum *below* the dissociation limit $U_2(\infty)$ and a *very shallow* secondary minimum at large x; the asymptotic limit $E \to U_2(\infty)$ corresponds to a *maximum*. Note that the minimum near the molecular attractor ξ^1 deepens and shifts slightly towards larger x values when coupling strongly to the field.

This simple example suggests that the GED methodology can retrieve the familiar notions of "energy barrier" and "avoided crossing" without resorting to nonadiabatic couplings. These features appear naturally as effects in the model, where transitions are mediated by the couplings to the electromagnetic field. Depending on the intensity of
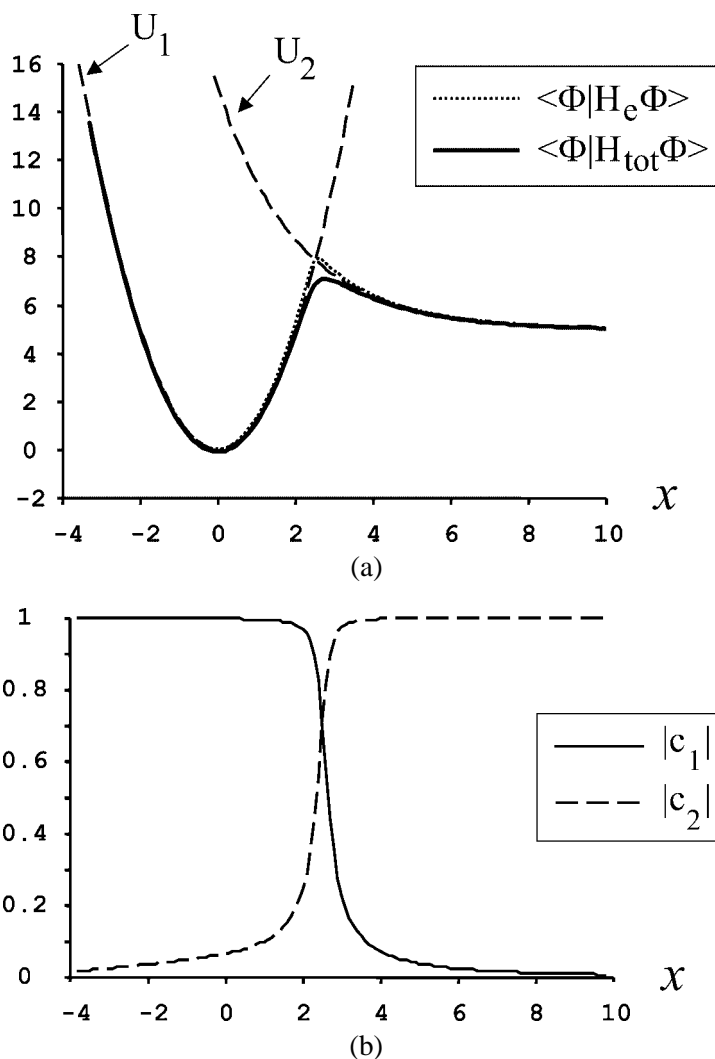
Figure 1. Evolution of a general quantum state $|\Phi\rangle$ describing the dissociation of an open-shell molecular diatomic attractor. The dissociation is mediated by an external electromagnetic field and requires no transition state. The top diagram shows the diabatic potential energies for reactant and product (U_1 and U_2, respectively, in dashed lines), as well as the total energy ($\langle\Phi|H_{tot}\Phi\rangle$) and the intrinsic molecular energy in the field ($\langle\Phi|H_e\Phi\rangle$) as a function of the elongation variable x. The bottom diagram shows how the two diabatic basis functions contribute to the total quantum state. The results correspond to the case of diabatic states *weak-coupled* in the field ($V_{12} = 1$). There is a sharp transition from reactant to product and an apparent barrier in $\langle\Phi|H_{tot}\Phi\rangle$.

the latter, our model predicts the disappearance of barriers, the stabilization of attractors in the field, and the occurrence of weakly-bound states at large internuclear separations. All these features have a counterpart in the behaviour of real diatomic systems.
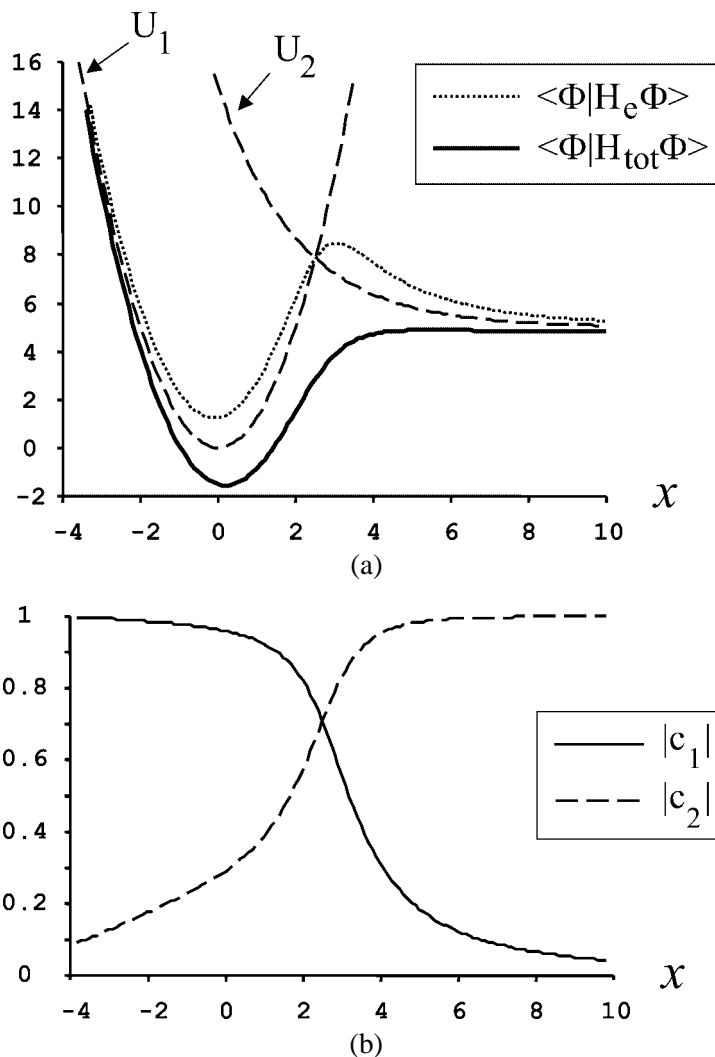
Figure 2. Evolution of the quantum state $|\Phi\rangle$ for the dissociation of an open-shell molecular diatomic attractor in the presence of an intense external electromagnetic field. Symbols and parameters are the same as in figure 1, except for the value $V_{12} = 5$ for the coupling of diabatic functions. In this case, the transition from reactant to product is broader over a range of x values. Moreover, instead of a barrier above the asymptotic limit $U_2(x \to \infty)$, we find a broad flat maximum and a shallow minimum for $\langle \Phi | H_{\text{tot}} \Phi \rangle$.

4.2. Three-state model for a reaction involving two molecular attractors

We can extend the previous model to the case of two states $\psi_1(\mathbf{q})$ and $\psi_2(\mathbf{q})$ with the same symmetry with respect to inversion. This situation can be found, for instance, in the isomerization of closed-shell species. (A different case, corresponding to the dissociation of a closed-shell molecule into a singlet asymptotic attractor can be found in [26].) For symmetry reasons, the diabatic states of two closed-shell isomers are not

coupled in the external field: $[H_{tot}]_{12} = V_{12} = 0$. Thus, the electronic change $\psi_1(\mathbf{q}) \rightarrow \psi_2(\mathbf{q})$ requires *a transition state* associated with an open-shell (yet singlet) diabatic state $\psi_3(\mathbf{q})$.

We consider a minimal model consisting of three bound diabatic states $\psi_1(\mathbf{q})$, $\psi_2(\mathbf{q})$, and $\psi_3(\mathbf{q})$ associated with three harmonic potential energy functions $U_i(x)$. For the sake of simplicity, we describe the reactant and product by diabatic energy functions differing only in the location of the respective minima: $U_1(x) = 1.25x^2$ and $U_2(x) = 1.25(x - 3)^2$ (in arbitrary units). Finally, for the diabatic transition state (TS), we use a potential energy function with an attractor shifted towards the product $U_3(x) = 2 + 2.5(x - 2.5)^2$. Using these functions, the standard BO approximation would yield an artificial transition between $\psi_1(\mathbf{q})$ and $\psi_2(\mathbf{q})$, and an effective energy barrier, at the diabatic curve crossing $U_1 = U_2$, i.e., $x = 1.5$. As we show below, the GED approach produces also an effective barrier, but its location and height depends on the TS-function and the applied external field.

Using a superposition function $\Phi(\mathbf{q}, x) = c_1(x)\psi_1(\mathbf{q}) + c_2(x)\psi_2(\mathbf{q}) + c_3(x)\psi_3(\mathbf{q})$ for the total quantum state, the matrix for the complete Hamiltonian $H_{tot} = H_e + V_{e\text{-field}}$ becomes:

$$\left([H_{tot}]_{ij}\right) = \begin{pmatrix} U_1 & 0 & V_{13} \\ 0 & U_2 & V_{23} \\ V_{13} & V_{23} & U_3 \end{pmatrix}, \tag{18}$$

where we have considered: (i) $[H_{tot}]_{ii} = U_i$, given that $V_{ii} = \langle\psi_i(\mathbf{q})|V_{e\text{-field}}\psi_i(\mathbf{q})\rangle = 0$ because of the symmetry of the interaction operator $V_{e\text{-field}}$, (ii) $[H_{tot}]_{12} = 0$ because $\psi_1(\mathbf{q})$ and $\psi_2(\mathbf{q})$ are nondegenerate (i.e., $[H_e]_{12} = 0$), yet their parity is opposite that of $V_{e\text{-field}}$ (i.e., $V_{12} = 0$), and (iii) the $\psi_3(\mathbf{q})$ function has the same parity as $V_{e\text{-field}}$, and thus V_{13} and V_{23} need not be zero. By monitoring the lowest eigenvalue of (18), $E(x) = \langle\Phi|H_{tot}\Phi\rangle$, we can follow the onset of electronic transitions as a function of the control variable x. The corresponding coefficients for the wave function of the total quantum state in the diabatic states are: $|c_1| = V_{13}c_3/|E - U_1|$, $|c_2| = V_{23}c_3/|E - U_2|$, and $|c_3| = \{(V_{13}/|E - U_1|)^2 + (V_{23}/|E - U_2|)^2 + 1\}^{-1/2}$. This result implies that the diabatic curve crossing ($U_1 = U_2$) does not produce a state with the same weight in reactant and product (i.e., $c_1 = c_2$) unless both states are coupled to the TS with the same strength (i.e., only if $V_{13} = V_{23}$). Note that, since $\psi_i(\mathbf{q})$ is diabatic, the matrix elements V_{ij} are independent of x and proportional to the intensity of the applied electromagnetic field.

As an illustrative example, figure 3 shows the results in the case where reactant and product are equally coupled to the TS: $V_{13} = V_{23} = 2$. In figure 3(a), the diabatic potentials $\{U_i(x)\}$ appear in dashed lines and the total energy in the field, $E(x) = \langle\Phi|H_{tot}\Phi\rangle$, appears in thick line. The $E(x)$ function produces a one-dimensional barrier that interpolates between the reactant and product potentials, leading to an effective "avoided crossing" between $U_1(x)$ and $U_2(x)$. The bottom diagram in figure 3 indicates that the state function Φ evolves slowly from $\psi_1(\mathbf{q})$ to $\psi_2(\mathbf{q})$ over a range of x-configurations. The key role of the TS in the electronic transition is apparent by the strong, broad maximum in $|c_3|$.
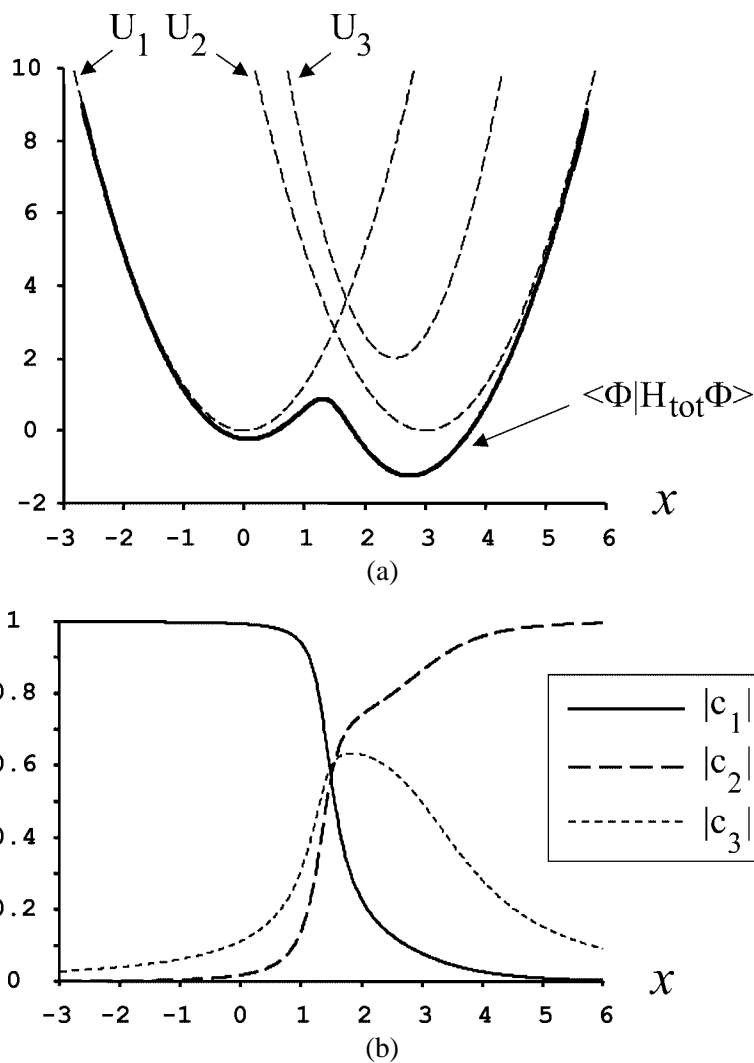
Figure 3. Evolution of the quantum state $|\Phi\rangle$ for the isomerization of two closed-shell molecular species. The reactant and product attractors are represented by diabatic potential energies U_1 and U_2 which differ only the x value for the location of their minima (dashed lines). A transition between these diabatic states is mediated by the external field and a bound *transition state* (TS) with diabatic potential U_3 (also in dashed line). The total energy in the field ($\langle\Phi|H_{tot}\Phi\rangle$, thick line) was computed using equal couplings to the TS, $V_{13} = V_{23} = 2$. In this case, the product is effectively stabilized in the field; its quantum state which has a strong contribution from the TS. Note that the effective barrier in $\langle\Phi|H_{tot}\Phi\rangle$ decreases, and adopts an x-geometry that is closer to the reactant state, in agreement with the familiar Hammond postulate.

Due to the coupling mediated by the external field, the $E(x)$ function is no longer symmetric with respect to the diabatic crossing at $x = 1.5$. The three extrema of $E(x)$, located at geometries denoted by x_i^*, $i = 1, 2, 3$, are shifted with respect to the barrier implied by the standard two-state BO approximation. The product is stabilized since

Table 1

Contribution of the diabatic reactant, product, and transition states (ψ_1, ψ_2, and ψ_3, respectively) to the total quantum state $|\Phi\rangle$ at selected geometries of the three-state system in figure 3. The selected x values correspond to the extrema of the total energy in the field $E(x) = \langle\Phi|H_{tot}\Phi\rangle$, using the parameters in figure 3. The $E(x)$ maximum plays the role of an effective *pseudo*-transition-structure; the latter resembles the reactant, as it would be expected for an exothermic reaction (i.e., an "early" barrier). The diabatic states are mixed, although the minima 1 and 2 resemble more the reactant and product, respectively.

x^*	$E(x^*)$	$|c_1|$	$|c_2|$	$|c_3|$
0.07 (min)	-0.2344	0.9926	0.0218	0.1194
1.31 (max)	0.8829	0.7859	0.3692	0.4960
2.74 (min)	-1.2439	0.1036	0.8285	0.5503

the minimum $E(x_3^*)$ is lower than $E(x_1^*)$ for the reactant; table 1 indicates an effective endothermic barrier with $E(x_2^*) - E(x_1^*) = -1.0095$. In this barrier, the x_2^* maximum plays the role of a *pseudo*-transition structure, with its energy value $E(x_2^*)$ located below that of the diabatic crossing at $x = 1.5$. Moreover, the barrier maximum is closer to the reactant ($x_2 - x_1 = 1.24$) than to the product ($x_3 - x_2 = 1.43$). Table 1 gives also the structure of the wave function Φ at x_i^* in terms of the diabatic states. From table 1, it is clear that the quantum state $|\Phi\rangle$ at x_2^* has a strong contribution from the diabatic reactant state ψ_1. This result is in agreement with the Hammond postulate ([27] and references therein), whereby a reactant-like (or "early") TS is expected for endothermic reactions and a product-like (or "late") TS for exothermic ones. Our analysis recovers these notions by quantifying the similarity between the total state and diabatic basis functions in terms of the $\{c_i(x)\}$ coefficients. This measure of similarity is physically more appealing than one based on comparing reaction coordinate values.

5.   Conclusions

In the GED approach, the quantum states of an electronic system are represented as superpositions of diabatic functions; all information on the positive charge geometry is contained in the linear superposition coefficients, not in the diabatic basis functions. If an isolated electronic system is prepared initially at an eigenstate of the electronic Hamiltonian (i.e., a diabatic state), no transition takes place; the latter occur only if the proper physical conditions are provided (e.g., an electromagnetic field is present). In addition, some systems may require the mediation of a transition state that couples reactants and products. Finally, it should be noted that transitions will be observed *within a range of configurations for the positive charge background*. The GED model is consistent with the notion that one can manipulate the background of positive charges so as to reach the ξ-geometries with large amplitudes in the product state. In catalytic reactions, these ξ-geometries should span a region of configurational space commensurable with that of an active site or a conventional transition structure. Depending on the region's size, and the residence time of the reactant in it, one could translate product probabilities into kinetic data such as rate constants.

It is worth restating some key conceptual differences with the standard BO approach. First, in the GED scheme, the operator $\mathcal{H}_e$ is *not* derived from a molecular Hamiltonian using approximations dealing with nuclear masses. Instead, a background of *classical massless* positive test charges is introduced merely as a *tool* to build a complete basis set of diabatic electronic functions. If desired, these functions can then be used to represent the general states of a fully quantum electro-nuclear system. Secondly, nuclear masses do *not* appear in the GED analysis either explicitly or implicitly for the electronic system, even though $\mathcal{H}_e$ is isomorphic to the BO electronic Hamiltonian in an inertial frame and clamped nuclei. The differences are subtle yet significant, since they allows us to circumvent some known difficulties associated with interpreting the BO internal electronic Hamiltonian after the removal of centre-of-mass translations [8]. Using the diabatic basis functions, equation (13) provides the most general representation for the quantum states of the complete molecular system of *m*-nuclei and *n*-electron system:

$$\Psi_i(\mathbf{q}, \xi) = \sum_j B_{ij}(\xi)\psi_j(\mathbf{q}).$$

If the nuclear charges are taken as classical particles, the geometry-dependent coefficients $\{B_{ij}(\xi)\}$ contain no information on nuclear masses and represent the coupling between electronic states mediated by the electromagnetic field. When the field is absent and the nuclei are included as quantum particles, the $B_{ij}(\xi)$-coefficients couple electronic states whose diabatic potential energy surfaces yield degenerate functions for the nuclear dynamics. These geometry-dependent coefficients couple *all* electronic states whenever we consider a fully quantum-mechanical molecule embedded in an external field.

In closing, it is worth restating that useful concepts commonly employed in the BO separation scheme also find their place in the GED approach, although in a different guise. For instance, avoided crossings in absence of a field are artifacts in the BO approximation resulting from either re-labeling the electronic functions after a diabatic crossing, or basis set dependence on nuclear positions. In contrast, "avoided" crossings appear naturally in the GED approach of field-mediated transitions; their overall location and shape, however, depend on the geometry of the TS-attractor and its coupling with reactant and product. The total molecular energy function $\langle\Phi|H_{tot}\Phi\rangle$ of a general quantum state $|\Phi\rangle$ allows us to recover notions such as those of energy barrier, shallow double minima, and the Hammond postulate for the similarity between molecular species along a reaction coordinate.

Acknowledgments

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