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Citation	Van Voorhis, Troy et al. “The Diabatic Picture of Electron Transfer, Reaction Barriers, and Molecular Dynamics.” Annual Review of Physical Chemistry 61.1 (2010): 149–170.
As Published	http://dx.doi.org/10.1146/annurev.physchem.012809.103324
Publisher	Annual Reviews
Version	Author's final manuscript
Accessed	Sat Oct 31 15:51:52 EDT 2015
Citable Link	http://hdl.handle.net/1721.1/69649
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The diabatic picture of electron transfer, reaction barriers and molecular dynamics

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(Dated: July 15, 2009)

Abstract

Diabatic states have a long history in chemistry, beginning with early valence bond pictures of molecular bonding and stretching through the construction of model potential energy surfaces to the modern proliferation of methods for computing these elusive states. In this review we summarize the basic principles that define the diabatic basis and demonstrate how they can be applied in the specific context of constrained density functional theory. Using illustrative examples from electron transfer and chemical reactions, we show how the diabatic picture can be used to extract qualitative insight and quantitative predictions about energy landscapes. The review closes with a brief resumé of the challenges and prospects for the further application of diabatic states in chemistry.

Key Words: Reaction Dynamics, Nonadiabatic, Density Functional

I. INTRODUCTION

Qualitatively, a diabatic electronic state is one that does not change its physical character as one moves along a reaction coordinate. This is in contrast to the adiabatic, or Born-Oppenhimer, electronic states which change constantly so as to remain eigenstates of the electronic Hamiltonian. A classic example of the interplay between diabatic and adiabatic pictures is given by sodium chloride dissociation (Figure 1). Here, the ground adiabatic state is thought of as arising from the avoided crossing between an ionic and a covalent state. The adiabatic state thus changes character - transforming from Na-Cl to Na^{+}-Cl^{-} as the bond gets shorter - while the ionic and covalent configurations play the role of diabatic states.

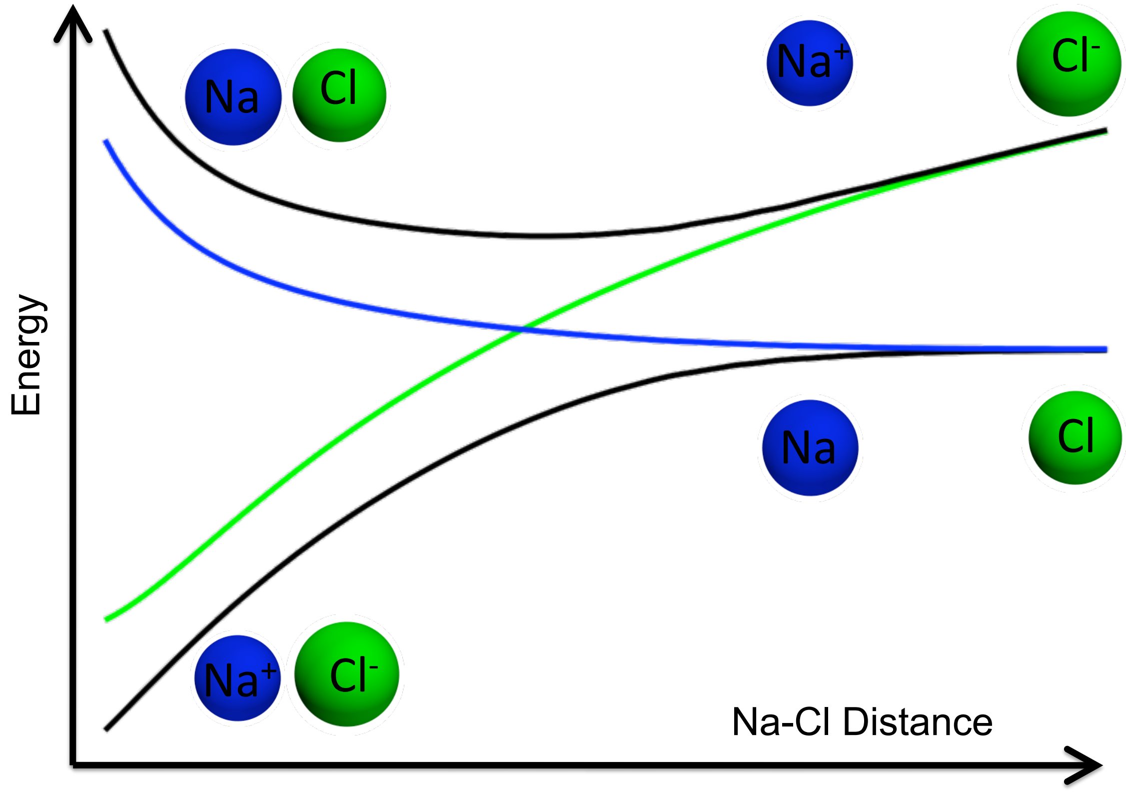

FIG. 1: NaCl dissociation in the diabatic and adiabatic representations. The ionic (green) and covalent (blue) diabatic states maintain the same character across the potential energy surface, while the adiabatic states (black) change.

Diabatic electronic states play a role in a variety of chemical phenomena but are, at the same time, under-appreciated by many chemists. For example, diabats are often used in the construction of potential energy surfaces because they are smooth functions of the nuclear coordinates [1–3]. In spectroscopy, diabatic states are invoked to assign vibronic transitions and rationalize the rates of interstate transitions [4–6]. When describing electronically excited dynamics more generally, diabatic states are advantageous because they typically have a small derivative coupling, simplifying the the description of electronic transitions [7–11]. In scattering theory, diabatic states connect to clearly-defined product channels [12–14]. Finally, diabatic states play a qualitative role in our understanding of molecular bonding [15–17] (as illustrated by the NaCl example above), electron transfer [18, 19] and proton tunnelling [20–22]

This review article is intended as an introduction the basic concepts about how diabatic states are constructed and how they are used to describe chemical phenomena. After a summary of different definitions of diabatic states - and in particular why so many competing definitions exist - we focus on a particular definition based on constrained density functional theory (CDFT). We show how CDFT-derived diabatic states are computed in practice and discuss several illustrative chemical applications.

II. STRICT DIABATS CANNOT BE OBTAINED FROM ADIABATS

Of central importance to the study of diabatic electronic states is the idea of a strictly diabatic basis (SDB)[23]. By definition, for a set of strict diabats, $|\Phi_i\rangle$, the derivative coupling between any two states vanishes at every possible nuclear configuration, $\mathbf{R}$:

$$\mathbf{d}_{ij}(\mathbf{R}) \equiv \langle \Phi_i | \frac{\partial}{\partial \mathbf{R}} \Phi_j \rangle = 0 \ \ \forall \ i, j, \mathbf{R} \tag{1}$$

This definition is in line with our qualitative idea that diabatic states do not change when the nuclei move (e.g. the derivative is zero). Given an arbitrary set of M adiabatic states, $|\Psi_i\rangle$ - say, a few important electronic states involved in a photochemical reaction - it would clearly be desirable to develop a formula for a set of M strictly diabatic states that span the same Hilbert space as the given adiabats. That is to say, one would like to have a set of orthonormal states that satisfy Eq. 1 and for which

$$|\Phi_i(\mathbf{R})\rangle = \sum_j A_{ij}(\mathbf{R}) |\Psi_j(\mathbf{R})\rangle \tag{2}$$

for some matrix $\mathbf{A}$. The matrix $\mathbf{A}$ is called the adiabatic-to-diabatic transformation matrix, for obvious reasons[24, 25].