The Parallel-Transported (Quasi)-Diabatic Basis

Robert Littlejohn,[1] Jonathan Rawlinson,[2] and Joseph Subotnik[3]

[1)]Department of Physics, University of California, Berkeley, California 94720 USA

[2)]School of Mathematics, University of Manchester, Manchester UK

[3)]Department of Chemistry, University of Pennsylvania, Philadelphia, PA, USA

(*Electronic mail: subotnik@sas.upenn.edu)

(*Electronic mail: jonathan.rawlinson@manchester.ac.uk)

(*Electronic mail: robert@wigner.berkeley.edu)

(Dated: 19 October 2022)

This article concerns the use of parallel transport to create a diabatic basis. The advantages of the parallel-transported basis include the facility with which Taylor series expansions can be carried out in the neighborhood of a point or a manifold such as a seam (the lo-cus of degeneracies of the electronic Hamiltonian), and the close relationship between the derivative couplings and the curvature in this basis. These are important for analytic treatments of the nuclear Schrödinger equation in a neighborhood of degeneracies. The parallel-transported basis bears a close relationship to the singular-value basis; in this arti-cle both are expanded in power series about a reference point and they are shown to agree through second order but not beyond. Taylor series expansions are effected through the projection operator, whose expansion does not involve energy denominators or any type of singularity, and in terms of which both the singular-value basis and the parallel-transported basis can be expressed. The parallel-transported basis is a version of Poincaré gauge, well known in electromagnetism, which provides a relationship between the derivative cou-plings and the curvature and which, along with a formula due to Mead, affords an efficient method for calculating Taylor series of the basis states and the derivative couplings. The case in which fine structure effects are included in the electronic Hamiltonian is covered.

I. INTRODUCTION

This article concerns bases of electronic wave functions in polyatomic molecules that span a chosen subspace of strongly coupled states. We are especially interested in the parallel-transported basis and the closely related singular-value basis. The context of this work is Born-Oppenheimer theory, applied to multiple, strongly coupled electronic states, a subject that is treated and reviewed in many places (Cederbaum (2004); Faraji, Gómez-Carrasco, and Köppel (2012); Köppel (2004); Matsunaga and Yarkony (1998); Yarkony (1996, 2004, 2001, 2012); Zhu and Yarkony (2016); Kendrick, Mead, and Truhlar (2002); Mead (1988, 1992); Mead and Truhlar (1979, 1982); Richings and Worth (2015); Richings and Habershon (2020)). The bases we refer to are really fields of bases, that is, defined over some region of the nuclear configuration space.

In this article we refer to any basis that is smooth over the region in question as "diabatic," without any assumption that the derivative couplings vanish and without the common prefix "quasi." We do this because as a practical matter the derivative couplings in polyatomic molecules never vanish; if we wish to refer to the (rare) cases in which they do, we will refer to a "strictly diabatic" basis. In addition, the designation "quasi" implies that a quasi-diabatic basis is close to a strictly diabatic basis, that is, that the derivative couplings are small. There is much wishful thinking in the literature that the derivative couplings can be made small enough to be ignored, but without quantitative justification. A careful analysis by Kendrick, Mead, and Truhlar (2002), however, shows that the derivative couplings are generically of order unity over a range of the order of one atomic unit, unless forced to be even larger by small energy denominators. In addition numerical evidence (Choi and Vaníček (2021)) supports the conclusion that these couplings must be taken into account for accurate results.

There is some subtlety in the question of the magnitude of the derivative couplings, however, because these couplings are components of a vector potential of a gauge theory (Pacher et al. (1989); Pacher, Cederbaum, and Köppel (1993); Wittig (2012); Kendrick and Mead (1995); Mead (1980b, 1987, 1992); Bohm, Boya, and Kendrick (1991); Bohm et al. (1992); Bohm, Kendrick, and Loewe (1992); Kendrick (2004); Berry (1984)), in which the gauge transformations are changes of frame, specified by (ideally) smooth fields of unitary matrices. We call this the Mead-Truhlar-Berry vector potential or connection (Mead and Truhlar (1979); Berry (1984)). In this article, the derivative couplings and the Mead-Truhlar-Berry connection or vector poten-tial (the only vector potential we consider) are almost the same thing (the small differences are

explained in Sec. IV D).

Thus, diabatic bases are not unique, and different choices have different advantages and disadvantages. Several choices of diabatic basis have been reviewed by Pacher, Cederbaum, and Köppel (1993), including the singular-value basis (Pacher, Cederbaum, and Köppel (1988)) and the Lorentz-gauge basis (Pacher et al. (1989)), which minimizes the mean square of the connection over a region of nuclear configuration space.

In addition there is the basis of Werner and Meyer (1981), which diagonalizes the dipole operator in a single dimension, and of Cave and Newton (1996, 1997) and Subotnik et al. (2008) who generalized this diagonalization to multidimensional problems. Historically, within the chemistry literature, the emphasis has been on finding a good set of diabatic states that serve as initial and final states for electron transfer problems, e.g., Subotnik et al. (2009), so that one can apply Mar-cus theory; that being said, our treatment here is more general dynamically (rather than serving as a platform for a spin-boson model Hamiltonian (Xu and Schulten (1994); Rosso and Dupuis (2006))). In such a case, there is no need to have an element of electronic locality inherent within a smooth diabatic basis.

The advantages of the parallel-transported basis include the facility with which it can be expanded in Taylor series about given points or even given manifolds, such as seams or degeneracy manifolds, and the close relationship it bears to the curvature. These features will be explained in detail in this article, but the following is some of the basic ideas.

It turns out that by means of a gauge transformation it is possible to make the vector potential vanish at any given point. Indeed, both the parallel-transported basis and the singular-value basis do this, as will be explained below. In fact, in some circumstances (triatomics in the electrostatic model) there exists a parallel-transported frame that causes the vector potential to vanish over the entire degeneracy manifold or seam, which is a one-dimensional curve. In the neighborhood of such a point or such a manifold in such a basis, the derivative couplings are indeed small. Then the question is how rapidly the couplings grow as we move away from the chosen point or manifold.

This question draws attention to the curvature, a tensor that is a function of the derivative couplings and their derivatives. Here the important fact is that the curvature tensor, unlike the vector potential, is a tensor, so that it transforms under a gauge transformation by simple conjugation by the unitary matrix specifying the transformation, see (68). Thus, the magnitude of the curvature tensor, whose square is the sum of squares of its components, is invariant under a gauge transformation. In a sense the curvature represents the part of the connection that is gauge-invariant,

while the part that is not is what is changed by a gauge transformation. We will not attempt to make this notion precise but merely use it to motivate the idea that to minimize the connection we should find a gauge that expresses the connection in terms of the curvature. As we will show, the parallel-transported basis does this.

Our interest in the parallel-transported basis is part of a larger project in which we aim to find analytical treatments of the nuclear Schrödinger equation in the neighborhood of conical intersections. Part of that work involves normal forms for Landau-Zener transitions in many dimensions; these are illustrated by Littlejohn and Flynn (1992), in which a 2-dimensional Landau-Zener problem is treated. A conical intersection has an effective range in the nuclear configuration space, outside of which the potential energy surfaces can be decoupled by adiabatic means (Weigert and Littlejohn (1993); Panati, Spohn, and Teufel (2002); Teufel (2003)). That range depends on the nuclear momentum and gets larger as that momentum grows, but even for fairly large nuclear momenta by ordinary standards, that is, momenta such that the nuclear kinetic energy is of the order of one atomic unit, the range of a conical intersection is still quite small in atomic units. Thus, Taylor series expansions are a viable approach for covering the strongly coupled region.

Expansions in Taylor series about a conical intersection have a long history, including the works by Mead (1983); Thompson and Mead (1985); Yarkony (1997) on derivative couplings and their singularities in the neighborhood of a conical intersection and by Yarkony (2000) on the bifurcations of degeneracy manifolds. This work focuses on the projection operator and its expansion, an attractive intermediate goal since the projection operator is smooth and diabatic bases such as the singular-value and parallel-transported basis can be expressed in terms of it. The usual approaches work with the adiabatic basis, which leads to small or vanishing energy denominators when one moves tangent or nearly tangent to the degeneracy manifold or seam. In this article we avoid the adiabatic basis as much as possible, mainly using the projection operator as a substitute; this gives us expansions that are valid even when one moves tangent to the degeneracy manifold.

In Sec. II we discuss aspects of the singular-value diabatic basis, which is due to Pacher, Cederbaum, and Köppel (1988, 1993). We begin with a variational principle for the singular-value diabatic basis that differs somewhat from the one used in the original work on the subject, but which shows a closer connection with the variational foundations of the parallel-transported basis, which is our main topic. We emphasize the issue of the smoothness of the solution; although the singular-value diabatic basis is smooth, some of the the objects used in its derivation and construction are

not. We express the singular-value basis in terms of the projection operator, an important step since the latter is smooth. In addition, the projection operator can be expanded about a reference point, possibly on a conical intersection, something that we carry out in Sec. III. We then use that to expand the singular-value basis to third order about the reference point.

In Sec. IV we develop the theory of parallel transport and use it to construct the parallel-transported basis and its expansion about a reference point, which we show agrees with the singular-value basis through second order but differs at third order. We then express the Hamiltonian, connection and curvature in the parallel-transported bases as power series expansions about a reference point. We point out that the parallel-transported frame is a version of Poincaré gauge, which in electromagnetism is a gauge that is transverse in real space. This allows us to express the connection in terms of an integral involving the curvature, which provides an efficient method of calculating the connection in the parallel-transported frame. Finally we point out that construc-tions of diabatic bases are only needed in 3N 3 directions of nuclear configuration space, because in the remaining 3 directions the nuclear configuration changes by a pure rotation, and in those di-rections the basis should transform by a rotation operator. Thus the construction of diabatic bases takes place on a (3N 6)-dimensional "section" of the nuclear configuration space.

In Sec. V we discuss degeneracy manifolds, usually called seams, and the construction of diabatic bases in the neighborhood of them. For example, in triatomic molecules in the electrostatic model for the electronic Hamiltonian, for which the degeneracy manifold is a 1-dimensional curve in the 3-dimensional section, we construct a diabatic basis in a tubular region surrounding the curve. Again the connection is expressed in terms of the curvature, but the components of the connection along the degeneracy manifold and transverse to it have different expansions. We also point out that in the case of triatomics with the electrostatic model, it is possible to choose a gauge such that the derivative couplings (in all of their components) vanish on the degeneracy manifold. Finally, in Sec. VI we present some conclusions.

In this article we denote the adiabatic basis by $|a(x);k\rangle$, the singular-value diabatic basis by $|d(x);k\rangle$, the basis that is parallel transported away from a reference point by $|p(x);k\rangle$ and the basis that is parallel transported away from the degeneracy manifold by $|D(x);k\rangle$, where x is a point of nuclear configuration space and k is a quantum number or sequencing number for the basis state.

II. THE SINGULAR-VALUE DIABATIC BASIS

In this section we cover some aspects of the singular-value diabatic basis, which is due to Pacher, Cederbaum, and Köppel (1988, 1993). This basis is easy to compute at a point x of configuration space, and it does not require integration along some path starting at another point x_0. For these reasons it is popular in numerical work. It is also conceptually simple and geometrically compelling. In this article we present some new results on the singular-value basis, including a discussion of its smoothness properties, its relation to the projection operator, and Taylor series expansions about a reference point.

We begin by showing that the singular-value basis satisfies a certain variational principle. This differs only slightly from the original variational principle used by Pacher, Cederbaum, and Köppel (1993), but we present it anyway because it reveals a close connection with parallel transport which is the main topic of this paper. Both variational principles lead to the same (singular-value) diabatic basis. Other variational principles that have been considered, for example, the one by Cimiraglia et al. (1985), are not equivalent and lead to different diabatic bases.

We also emphasize the issue of the smoothness of the singular-value diabatic basis, something that takes some effort since the adiabatic basis with which the construction begins is not smooth. Finally we show that the singular-value diabatic basis can be expressed in terms of the projection operator onto the coupled subspace of the electronic Hilbert space. Since the projection operator is smooth, this shows that the singular-value diabatic basis is, too, and it also provides a method for expanding the singular-value basis in a Taylor series about a reference point.

A. Terminology and Notation

We let x represent a point of the nuclear configuration space in the center-of-mass frame, so that x stands for the collection of N 1 Jacobi vectors (Aquilanti and Cavalli (1986); Smirnov and Shitikova (1977)) or their 3(N 1) components, where N 3 is the number of nuclei. We let H(x) be the electronic Hamiltonian, which initially we assume is taken in the electrostatic model, although later we make some comments about the changes necessary when fine structure effects are included. We label the energy levels of H(x) by a sequencing number k, and define a "coupled subspace" by a set of adjacent energy levels,

$$A = \{k_0; k_0 + 1; \ldots; k_0 + N_l \quad 1\}; \tag{1}$$

where N_l is the number of coupled levels. Usually in practice k_0 is the ground state and N_l is small. We consider a region of nuclear configuration space in which energy level k_0 is not degenerate with level $k_0 - 1$ and level $k_0 + N_l - 1$ is not degenerate with level $k_0 + N_l$, that is, a region in which there are no degeneracies that cross the boundaries of A. Degeneracies within A ("internal degeneracies") are allowed, however (and these require $N_l \geq 2$). In practice, if the region we are interested in does have degeneracies that cross the boundaries of A (caused by "intruder states" (Venghaus and Eisfeld (2016))), we can either excise the locations where those degeneracies occur from the region in question, or we can expand the definition of A to make the problematic degeneracies internal. If we choose the first option then the region after the excision will often fail to be simply connected, which has topological implications for the existence of smooth fields of frames.

For $k \in A$ we denote the energy eigenstates by $|a x; k\rangle$, so that

$$H(x)|a x; k\rangle = e_k(x)|a x; k\rangle; \qquad k \in A; \tag{2}$$

where, as indicated, the energy eigenvalues are $e_k(x)$. The a in the notation $|a x; k\rangle$ indicates the adiabatic basis, and the x-dependence of the eigenstate is separated by a semicolon from the quantum number k.

We let $S_\parallel(x)$ be the subspace of the electronic Hilbert space spanned by the set of vectors $|a x; k\rangle$ for $k \in A$, what we will call the "coupled subspace." The projection operator onto this subspace is

$$P(x) = \sum_{k \in A} |a x; k\rangle\langle a x; k|: \tag{3}$$

We denote the subspace of the Hilbert space orthogonal to $S_\parallel(x)$ by $S^\perp(x)$, and denote the projection operator onto $S^\perp(x)$ by

$$Q(x) = 1 - P(x): \tag{4}$$

For $k \notin A$ we write $|a x; k\rangle$ for a basis in $S^\perp(x)$ that is discrete and orthonormal but otherwise arbitrary. We will call the set of states $\{|a x; k\rangle\}$ for all k the "adiabatic basis", even though the basis states for $k \notin A$ are not energy eigenstates. This is not exactly standard terminology but in fact normal usage is often restricted to the states $k \in A$. In addition there are reasons not to deal with energy eigenstates when $k \notin A$, which present a number of difficulties, both computational and theoretical. Computationally the high lying energy eigenstates are seldom accessible, and theoretically they present problems because their phase and frame conventions have singularities

on surfaces that proliferate at k is increased. In addition there is the problem of the continuum and the transition thereto, which changes as x changes. Actually one never needs to refer to energy eigenstates when $k \not\in A$ and we shall not do so. We must remember, however, that in our "adiabatic basis" the vectors $|a_x; k\rangle$ are energy eigenstates only when $k \in A$.

B. Phase Conventions and Smoothness

Energy eigenstates are defined only to within a phase convention (when nondegenerate) or a frame convention inside the degenerate eigenspace (when degenerate), and this must be kept in mind when using the notation $|a_x; k\rangle$ for $k \in A$. Although it is always possible to assign those conventions at any given point x of the region in question, in general this assignment is not smooth on certain submanifolds of the region as x is varied. Notably this occurs when x lies on an internal degeneracy (usually a conical intersection). There may be additional singularities when x is not on an internal degeneracy; these occur on surfaces that can be moved about by a gauge transformation like a branch cut in the complex plane or the strings of monopoles but that cannot be eliminated. These singularities (of both types) are the main drawback of the adiabatic basis.

In this article when we say that something is smooth we mean that it is a continuous function of x and that it has as many continuous derivatives as needed for any applications we might make. A function is continuous at a point x_0 if it is defined at x_0 and its limit as $x \to x_0$ is independent of the direction of approach and equals the value of the function at x_0. It is precisely in this sense that the adiabatic basis is not continuous at an internal degeneracy (the limit exists as $x \to x_0$ but it depends on the direction of approach), and the lack of continuity implies that the derivatives of the adiabatic basis diverge at such points.

In fact the singularities of the adiabatic basis occur only on a subset of measure zero, so elsewhere, on a subset of full measure, it is possible to talk about the derivatives of the adiabatic basis vectors, as is commonly done in the literature. Such derivatives occur in the derivative couplings and other quantities of interest. Such quantities diverge as a degeneracy is approached, and a great deal of literature is devoted to analyzing and eliminating these divergences. In this article we will simply refrain from ever assuming that the vectors $|a_x; k\rangle$ are smooth functions of x, and, in particular, we never talk about derivatives of these vectors with respect to x. This applies both for $k \in A$ and $k \not\in A$; at any given x we can choose $|a_x; k\rangle$ for $k \not\in A$ as a basis that spans $S^{?}(x)$, but we will not assume that that assignment can be made in a smooth manner as x is varied.

The singularities of the adiabatic basis vectors $|a(x);k\rangle$ for $k \in A$ are always due the impossibility of making phase and/or frame conventions in a smooth manner as x is varied. Granting this, an object constructed out of the basis vectors $|a(x);k\rangle$ can be smooth only if it is independent of the phase and/or frame conventions of the basis.

This applies in particular to the projection operator P(x), defined by (3). The definition is just the expression of the projector onto $S(x)$ in terms of an orthonormal basis in that subspace. But any orthonormal basis can be used for that purpose, including those which differ from $|a(x);k\rangle$ by a change of phase and/or frame conventions. Therefore P(x) is independent of the phase and/or frame conventions for the energy eigenstates $|a(x);k\rangle$ for $k \in A$.

Moreover there are no other reasons why the projection operator might not be smooth. It is true that the projection operator is not defined where degeneracies cross the boundaries of A, but we are excluding such points from the region under consideration.

Thus, the derivatives of P(x) exist and P(x) can be expanded in a Taylor series about any point x_0 in the region in question, in which all derivatives are well defined. Since P(x) is smooth, $Q(x) = 1 - P(x)$ is too.

We have presented a more careful argument for the smoothness of P(x) in Appendix A, in which the basic idea is to use the Cauchy-Kato formula to express P(x) in terms of the electronic Hamiltonian H(x), which is assumed to be a smooth function of x.

C. A Definition of Diabatic Basis

Originally a diabatic basis was defined as one for which the derivative couplings vanish. This would cure the drawback of the adiabatic basis, that the derivative couplings are not only nonzero, they diverge at conical intersections. Unfortunately, such bases do not exist in polyatomic molecules, for which the derivative couplings cannot be transformed away.

Since the main difficulties with the adiabatic basis are due to its lack of smoothness, we suggest that a diabatic basis be defined as one that is smooth in the region in question. This does not quite solve all the problems with the adiabatic basis, however, since if the new basis is rapidly varying then the derivative couplings will be large (not infinite, but large). Thus there must be some understanding on how rapidly the basis vectors change with x.

Given a configuration x_0 we define a diabatic basis as one that is not only smooth (free of singularities) in a neighborhood of x_0 but also smooth enough, in a manner to be specified. In

the literature one is usually interested in the case that x_0 lies on a degeneracy manifold (usually a seam or surface of conical intersection) but there are applications for which this is not so and in the following we shall make no assumptions about x_0.

A diabatic basis so defined is not unique, since any smooth field of unitary transformations on S (x) and another on S ?(x) will map one smooth basis into another. As is well known (Pacher et al. (1989); Bohm et al. (1992); Mead (1992); Pacher, Cederbaum, and Köppel (1993)), such changes of frame are gauge transformations of the theory. Thus additional criteria must be imposed for the selection of a unique diabatic basis.

The derivative couplings (59) involve the derivatives of the basis states and these change when a gauge transformation is carried out. One could take a smooth diabatic basis and subject it to a gauge transformation (a change of frame) based on a unitary transformation that was a smooth function of x in the mathematical sense but rapidly varying on the atomic length scale. The resulting basis would still be smooth in a mathematical sense but it would have large derivative couplings. To avoid this we must require that a diabatic basis be not only smooth, but smooth enough.

Intuitively, a diabatic basis is smooth enough if one must move a distance of order unity in atomic units for the basis vectors to change by an amount of order unity. Both the singular-value basis and the parallel-transported basis satisfy this criterion. Such bases are related by fields of unitary matrices that themselves have a variation on the atomic length scale but not smaller. By this definition, the derivative couplings in a diabatic basis are of order unity when measured in atomic units. They do not vanish, but they do not diverge, either.

We can formalize this by speaking, not of the numerical values of the derivative couplings (or other quantities), but rather their dependence on the Born-Oppenheimer ordering parameter $k = (m/M)^{1/4}$. Many quantities of interest can be assigned an order in k. That is, a quantity that scales as k^n as $k \to 0$ is considered of order k^n. In particular, a quantity that scales as $k^0 = 1$, that is, a quantity that is independent of k for small k, is of order unity in this sense.

This leads us to suggest that a diabatic basis should be defined as one that is smooth and independent of k. This means that the diabatic basis is independent of the nuclear masses M, so that its derivatives and the derivative couplings are of order unity when measured in atomic units. Both the singular-value and the parallel-transported diabatic bases satisfy this condition, since, as we will show, both bases can be expressed in terms of the projection operator (3). The latter depends on the electronic Hamiltonian but not on the nuclear masses, and so is of order $k^0 = 1$,

that is, it is independent of k.

The dependence of the diabatic basis and the derivative couplings on k is important when adiabatic perturbation theory, which is an expansion in powers of k, is carried out (Littlejohn and Flynn (1991); Weigert and Littlejohn (1993); Teufel (2003); Panati, Spohn, and Teufel (2002)). For this purpose one wants the diabatic basis and all of its derivatives to be independent of k.

For reference we will need a basis in the electronic Hilbert space that is independent of x. For convenience we choose this basis to be $|a x_0; k\rangle$, which is the adiabatic basis at x_0. In the literature when this basis is used to study dynamics at points $x = x_0$ it is sometimes called the "crude adiabatic basis."

D. A Variational Criterion

We now present a variational criterion for a diabatic basis, which leads to the singular-value basis. Initially we focus on the part $k \in A$ of the basis that spans the coupled subspace $S(x)$. We define the diabatic basis at x, denoted $|d x; k\rangle$ with a designation d for "diabatic," as the frame at x that is closest to the adiabatic frame at x_0, in the sense that it minimizes the quantity

$$\sum_{k\in A} \big\| |d x; k\rangle - |a x_0; k\rangle \big\|^2 = \sum_{k\in A} (2 - \langle a x_0; k | d x; k\rangle - \langle d x; k | a x_0; k\rangle). \tag{5}$$

According to our definition, to use the notation $|d; x\rangle$ and to call the basis "diabatic" we should both define the basis and show that it is smooth. We defer the latter task to subsection II E and in the meantime refer to the basis provisionally as "diabatic" (which it turns out to be).

Both the diabatic basis $|d x; k\rangle$ and the adiabatic one $|a x; k\rangle$ for $k \in A$ span $S(x)$, so we must have

$$|d x; k\rangle = \sum_{l\in A} |a x; l\rangle U_{lk}(x); \tag{6}$$

where $U_{lk}(x)$ is an $N_l \times N_l$ unitary matrix. Thus the quantity (5) can be written,

$$\sum_{k\in A} 2 \left[1 - \sum_{l\in A} (S_{kl} U_{lk} + S_{kl}^* U_{lk}^*) \right]; \tag{7}$$

where

$$S_{kl} = \langle a x_0; k | a x; l\rangle. \tag{8}$$

The notation S for this matrix is the same as in Pacher, Cederbaum, and Köppel (1993).

With no restrictions on k and l, (8) defines S as an infinite-dimensional, unitary matrix, but for use in the variational principle we only need the $N_l N_l$ block of this matrix, S_{kl} for $k;l \in A$. We find it convenient to partition infinite dimensional matrices like this according to what we will call the a and b subsets of indices, which are those for which $k \in A$ and $k \notin A$, respectively. For example, we partition the infinite dimensional matrix S as follows:

$$S = \begin{pmatrix} S^{aa} & S^{ab} \\ S^{ba} & S^{bb} \end{pmatrix}; \tag{9}$$

so that S^{aa} is an $N_l N_l$ matrix, etc. In terms of this notation, the quantity (5) or (7) can be written

$$2N_l \quad [\mathrm{tr}(S^{aa}U) + \mathrm{c.c.}]: \tag{10}$$

We assume that the adiabatic basis is given as a function of x so that the matrix S^{aa} is known (but it is not assumed to be a smooth function of x). We wish to minimize the quantity (7) with respect to the choice of the unitary matrix U_{kl} (where $k;l \in A$). We enforce the unitarity of U by adding the term,

$$\mathrm{tr}[L(UU^{\dagger} \quad I)] = \sum_{k;l \in A} L_{lk} \left(\sum_{m \in A} U_{km}U_{lm} \quad d_{kl} \right); \tag{11}$$

where L_{kl} is a Hermitian matrix of Lagrange multipliers. Now varying with respect to either U or $U^{\dagger}$ we find

$$S^{aa} = U^{\dagger}L; \tag{12}$$

in which S^{aa} is given and unitary U and Hermitian L are to be determined. The theory of the polar decomposition tells us that if S^{aa} is nonsingular then (12) has a unique solution for a unitary matrix U and a positive definite, Hermitian matrix L. We will show below that S^{aa} is, in fact, nonsingular in a neighborhood of x_0 and that L must be positive definite for a meaningful solution; thus we obtain unique results for U and L over the neighborhood in question. That is, since $(S^{aa})^{\dagger}S^{aa} = L^2$, $L = [(S^{aa})^{\dagger}S^{aa}]^{1=2}$, where here and below by the square root of a positive definite, Hermitian matrix we mean the unique positive definite, Hermitian square root; and given L, $U = L(S^{aa})^{\quad 1}$. Then (6) gives us the diabatic basis at x in terms of a finite linear combination of adiabatic basis vectors at x. This is identical to the singular-value diabatic basis of Pacher, Cederbaum, and Köppel (1988).

E. Smoothness of the Solution

To complete the construction of the basis $|d(x);k\rangle$ we must prove that it is smooth, thereby justifying the use of the terminology "diabatic." In fact, $|d(x);k\rangle$ is smooth, but neither S^{aa}, U or L are. Since singularities are due to the phase and frame conventions for the adiabatic basis states $|a(x);k\rangle$ (frame conventions applying inside a degenerate subspace), let us change these conventions for $k \in A$ by means of an $N_I \times N_I$ unitary matrix V,

$$|a'(x);k\rangle = \sum_{l \in A} |a(x);l\rangle V_{lk}; \tag{13}$$

and study how various quantities transform under such a change. In (13) V is allowed to be a nonsmooth function of x. Combining (13) with (6), the definition of U, and with (8), the definition of S^{aa}, we find

$$S^{aa\prime} = S^{aa}V; \qquad U' = V^{\dagger}U; \qquad L' = V^{\dagger}LV: \tag{14}$$

Thus neither S^{aa}, U nor L is smooth, in general.

On the other hand, the products $S^{aa}U = U^{\dagger}LU$ and $S^{aa}(S^{aa})^{\dagger} = UL^2U$ are invariant under the change (13) and are therefore smooth (for example, $S^{aa\prime}U' = S^{aa}U$), as is the quantity $|\det S^{aa}|$. As for the latter, we note that at $x = x_0$, $S^{aa} = I$ so $|\det S^{aa}| = 1$. Therefore by continuity $\det S^{aa}$ is bounded away from 0 in some finite neighborhood of x_0 (and note that we can use continuity arguments only on smooth functions), and therefore S^{aa} is nonsingular in this neighborhood.

Let us define

$$S = S^{aa}U = U^{\dagger}LU = S^{\dagger}; \tag{15}$$

which, as noted, is a smooth function of x. To get its value at x_0 we require of our diabatic basis that $|d(x_0);k\rangle = |a(x_0);k\rangle$, that is, it agree with the adiabatic basis at x_0. This means that $U = I$ at $x = x_0$, and thus also $L = S = I$ at x_0. But since S is a smooth function of x, it must be positive definite in a neighborhood of x_0. This means that $L = USU^{\dagger}$, which is not smooth, is also positive definite in the same neighborhood (the eigenvalues are not changed by unitary conjugation).

These considerations suggest that rather than factoring S^{aa} via the polar decomposition as in (12), we factor it the other way using $S^{aa} = SU^{\dagger}$ to obtain S and U. That is, we compute $S = [S^{aa}(S^{aa})^{\dagger}]^{1=2}$, and then compute $U = (S^{aa})^{-1}S$. The advantage of this approach is that S, a smooth function of x, takes the place of the nonsmooth L, which is never needed.

F. Relation to the Projection Operator

We still have not shown that the diabatic basis $|d(x);k\rangle$ is a smooth function of x, but if it is we guess that it should be possible to express it purely in terms of the projection operator $P(x)$, which is known to be smooth. This turns out to be the case, as we now show.

For $k \in A$ the procedure above gives the diabatic basis $|d(x);k\rangle$ as a finite linear combination of the adiabatic basis $|a(x);k\rangle$, also for $k \in A$. For some purposes, however, it is convenient to have the diabatic basis expressed as a linear combination of the reference basis $|a(x_0);k\rangle$, in spite of the fact that this involves an infinite number of terms. We obtain a useful form of this expansion by writing, for $k \in A$,

$$\begin{aligned} |d(x);k\rangle = P(x)|d(x);k\rangle &= \sum_{\text{all } l} |a(x_0);l\rangle\langle a(x_0);l| \sum_{m\in A} |a(x);m\rangle\langle a(x);m|d(x);k\rangle \\ &= \sum_{l,m\in A} |a(x_0);l\rangle S^{aa}_{lm} U_{mk} + \sum_{l\notin A,\, m\in A} |a(x_0);l\rangle S^{ba}_{lm} U_{mk} \\ &= \sum_{l\in A} |a(x_0);l\rangle (S^{aa}U)_{lk} + \sum_{l\notin A} |a(x_0);l\rangle (S^{ba}U)_{lk}. \end{aligned} \tag{16}$$

Evidently, for this expansion we need the matrices $S^{aa}U = S$ and $S^{ba}U$.

We define the matrix representation of the projection operator $P(x)$ in the reference basis,

$$P_{kl}(x) = \langle a(x_0);k|P(x)|a(x_0);l\rangle = \sum_{m\in A} \langle a(x_0);k|d(x);m\rangle\langle d(x);m|a(x_0);l\rangle; \tag{17}$$

for all k, l. Now substituting (16) into (17), we obtain

$$\begin{aligned} P^{aa} &= (S^{aa}U)(S^{aa}U)^\dagger = S^{aa}(S^{aa})^\dagger = S^2; \\ P^{ba} &= (S^{ba}U)(S^{aa}U)^\dagger = S^{ba}(S^{aa})^\dagger; \end{aligned} \tag{18}$$

where we partition $P(x)$ as in (9). Thus the matrix $S^{aa}U$ that appears in (16) is the positive definite matrix $S = (P^{aa})^{1/2}$. As for the matrix $S^{ba}U$, we have

$$P^{ba} = S^{ba}U(S^{aa}U)^\dagger = S^{ba}US^\dagger = S^{ba}US; \tag{19}$$

or,

$$S^{ba}U = P^{ba}(P^{aa})^{-1/2}. \tag{20}$$

Thus, both matrices needed in the expansion (16) can be expressed in terms of the projection operator.

Let us write T for the infinite-dimensional unitary matrix that connects the diabatic basis $|dx;k\rangle$ with the reference basis $|ax_0;k\rangle$,

$$|dx;k\rangle = \sum_{\text{all } l} |ax_0;l\rangle T_{lk}; \tag{21}$$

which holds for all k, l. Again, this notation follows Pacher, Cederbaum, and Köppel (1988, 1993), and we note that their variational principle minimizes the quantity

$$\|T - I\|^2: \tag{22}$$

So far we have worked on the case $k \in A$ and found $T^{aa} = S^{aa}U$ and $T^{ba} = S^{ba}U$ in terms of the projection operator. We can find the other blocks, T^{ab} and T^{bb}, by repeating the same procedure we have just been through, but now taking $k \notin A$ and swapping subspaces $a \leftrightarrow b$ and projectors $P \leftrightarrow Q$. This gives altogether,

$$\begin{aligned} T &= \begin{pmatrix} (P^{aa})^{1/2} & Q^{ab}(Q^{bb})^{-1/2} \\ P^{ba}(P^{aa})^{-1/2} & (Q^{bb})^{1/2} \end{pmatrix} \\ &= \begin{pmatrix} P^{aa} & Q^{ab} \\ P^{ba} & Q^{bb} \end{pmatrix} \begin{pmatrix} (P^{aa})^{-1/2} & 0 \\ 0 & (Q^{bb})^{-1/2} \end{pmatrix}; \end{aligned} \tag{23}$$

where we note that $Q^{ab} = -P^{ab}$ and $Q^{bb} = I^{bb} - P^{bb}$, so that the entire result can be expressed in terms of P. It can be directly checked that $TT^\dagger = T^\dagger T = I$; for this one must use the facts that $P = P^\dagger$ and $P^2 = P$.

Now (21) and (23) show that the transformation from the reference basis to the singular-value diabatic basis can be expressed purely in terms of the projection operator. This not only shows that the diabatic basis is smooth in a neighborhood of x_0 but it also allows us to expand the diabatic basis in a Taylor series about x_0.

III. EXPANSION OF THE PROJECTION OPERATOR

In the following we will use the symbol P or $P(x)$ for both the projection operator and its matrix in the reference basis, as in (17), with hopefully little danger of confusion. We wish to expand P in a power series about the reference point x_0. We write $x = x_0 + \Delta x$, where Δx is a displacement vector in nuclear configuration space. We think of all the symbols, x, x_0 and Δx, as standing for the $N - 1$ Jacobi vectors or their $3(N - 1)$ components, effectively using these as coordinates on the nuclear configuration space in the center-of-mass system. We will write these coordinates explicitly as

x^m, x_0^m, x^m, etc., where $m = 1;\ldots;3N$ 3. We use the summation convention on such coordinate indices m, n, etc.

The expansion of the projection operator is a part of degenerate or quasidegenerate perturbation theory, see for example Kato (1949); Bloch (1958); des Cloizeaux (1960); Klein (1974), which discuss, among other techniques, the use of Cauchy's theorem and the resolvent operator to obtain expansions of the projection operator. In the following we summarize a straightforward approach, which is suitable to the order to which we carry the expansion. We simply note that the usual goal of perturbation theory is to expand the energy eigenstates (which in our case would be the adiabatic basis) in a power series, something which however must cope with degeneracies, near degeneracies and small or vanishing energy denominators, none of which is an issue in the expansion of the projection operator. These complications are due to the singularity of the adiabatic basis at a degeneracy, which we are avoiding by using the projection operator.

We expand the projection operator in a power series in x,

$$P(x) = P_0 + P_1 + P_2 + \ldots; \tag{24}$$

where

$$P_0 = P(x_0);\ P_1 = x^m \frac{\P P}{\P x}(x_0);\ P_2 = \frac{1}{2} x^m x^n \frac{\P^2 P}{\P x^m \P x^n}(x_0); \tag{25}$$

etc., and similarly we expand the Hamiltonian,

$$H(x) = H_0 + H_1 + H_2 + \ldots \tag{26}$$

We carry out the perturbation expansion by requiring $P(x)^\dagger = P(x)^2 = P(x)$ and $[P(x); H(x)] = 0$. At zeroth order, that is, at $x = x_0$, we have

$$P_0 = \begin{pmatrix} I^{aa} & 0 \\ 0 & 0 \end{pmatrix}; \qquad H_0 = \begin{pmatrix} H_0^{aa} & 0 \\ 0 & H_0^{bb} \end{pmatrix}; \tag{27}$$

where matrices are partitioned as in (9). Since the reference basis is an energy eigenbasis at x_0 for $k \in A$, we have

$$H^{aa}_{0;kl} = e_{0k}\, d_{kl}; \tag{28}$$

where $e_{0k} = e_k(x_0)$ for $k \in A$. Equation (28) applies when $k; l \in A$; in equations like this we shall not indicate the ranges of indices when they are evident from the superscripts (for example, aa in this case).

At first order we must satisfy $P_0P_1 + P_1P_0 = P_1$, which gives $P_1^{aa} = 0$ and $P_1^{bb}=0$. In addition, when we require $[P_0; H_1] + [P_1; H_0] = 0$, we find

$$P_{1;kl}^{ab} = \sum_{m \in A} H_{1;km}^{ab} R(e_{0k})_{ml}; \tag{29}$$

where the resolvent $R(e)$ is a bb-type matrix defined by

$$\sum_{m \in A} R(e)_{km} \, (e\, d_{ml} - H_{0;ml}^{bb}) = d_{kl}; \tag{30}$$

that is,

$$R(e) = (eI^{bb} - H_0^{bb})^{-1}. \tag{31}$$

The resolvent $R(e)$ is defined when $e = e_{0k}$ for $k \in A$, which is outside the range of eigenvalues of H_0^{bb}. Thus we can write

$$P_1 = \begin{pmatrix} 0 & P_1^{ab} \\ P_1^{ba} & 0 \end{pmatrix}; \tag{32}$$

where $P_1^{ba} = (P_1^{ab})^\dagger$.

At second order we require $P_0P_2 + P_1^2 + P_2P_0 = P_2$, which gives $P_2^{aa} = -P_1^{ab}P_1^{ba}$ and $P_2^{bb} = +P_1^{ba}P_1^{ab}$. We also require $[P_0; H_2] + [P_1; H_1] + [P_2; H_0] = 0$, which gives

$$P_{2;kl}^{ab} = \sum_{m \in A} \left(H_2^{ab} + P_1^{ab} H_1^{bb} - H_1^{aa} P_1^{ab} \right) R(e_{0k})_{ml}. \tag{33}$$

Thus we can write

$$P_2 = \begin{pmatrix} P_1^{ab}P_1^{ba} & P_2^{ab} \\ P_2^{ba} & P_1^{ba}P_1^{ab} \end{pmatrix}. \tag{34}$$

Finally, at third order we find

$$P_3 = \begin{pmatrix} P_1^{ab}P_2^{ba} - P_2^{ab}P_1^{ba} & P_3^{ab} \\ P_3^{ba} & P_1^{ba}P_2^{ab} + P_2^{ba}P_1^{ab} \end{pmatrix} \tag{35}$$

where

$$P_{3;kl}^{ab} = \sum_{m \in A} \left(H_3^{ab} + P_1^{ab} H_2^{bb} - H_2^{aa} P_1^{ab} - P_1^{ab} P_1^{ba} H_1^{ab} + P_2^{ab} H_1^{bb} - H_1^{aa} P_2^{ab} - H_1^{ab} P_1^{ba} P_1^{ab} \right)_{km} R(e_{0k})_{ml}; \tag{36}$$

and $P_3^{ba} = (P_3^{ab})^\dagger$.

Now we can take the square roots indicated in (23), which to third order are given by

$$(P^{aa})^{1=2} = I^{aa} \quad \frac{1}{2}P_1^{ab}P_1^{ba} \quad \frac{1}{2}(P_1^{ab}P_2^{ba} + P_2^{ab}P_1^{ba}); \tag{37a}$$

$$(Q^{bb})^{1=2} = I^{bb} \quad \frac{1}{2}P_1^{ba}P_1^{ab} \quad \frac{1}{2}(P_1^{ba}P_2^{ab} + P_2^{ba}P_1^{ab}): \tag{37b}$$

These allow us to write out the expansion of T,

$$\begin{aligned} T = {} & \begin{pmatrix} 0 & 1 \\ I^{aa} & 0 \end{pmatrix} + \begin{pmatrix} 0 & 1 \\ 0 & P_1^{ab} \\ P_1^{ba} & 0 \end{pmatrix} + \begin{pmatrix} 0 & 1 \\ (1=2)P_1^{ab}P_1^{ba} & P_2^{ab} \\ P_2^{ba} & (1=2)P_1^{ba}P_1^{ab} \end{pmatrix} \\ & + \begin{pmatrix} 0 & 1 \\ (1=2)(P_1^{ab}P_2^{ba} + P_2^{ab}P_1^{ba}) & P_3^{ab} \\ P_3^{ba} + (1=2)P_1^{ba}P_1^{ab}P_1^{ba} & (1=2)(P_1^{ba}P_2^{ab} + P_2^{ba}P_1^{ab}) \end{pmatrix} + \cdots; \end{aligned} \tag{38}$$

which gives the expansion of the singular-value diabatic basis about an arbitrary point x_0 to third order.

IV. A DIABATIC BASIS VIA PARALLEL TRANSPORT

Parallel transport is a standard topic in gauge theories (Kobayashi and Nomizu (1963); Nakahara (2003)) and is an important part of the theory of Berry's phases (Berry (1984); Simon (1983)). Its role in Born-Oppenheimer theory is also well known (Mead (1992); Bohm, Boya, and Kendrick (1991)). Parallel transport can be used to create a diabatic basis; one simply takes a basis at a reference point x_0, possibly on a conical intersection, and parallel transports it along radial lines emanating from x_0 to fill in a basis defined over a neighborhood of x_0. Such bases have a long history in the chemical literature, going back at least to Smith (1969), who used parallel transport in diatomics to create a strictly diabatic basis, possible in his case because his parameter space was 1-dimensional. Strictly diabatic bases (by any means of construction) do not exist in the poly-atomic molecules considered in this article (Mead and Truhlar (1982)), but for a contrary opinion see Baer (1975, 1976, 1980); Baer and Englman (1992); Baer and Alijah (2000); Baer (2000a,b, 2001, 2002).

A. Parallel Transport

We review some aspects of parallel transport that we will need; for a slightly different perspective see Mead (1992). Given a vector $y(x) \; 2 \; S \; (x)$, we wish to find the vector $y(x + dx) =$

$y(x) + dy$ at a nearby point such that $y(x + dx) \in S(x + dx)$ and such the square distance in Hilbert space

$$y(x + dx) \quad y(x)^2 \tag{39}$$

is minimum. Writing simply y for $y(x)$ and likewise P for $P(x)$, we have $Py = y$ and $(P + dP)(y + dy) = y + dy$, or,

$$dy = Pdy + (dP)y: \tag{40}$$

We regard y as given and dy as unknown. Since $dy = Pdy + Qdy$ we see that $(dP)y = Qdy$ and that the two terms in (40) are orthogonal. Also, the term $(dP)y$, the component of dy orthog-onal to $S(x)$, is fixed; therefore to minimize the square distance (39) we choose dy so that it is orthogonal to $S(x)$, that is, so that $Pdy = 0$.

This gives $dy = (dP)y$. If now the step from x to $x + dx$ is taken along a curve $x(\lambda)$, then by dividing by $d\lambda$ we obtain an equation of parallel transport along the curve,

$$y' = P'y; \tag{41}$$

where the prime means $d/d\lambda$. This equation is to be used only for vectors $y(x)$ that lie in $S(x)$, that is, that satisfy $Qy = 0$. It can be shown (see Appendix A) that (41) implies

$$\frac{d}{d\lambda} + P' \quad (Qy) = 0; \tag{42}$$

so that if $Qy = 0$ at $\lambda = 0$ then $Qy = 0$ for all λ (this follows from the uniqueness of the solution of the differential equation). Similarly, if we wish to transport a vector that remains in $S^{\perp}(x)$ if it starts out in that space, then we use the transport equation

$$y' = Q'y = \quad P'y: \tag{43}$$

We can combine both types of parallel transport into a single equation by writing

$$y' = (P'P \quad PP')y = [P'; P]y: \tag{44}$$

It can be shown that if y satisfies this equation then Qy satisfies (42), so that if $y \in S(x)$ initially then it remains in $S(x)$; and it can be shown that if y satisfies this equation and $Qy = 0$ then y satisfies the simpler equation (41). (See Appendix A.) Thus, (41) and (44) are equivalent if $y \in S(x)$. Similarly it can be shown that (43) and (44) are equivalent if $y \in S^{\perp}(x)$.

The form (44) is convenient because it applies to the transport of any vector, one in $S(x)$, one in $S^{\perp}(x)$, or any linear combination thereof. Also, since the commutator $[P'; P]$ is anti-Hermitian,

it follows that parallel transport via (44) is unitary, and preserves the scalar product of vectors. In particular, the parallel transport of an orthonormal frame is orthonormal. Furthermore, if we parallel transport a frame that block diagonalizes the Hamiltonian, it continues to do so as we evolve along the curve. Finally, we note that another useful form for (44) is

$$y^0 = (P^0 P + Q^0 Q)y: \tag{45}$$

We mention this because it makes it evident how parallel transport is generalized to the case in which there are multiple subspaces of the electronic Hilbert spaee under consideration (not just two).

B. The Parallel Transported Basis

Now let us replace the displacement x by λx, so that

$$x^m(\lambda) = x_0^m + \lambda x^m; \tag{46}$$

which represents a radial line parameterized by λ starting at x_0 when $\lambda = 0$. We expand the Hamiltonian $H(x)$ and projector $P(x)$ as before, except now with a λ dependence, so that for example

$$H(x(\lambda)) = H_0 + \lambda H_1 + \lambda^2 H_2 + \lambda^3 H_3 + :::; \tag{47}$$

instead of (26). We expand $P(x(\lambda))$ and a parallel-transported wave function $y(\lambda)$ similarly. The wave function y is initially defined only along a single curve, so it is a function of λ but not of x.

Then we have

$$P(x) = P_0 + \lambda P_1 + \lambda^2 P_2 + \lambda^3 P_3 + :::; \tag{48a}$$

$$P^0(x) = P_1 + 2\lambda P_2 + 3\lambda^2 P_3 + :::; \tag{48b}$$

$$\begin{aligned}[P^0; P] = {} & [P_1; P_0] + 2\lambda [P_2; P_0] \\ & + \lambda^2 \, 3[P_3; P_0] + [P_2; P_1] + :::\end{aligned} \tag{48c}$$

and with $y = y_0 + \lambda y_1 + \lambda^2 y_2 + \lambda^3 y_3 + :::$, (44) becomes

$$y_1 = [P_1; P_0] y_0; \tag{49a}$$

$$2y_2 = [P_1; P_0] y_1 + 2[P_2; P_0] y_0; \tag{49b}$$

$$\begin{aligned}3y_3 = {} & [P_1; P_0] y_2 + 2[P_2; P_0] y_1 \\ & + 3[P_3; P_0] + [P_2; P_1] y_0;\end{aligned} \tag{49c}$$

etc. These allow us to express y_1, y_2, etc., in terms of y_0.

We write the result in the following way. Define $y_k(l)$ as the components of $y(l)$ with respect to the reference basis $|a(x_0);k\rangle$, that is, $y_k(l) = \langle a(x_0);k|y(l)\rangle$. Then $y_k(l)$ is a linear function of $y_k(0)$, which is expressed by

$$y_k(l) = \sum_{\text{all } l} T_{p;kl}\, y_l(0); \tag{50}$$

where T_p is an infinite-dimensional matrix that depends on l along a single curve, or, with $l = 1$ and x regarded as a variable, on $x = x_0 + x$. This matrix plays a similar role to T for the singular-value diabatic basis and, in particular, if we define $|p(x);k\rangle$ as the basis that is parallel transported along radial lines from x_0, with the initial values being the reference basis $|a(x_0);k\rangle$ at x_0, then

$$|p(x);k\rangle = \sum_{\text{all } l} |a(x_0);l\rangle [T_p(x)]_{lk}; \tag{51}$$

which may be compared to (21). The subscript on T_p refers to the parallel-transported basis.

Now we expand $T_p = T_{p0} + l\,T_{p1} + l^2 T_{p2} + \cdots$ and use (49) to obtain

$$T_{p1} = [P_1; P_0]; \tag{52a}$$

$$T_{p2} = \frac{1}{2}[P_1; P_0]T_{p1} + [P_2; P_0]; \tag{52b}$$

$$T_{p3} = \frac{1}{3}[P_1; P_0]T_{p2} + \frac{2}{3}[P_2; P_0]T_{p1} + [P_3; P_0] + \frac{1}{3}[P_2; P_1]. \tag{52c}$$

Then we set $l = 1$ and work out the commutators to obtain T_p through third order,

$$T_p = \begin{pmatrix} 0 & 0 \\ 0 & I^{bb} \end{pmatrix} + \begin{pmatrix} I^{aa} & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & P_1^{ab} \\ P_1^{ba} & 0 \end{pmatrix} + \begin{pmatrix} (1/2)P_1^{ab}P_1^{ba} & P_2^{ab} \\ P_2^{ba} & (1/2)P_1^{ba}P_1^{ab} \end{pmatrix} + \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$
$$+ \begin{pmatrix} (2/3)P_1^{ab}P_2^{ba} & (1/3)P_2^{ab}P_1^{ba} \\ P_3^{ba} + (1/2)P_1^{ba}P_1^{ab}P_1^{ba} & (2/3)P_1^{ba}P_2^{ab} \end{pmatrix} + \begin{pmatrix} P_3^{ab} & (1/2)P_1^{ab}P_1^{ba}P_1^{ab} \\ (1/3)P_2^{ba}P_1^{ab} & 0 \end{pmatrix}. \tag{53}$$

Comparing this with (38) we see that the singular-value diabatic basis and the parallel-transported diabatic basis are identical through second order in an expansion about x_0 but differ at third order. The two expansions cannot be identical to all orders, since in effect each small step of the parallel transport involves an infinitesimal version of the singular-value basis, but one that compares frames between x and $x + dx$ rather than between x_0 and x.

C. Hamiltonian in Parallel-Transported Basis

Let us write

$$H_{p;kl}(x) = \langle px;k|H(x)|px;l\rangle \tag{54}$$

for the Hamiltonian matrix in the parallel-transported basis, while other matrices (H_1, P_2, etc.) are understood to be in the reference basis $|ax_0;k\rangle$, as previously. Then

$$H_p(x) = T_p(x)^\dagger H(x) T_p(x): \tag{55}$$

Now we expand $H(x)$ as in (26) and $T_p(x)$ as in (52) and multiply series to compute $H_p(x)$ to second order. We find that the off-diagonal elements vanish, $H_p^{ab}(x) = H_p^{ba}(x) = 0$, as they should, while through first order the diagonal elements of $H_p(x)$ are the same as those of $H(x)$, that is, $H_{p0}^{aa} = H_0^{aa}$, $H_{p1}^{aa} = H_1^{aa}$, $H_{p0}^{bb} = H_0^{bb}$ and $H_{p1}^{bb} = H_1^{bb}$. As for the diagonal elements at second order, we find

$$H_{p2}^{aa} = H_2^{aa} + \frac{1}{2}(H_1^{ab}P_1^{ba} + P_1^{ab}H_1^{ba}); \tag{56}$$

$$H_{p2}^{bb} = H_2^{bb} \quad \frac{1}{2}(H_1^{ba}P_1^{ab} + P_1^{ba}H_1^{ab}): \tag{57}$$

We note that if the electronic Hamiltonian at x_0 is completely degenerate in the coupled subspace, then we can use (90) to obtain

$$H_{p2}^{aa} = H_2^{aa} + H_1^{ab}R(e_0)H_1^{ba}; \tag{58}$$

the usual result from degenerate perturbation theory.

Now by diagonalizing H_p^{aa} we obtain the adiabatic basis $|ax;k\rangle$, if we want it. If x_0 is on an internal degeneracy (a seam or conical intersection), then this will reveal the usual singularities of the adiabatic basis, for example, the dependence of $|ax;k\rangle$ on the direction of approach as $x \to x_0$ and the π phase discontinuity as we encircle the degeneracy manifold in the case of a 2-fold degeneracy in the electrostatic model (Herzberg and Longuet-Higgins (1963); Longuet-Higgins (1975); Mead and Truhlar (1979)). In the case of a triatomic with an odd number of electrons and spin-orbit effects included it will reveal the string of a Dirac monopole (Mead (1980a, 1987)).

D. The Derivative Couplings and Connection

If $|x;k\rangle$ is any smooth basis that block diagonalizes the Hamiltonian then we define the derivative couplings by

$$F_{m;kl} = \langle x;k|\P_m|x;l\rangle = \quad (\P_m\langle x;k|)|x;l\rangle = \quad F_{m;lk}; \tag{59}$$

where $\P_m = \P/\P x^m$ and where the alternative forms follow from the orthonormality of the basis vectors. For example, the basis $|x;k\rangle$ could be $|dx;k\rangle$ or $|px;k\rangle$ or the adiabatic basis $|ax;k\rangle$ in regions where the latter is smooth. If we just write F_m we mean the infinite dimensional matrix whose components are $F_{m;kl}$; this can be decomposed into aa-, ab-, etc., blocks. As is well known, the derivative couplings appear when the molecular Schrödinger equation is transformed to the Born-Oppenheimer representation. The matrix of derivative couplings F_m, as well as its diagonal blocks, F_m^{aa} and F_m^{bb}, are anti-Hermitian and thus belong to the Lie algebra of the unitary group.

Any process of parallel transport gives rise to a connection, which in the general case is a rule for associating a unique object at a point $x + dx$, given that object at point x. The object in question could be a vector such as y, a frame, or other things. In the case of transporting the vector y as in Sec. IV A, the components of the connection, which we denote by $G_{m;kl}$, are defined by

$$\frac{dy_k}{dl} = \quad \sum_{all\,l} G_{m;kl}\frac{dx^m}{dl}y_l; \tag{60}$$

where the minus sign is conventional. If we now substitute

$$|y(l)\rangle = \sum_{all\,k}|x(l);k\rangle y_k(l) \tag{61}$$

into the equation of parallel transport (44) or (45) we find (see Appendix A),

$$G_m = \begin{pmatrix} 0 & 1 \\ F_m^{aa} & 0 \\ 0 & F_m^{bb} \end{pmatrix}; \tag{62}$$

that is, the diagonal blocks of the connection are the same as the derivative couplings. The off-diagonal components of the connection vanish because of the way we designed the process of parallel transport in Sec. IV A, that is, so that a vector that begins in one of the subspaces $S^{\|}(x)$ or $S^{?}(x)$ remains in that subspace.

If $|bx;k\rangle$ is any smooth basis that block-diagonalizes the Hamiltonian, where b just means "basis," then another such basis is given by

$$|b'x;k\rangle = \sum_l |bx;l\rangle U_{lk}(x); \tag{63}$$

where $U(x)$ is unitary, a smooth function of x and also block-diagonal. Then the derivative couplings in the new basis are given by

$$F'_m = U^\dagger F_m U + U^\dagger \partial_m U; \tag{64}$$

which, as is well known, is the transformation law for a (generally) non-Abelian gauge potential. Because of the inhomogeneous term the derivative couplings can be made to take on any value at any given point by means of such a gauge transformation. Indeed, in both the singular-value and parallel-transported basis the derivative couplings vanish at the reference point x_0. Since a common goal in practice is to minimize the derivative couplings over some region, naturally the question arises as to how fast these couplings grow (in some basis) as we move away from a point where they are known to vanish. This question leads us to the curvature, which we take up next.

E. Curvature

Let $|bx;k\rangle$ be an arbitrary, smooth basis that block-diagonalizes the Hamiltonian, as above, and let Δx^m and η^m be two infinitesimal displacements from a point x. Then let us carry out a parallel transport around the parallelogram, $x \to x + \Delta x \to x + \Delta x + \eta \to x + \eta \to x$. Initially we parallel transport the a-part of the frame, that is, the vectors $|bx;k\rangle$ for $k \in A$. This is a standard calculation in gauge theories (Kobayashi and Nomizu (1963); Nakahara (2003); Mead (1992)) and we just quote the results. Since parallel transport preserves orthonormality, the parallel-transported frame, once again back at the starting point x, must be related to the original frame at that point by a unitary matrix. Moreover, the unitary matrix must be infinitesimal, that is, the identity plus an infinitesimal, anti-Hermitian correction. If we denote the parallel-transported frame, back at x, by $|\tilde{b}x;k\rangle$, then we have

$$|\tilde{b}x;k\rangle = \sum_{l \in A} |bx;l\rangle [\delta_{lk} - \Delta x^m \eta^n G^{aa}_{mn;lk}(x)]; \tag{65}$$

which defines the aa-block of the curvature tensor $G_{mn;kl}$ at x. In this formula, G is understood to be expressed in the basis $|bx;k\rangle$; if we omit the $k;l$ indices, we refer to the matrix G^{aa}_{mn}. The calculation shows that

$$G^{aa}_{mn} = \partial_m F^{aa}_n - \partial_n F^{aa}_m + [F^{aa}_m, F^{aa}_n]. \tag{66}$$

If we carry out this calculation for the b-block, we find the same equation but with aa replaced by bb; and the off-diagonal blocks of G vanish, $G_{mn}^{\bar{a}b} = G_{mn}^{\bar{b}a} = 0$, for the same reason that the off-diagonal blocks of the connection do (see (62)).

Given the fact that F^{aa}_m and F^{bb}_m are anti-Hermitian, it follows from (66) that G^{aa}_{mn} and G^{bb}_{mn} are, too, that is, $G^{aa}_{mn;kl} = \quad G^{aa}_{mn;lk}$, etc.

The nuclear Hamiltonian involves the vector potential F, not the curvature G, but the curvature appears in the commutators of the velocity operators (Littlejohn and Reinsch (1997)) and in the classical equations of motion, which are useful for wave packet evolution (Berry and Robbins (1993); Wu, Miao, and Subotnik (2020); Bian et al. (2021)), especially when nuclear dynamics depend on spin.

We now present another formula for the curvature, which is a simplification of Eq. (3.42) of Mead (1992) and which connects the curvature with the projection operator. It is

$$G_{mn;kl}(x) = \langle kx|[P_m, P_n]|lx\rangle; \tag{67}$$

where $P_m = \nabla_m P$. This applies to the full, infinite-dimensional matrix G_{mn}, that is, for all k, l. In particular, it correctly gives zero for the off-diagonal elements. The proof is given in Appendix A 4. In our applications this turned out to be the most convenient means of calculating the curvature (much more convenient than (66)).

Under the change of basis (63) the curvature transforms as a tensor, that is,

$$G^c_{mn} = U G_{mn} U^\dagger; \tag{68}$$

(Mead (1992)), where U is the same (block-diagonal) unitary matrix as in (64). This means that the quantities

$$\sum_{k,l\in A} |G^{aa}_{mn;kl}|^2 \tag{69}$$

are independent of basis, as are the sums over the bb-block. These quantities, which constrain the derivatives of the derivative couplings, cannot be transformed away, not even at a single point. For this reason, there is some interest in finding a gauge that expresses F_m in terms of G_{mn}.

Finally, we quote the Bianchi identity, which is

$$\begin{aligned} &\nabla_s G^{aa}_{mn} + \nabla_m G^{aa}_{ns} + \nabla_n G^{aa}_{sm} \\ &+ [F^{aa}_m, G^{aa}_{ns}] + [F^{aa}_n, G^{aa}_{sm}] + [F^{aa}_s, G^{aa}_{mn}] = 0; \end{aligned} \tag{70}$$

with a similar formula for the bb-block. This is the analog of Maxwell's equation $\nabla \cdot B = 0$ in electromagnetism.

F. Non-Abelian Poincaré Gauge

In electromagnetism, Poincaré gauge (Cohen-Tannoudji, Dupont-Roc, and Grynberg (1989)) is transverse in real space, that is, $x \cdot A(x) = 0$. In a molecule, if x_0 is a reference point in nuclear configuration space and $x(l) = x_0 + l\,x$ is a radial line, as above, then the analog of Poincaré gauge for the Mead-Truhlar-Berry connection is a gauge such that

$$x^m F^{aa}_{m}\,x(l) = x^m F^{bb}_{m}\,x(l) = 0; \tag{71}$$

that is, the radial component of the connection vanishes.

It turns out that parallel-transported gauge is Poincaré gauge, in this sense. To prove this we start with $k; l \in A$ and note that in the parallel-transported frame we have

$$\begin{aligned} x^m F^{aa}_{m;kl} &= x^m \langle px;k|\nabla_m|px;l\rangle = \langle px;k|\frac{d}{dl}|px;l\rangle \\ &= \langle px;k|[P^0;P]|px;l\rangle = \langle px;k|P(P^0P - PP^0)P|px;l\rangle \\ &= 0; \end{aligned} \tag{72}$$

where we use $d=dl = x^m\nabla_m$ and (44). A similar proof holds for F^{bb}_{m}, but radial components of the off-diagonal blocks of the derivative couplings, F^{ab}_{m} and F^{ba}_{m}, do not vanish.

Poincaré gauge has the interesting property that the vector potential can be expressed in terms of the magnetic field. Thus one obtains Hamiltonians that are not expressed in terms of some arbitrary vector potential, but rather directly in terms of the magnetic field, which is fully physical. This is mainly useful in some neighborhood of a given point, by means of Taylor series expansions.

This property carries over to the non-Abelian case. Specifically, if F^{aa}_{m} is in parallel-transported gauge, then

$$F^{aa}_{m}(x) = \int_0^1 dl\, l\,x^n G^{nm}_{aa}\,x(l); \tag{73}$$

where x on the left-hand side means $x = x_0 + x$ and $x(l)$ under the integral means $x_0 + l\,x$, as above. The integral is carried along a radial line from x_0 to $x = x_0 + x$. A similar equation holds for the bb-block of the connection and curvature.

This is a rather remarkable formula, because it appears to give a linear relationship between F and G, which in the non-Abelian case are in fact connected by the nonlinear relationship (66). For us (73) is merely an identity connecting the curvature and connection in parallel-transported gauge, but if one were to interpret it as a map from a given curvature to a corresponding vector

potential, then it must be understood that the formula only works if G satisfies the Bianchi identity (70).

To prove (73) we assume that F is the parallel-transported connection and G is the curvature and we examine the integral on the right-hand side, but without assuming that it equals the left-hand side. Writing G in terms of F, the integral becomes

$$\int_0^1 d\lambda\, \lambda x^n \left(\partial_n F^{aa}_m - \partial_m F^{aa}_n + [F^{aa}_n, F^{aa}_m] \right); \tag{74}$$

where it is understood that everything under the integral is evaluated at $x(\lambda) = x_0 + \lambda x$. Because $x^n F^{aa}_n\, x(\lambda) = 0$ the commutator term vanishes. The first term in (74) can be written

$$\int_0^1 d\lambda\, \lambda \frac{dF^{aa}_m}{d\lambda}; \tag{75}$$

where we use $d/d\lambda = x^n \partial_n$. As for the second term, it is

$$\begin{aligned} \int_0^1 d\lambda\, x^n \frac{\partial F^{aa}_m}{\partial x} &= \int_0^1 d\lambda\, \frac{\partial}{\partial x}(x^n F^{aa}_n) - F^{aa}_m \\ &= \int_0^1 d\lambda\, F^{aa}_m; \end{aligned} \tag{76}$$

where we use $\partial/\partial x^m = \lambda \partial_m$ and where one major term vanishes on account of (71). Now adding (75) and (76) we obtain

$$\int_0^1 d\lambda\, \frac{d}{d\lambda}[\lambda F^{aa}_m\, x(\lambda)] = F^{aa}_m\, x(1) = F^{aa}_m(x); \tag{77}$$

which is the given left-hand side of (73).

Now we may expand the integrand in (73) in a power series in λ and do the integral, which through order λ^2 gives us

$$F^{aa}_m(x_0 + x) = \frac{1}{2} x^n G^{aa}_{nm}(x_0) + \frac{1}{3} x^n x^s (\partial_s G^{aa}_{nm})(x_0) + \cdots \tag{78}$$

This can be used to express F and its derivatives at x_0 in terms of the curvature,

$$F^{aa}_m = 0; \tag{79a}$$

$$\partial_n F^{aa}_m = \frac{1}{2} G^{aa}_{nm}; \tag{79b}$$

$$\partial_n \partial_s F^{aa}_m = \frac{1}{3} [\partial_s G^{aa}_{nm} + \partial_n G^{aa}_{sm}]; \tag{79c}$$

where it is understood that everything is evaluated at x_0. As we see, the Mead-Truhlar-Berry connection in the parallel-transported frame vanishes at x_0 and the curvature governs the rate at which it grows as we move away from x_0.

The facility of expressing the connection in terms of the curvature is one of the advantages of the parallel-transported frame over the singular-value frame.

G. Connection and Curvature in Parallel-Transported Basis

We can now work out the components of the connection and curvature in the parallel-transported basis. It is straightforward to do this with the expansion of the parallel-transported basis $|p(x);k\rangle$ in terms of the reference basis $|a(x_0);k\rangle$, given by (51), with coefficients given by (53). First we substitute this into the definition (59) of the derivative couplings to compute F_m, and then use (66) to compute G_{mn}. This will give expressions for F_m and G_{mn} in terms of the components of the projection operator, and, ultimately, in terms of the Hamiltonian and its derivatives.

It turns out to be much easier, however, to use first Mead's formula (67) in the parallel-transported basis to find G, and then to use (73) to find F. In this work we must be careful with notation. We will henceforth write P for the projection operator (previously simply denoted P), P for its matrix with respect to the reference basis $|a(x_0);k\rangle$ and $\bar{P}$ for its matrix with respect to the parallel-transported basis. Also, we will append (x) to a quantity if we mean it to be evalu-ated at $x = x_0 + x$, and we will omit the (x) if we mean it to be evaluated at x_0. Also, we define $P_m(x) = (\partial_m P)(x)$, etc.

We are interested in the curvature tensor in the parallel-transported basis, which according to Mead's formula (67) is

$$G_{mn;kl}(x) = \langle p(x);k|[P_m(x);P_n(x)]|p(x);l\rangle = [\bar{P}_m(x);\bar{P}_n(x)]_{kl}; \tag{80}$$

since the matrix of the commutator is the commutator of the matrices. (This holds when the matrices are the full, infinite-dimensional matrices, as here.) For this we need the matrix,

$$\bar{P}_m(x) = T_p(x)^\dagger P_m(x) T_p(x); \tag{81}$$

which is a change of basis from $|a(x_0);k\rangle$ to $|p(x);k\rangle$. This matrix vanishes on the diagonal blocks, for example, if $k;l \in A$ then

$$\begin{aligned}[\bar{P}_m(x)]_{kl} &= \langle p(x);k|P_m(x)|p(x);l\rangle \\ &= \langle p(x);k|P(x)P_m(x)P(x)|p(x);l\rangle = 0;\end{aligned} \tag{82}$$

as follows since $P(x)[\partial_m P(x)]P(x) = 0$.

The expansion of $P(x) = P(x_0 + x)$ is given by (27), (32), (34) and (35), which to second order

can be written

$$P(x) = \begin{pmatrix} I^{aa} & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & P^{ab}_m \\ P^{ba}_m & 0 \end{pmatrix} x^m + \begin{pmatrix} 0 & 1 \\ P^{ab}_m P^{ba}_n & (1/2) P^{ab}_{mn} \\ (1/2) P^{ba}_{mn} & P^{ba}_m P^{ab}_n \end{pmatrix} x^m x^n + \ldots; \tag{83}$$

where P^{ab}_m is the ab-block of $(\partial_m P)(x_0)$, P^{ab}_{mn} is the ab-block of $(\partial_m \partial_n P)(x_0)$, etc. Notice that in terms of our previous notation we have

$$P^{ab}_1 = P^{ab}_m x^m; \qquad P^{ab}_2 = \frac{1}{2} P^{ab}_{mn} x^m x^n; \tag{84}$$

etc. Differentiating (83) we obtain

$$P_m(x) = \begin{pmatrix} 0 & P^{ab}_m \\ P^{ba}_m & 0 \end{pmatrix} + \begin{pmatrix} 0 & 1 \\ P^{ab}_m P^{ba}_n + P^{ab}_n P^{ba}_m & P^{ab}_{mn} \\ P^{ba}_{mn} & P^{ba}_m P^{ab}_n + P^{ba}_n P^{ab}_m \end{pmatrix} x^n + \ldots \tag{85}$$

Now we use the expansion (53) of T_p, which we only need to first order and which we write as

$$T_p(x) = \begin{pmatrix} I^{aa} & 0 \\ 0 & I^{bb} \end{pmatrix} + \begin{pmatrix} 0 & P^{ab}_n \\ P^{ba}_n & 0 \end{pmatrix} x^n + \ldots; \tag{86}$$

to carry out the change of basis (81). This gives

$$\bar{P}_m(x) = \begin{pmatrix} 0 & P^{ab}_m \\ P^{ba}_m & 0 \end{pmatrix} + \begin{pmatrix} 0 & P^{ab}_{mn} \\ P^{ba}_{mn} & 0 \end{pmatrix} x^n + \ldots \tag{87}$$

which is off-diagonal, as predicted.

Now we can compute the commutator and thence the curvature. We find

$$G^{aa}_{mn}(x) = (P^{ab}_m P^{ba}_n - \text{h.c.}) + (P^{ab}_m P^{ba}_{ns} + P^{ab}_{ms} P^{ba}_n - \text{h.c.}) x^s + \ldots; \tag{88}$$

where subtracting the Hermitian conjugate of the indicated matrices is equivalent to antisymmetrizing in m;n. The expression for $G^{bb}(x)$ is obtained from this by swapping a $ b, and the off-diagonal blocks vanish, $G^{ab} = G^{ba} = 0$. Finally, replacing x by λx and carrying out the integral (73), we obtain the diagonal blocks of the Mead-Truhlar-Berry connection or derivative

couplings in the parallel-transported basis. We find

$$F_m^{aa}(x) = \frac{1}{2}(P_n^{ab}P_m^{ba} \quad \text{h:c:})x^n$$
$$+ \frac{1}{6}(P_n^{ab}P_{ms}^{ba} + P_s^{ab}P_{mn}^{ba} + 2P_{ns}^{ab}P_m^{ba} \quad \text{h:c:})x^n x^s + : : : ; \tag{89}$$

and similarly for the bb-block.

H. Coordinates and Rotations

So far we have been using the notation x to stand for a point of the nuclear configuration space in the center of mass frame and x^m for the collection of the 3N 3 components of the N 1 Jacobi vectors. We will call these "Jacobi coordinates." Thus derivatives ∂_m are understood to be taken with respect to Jacobi coordinates. However, there is nothing in our analysis so far that has required that the coordinates be these; everything goes through with an arbitrary coordinate system on nuclear configuration space, that is, a set of 3N 3 arbitrary, possibly nonlinear functions x'^m of x^m. We only require that the Jacobian matrix $\partial x'^m/\partial x^n$ be nonsingular in the neighborhood in which we are working. Therefore all our formulas so far are valid with x^m reinterpreted as an arbitrary coordinate system in this sense.

Our parallel-transported basis has been defined by integrating the (44) along radial lines emanating from a reference point x_0, which have the coordinate representation (46). This means that the parallel-transported basis at a point x depends on the coordinates, since a line that is straight in one coordinate system is not straight in another.

Another issue concerns the direction of integration. Let us assume that the configuration x_0 is noncollinear, the typical situation in polyatomic systems. Then there are three directions in which one can move away from x_0 that are purely rotational, and we do not want to use parallel transport to create a diabatic basis in those directions. In those directions the nuclear configuration trans-forms by a rigid rotation, that is, the shape of the molecule does not change, only its orientation. Those directions are tangent to the the 3-dimensional surfaces which are generated by applying rotations to a given configuration, which are the orbits or fibers of the action of rotations on the nuclear configuration space, as explained by Littlejohn and Reinsch (1997). When the nuclear configuration changes by a rigid rotation, the electronic basis functions should change by a rotation operator, not by parallel transport (or any other method for constructing a diabatic basis, such as the singular value method). Attention to those directions that are purely rotational versus

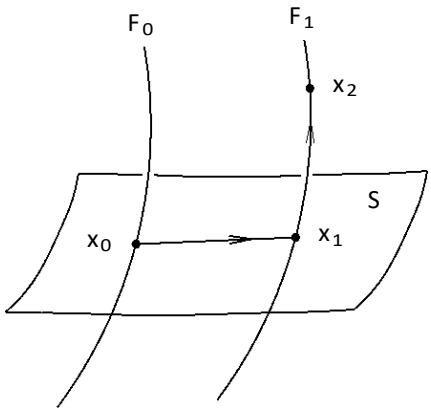

FIG. 1. Fibers F_0, F_1 are 3-dimensional surfaces swept out by applying rotations to nuclear configurations x_0, x_1. Section S is a (3N 6)-dimensional surface transverse to the fibers. To establish a frame of electronic wave functions over a region of nuclear configuration space, we may use parallel transport along a section S, such as along the path x_0 ! x_1, and then rotation operators to transport the frame along the fibers, such as along the path x_1 ! x_2.

those in which the shape changes is important in the construction of kinetic energy operators on the internal space (Wang and Tucker Carrington (2000)).

The situation is illustrated in Fig. 1, which is a schematic illustration of a region of the nuclear configuration space. Configuration x_0 is some configuration, and F_0 is the set of other configurations related to x_0 by rigid rotations, that is, configurations of the same shape as x_0 but different orientations. Surface F_0 is called the "fiber through x_0", as explained by Littlejohn and Reinsch (1997). Similarly F_1 is the fiber through x_1. Configurations x_1 and x_2 have the same shape but different orientations.

Surface S is a (3N 6)-dimensional surface that cuts transversally through the fibers in the given region, called a "section" of the fiber bundle (Littlejohn and Reinsch (1997)). Sections are needed to define orientational coordinates, that is, the section is the surface upon which the Euler angles are those of the identity rotation. The section also defines a body frame; it is the surface upon which the body frame coincides with the space frame. Sections are also implicitly used in electronic structure calculations, when it is attempted to fill in some region of nuclear configuration space. This is because one need only calculate the energy eigenvalues and eigenfunctions for a single orientation of a given shape; for other orientations the energy eigenvalues do not change and the energy eigenfunctions change simply by a rotation operator. Thus, electronic structure calculations take place on a section.

Now assume that x_0 is a reference configuration and we have an electronic basis at x_0 that block-diagonalizes the Hamiltonian, and suppose we wish to find a diabatic basis at neighboring points such as x_2 in the figure. Then the procedure is to use some rule (singular value, parallel transport, etc.) to create a diabatic basis at x_1 on the section, and then to use rotation operators to create a diabatic basis at x_2.

Thus we see that when we parallel transport a basis from a configuration x_0, we do not need to go out in all 3N 3 directions in nuclear configuration space, but rather only along the 3N 6 directions of a section passing through x_0. So far we have been interpreting the coordinates x^m as 3N 3 coordinates on nuclear configuration space, but all our results hold if we reinterpret them as 3N 6 coordinates on a section, and we will henceforth do this. These coordinates can be taken to be shape coordinates, that is, quantities such as bond lengths and angles that are invariant under overall rotations of the molecule. Similar considerations apply to all other methods (singular value, etc.) of constructing a diabatic basis in the neighborhood of x_0; the purely rotational directions are handled by rotation operators.

V. DEGENERACY MANIFOLDS

In the following it is assumed that we are working on a section with coordinates x^m, m = 1;:::;3N 6, or some subset of it which for simplicity we will call S. We assume the set A (see (1)) contains at least two levels, so that internal degeneracies are possible. We define the degeneracy manifold as the subset of S upon which there is an internal degeneracy. Degeneracy manifolds are usually called “seams” but we prefer the alternative terminology as it is more descriptive. Degeneracy manifolds are usually surfaces of conical intersections, but it should be noted that while all intersections of potential energy surfaces are degeneracies they are not always conical. We now address the construction of a parallel-transported basis in a neighborhood of the degeneracy manifold.

A. Models of the Electronic Hamiltonian

Up to this point we have been assuming that the electronic Hamiltonian was taken in the electrostatic model, but now we will address the more general case in which fine structure effects are included. We shall assume that no external fields are acting so that the molecular Hamiltonian has

time-reversal symmetry. This has an important effect in the case of an odd number of electrons, in which the electronic eigenstates become Kramers doublets. Let us agree to call a "level" a single Kramers doublet in the case of an odd number of electrons, which means the degeneracy is twice the number of levels. In other cases (electrostatic model or fine structure with an even number of electrons) the degeneracy is equal to the number of levels.

With this understanding, we now review the simplest case of two levels. If there is no symmetry in addition to time-reversal, the codimension of the degeneracy manifold is 2 in the electrostatic model or when fine structure is included and the number of electrons is even (von Neumann and Wigner (1929)), and it is 5 if fine structure is included and the number of electrons is odd (Mead (1980a)). If there are symmetries then the picture is more complicated since in general the symmetry only holds on submanifolds of configuration space, but an important exception is the C_s symmetry of triatomic molecules (reflection in the plane of the molecule), which is global. In the case of triatomics with fine structure and an odd number of electrons, the codimension of the degeneracy manifold is 3 (Mead (1980a)). We should also add that in the case of the electrostatic model we are assuming that one is working within a given subspace of spin states, that is, energy eigenstates of fixed S^2 and S_z, since degeneracies between states of different spin have codimension 1, whereas when fine structure is included we must enlarge the electronic Hilbert space to include all spin states.

Let us denote the degeneracy manifold by D; its codimension is counted inside the section S. For example, in triatomics S is 3-dimensional. Then in the electrostatic model or with fine structure and an even number of electrons, D has codimension 2 or dimension 1, that is, it is a curve in S; while if fine structure is included and number of electrons is odd, then the codimension of D is 3 and its dimension is 0, that is, D consists of isolated points inside S. These codimension counts apply at generic points of configuration space, where the Jacobian of the map from configuration space to Hamiltonian matrix space is of maximal rank; where this is not the case other phenomena arise, such as the bifurcation of degeneracy manifolds (Yarkony (2000)).

B. Reference point x_0 on Degeneracy Manifold

Henceforth we will assume that the reference point x_0 for the construction of a parallel-transported basis lies on D. We will also assume that at x_0 the electronic Hamiltonian is completely degenerate in the coupled subspace, so that $H^{aa}_{0;kl} = e_0 d_{kl}$, where e_0 is the degenerate eigenvalue.

In that case we note that P_n^{ab} can be expressed purely in terms of matrix products,

$$P_1^{ab} = H_1^{ab} R(e_0); \tag{90a}$$

$$P_2^{ab} = [H_2^{ab} + H_1^{ab} R(e_0) H_1^{bb} \quad H_1^{aa} H_1^{ab} R(e_0)] R(e_0); \tag{90b}$$

etc., with $P_n^{ba} = (P_n^{ab})^\dagger$. These are simplified versions of (29) and (33).

Let us also write the expansion of the Hamiltonian at $x = x_0 + x$ as a power series in x, just as we did for the projection operator in (84). We define, for example, $H_m^{ab} = (\partial_m H^{ab})(x_0)$, $H_{mn}^{ab} = (\partial_m \partial_n H^{ab})(x_0)$, etc., so that

$$H_1^{ab} = H_m^{ab} x^m; \qquad H_2^{ab} = \frac{1}{2} H_{mn}^{ab} x^m x^n; \tag{91}$$

etc., and similarly for the other blocks. Then with the aid of (90) the derivatives of P can be expressed in terms of the derivatives of H,

$$P_m^{ab} = H_m^{ab} R(e_0); \tag{92a}$$

$$P_{mn}^{ab} = [H_{mn}^{ab} + H_m^{ab} R(e_0) H_n^{bb} + H_n^{ab} R(e_0) H_m^{bb} \\ (H_m^{aa} H_n^{ab} + H_n^{aa} H_m^{ab}) R(e_0)] R(e_0); \tag{92b}$$

etc.

These can then be used to express the curvature and connection in terms of the derivatives of the Hamiltonian. For example, (67) gives us the curvature, which becomes

$$G_{mn}^{aa} = [H_m^{ab} R(e_0)^2 H_n^{ba} \quad h.c.] + \dots \tag{93}$$

Here we omit the first order correction as it is rather lengthy. As for the connection, in the parallel-transported basis $|x;k\rangle$ it is given in terms of the curvature by (78) or (79); thus, to first order we have

$$F_m^{aa}(x) = \frac{1}{2} [H_n^{ab} R(e_0)^2 H_m^{ba} \quad h.c.] x^n + \dots \tag{94}$$

The result (93) agrees with Eq. (56) of Mead and Truhlar (1982), in spite of the fact that those authors were not using the parallel-transported basis. The reason is that the curvature is a tensor, and has the same form in all frames. The same cannot be said for the connection. We believe the first order correction to the curvature seen in (67) is new.

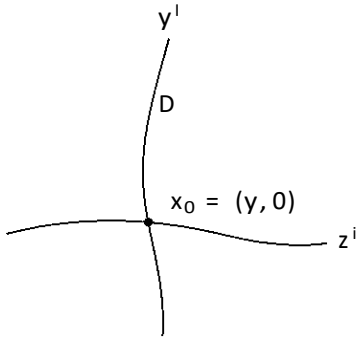

FIG. 2. The degeneracy manifold D as a subset of the section S and a neighborhood thereof are described by coordinates $x^m = (y^I; z^i)$, where y^I are coordinates along D and z^i are coordinates transverse to D. Coordinates $z^i = 0$ on D itself.

C. Diabatic Basis in a Neighborhood of the Degeneracy Manifold

We now construct a version of the parallel-transported basis in a neighborhood of the degeneracy manifold. So far we have constructed such a basis in the neighborhood of an arbitrary point x_0; we are free to choose x_0 to lie on D, but we still have just a small neighborhood of a single point, where Taylor series expansions are valid. We desire a construction that is valid over all of D, or at least the parts of D that form a smooth manifold. (Places where D bifurcates require a separate analysis, for which see Yarkony (2000)). For example, in triatomic molecules where D is a line inside the 3-dimensional section S, we desire a parallel-transported basis that is valid in a tubular neighborhood of D, where the two potential energy surfaces are strongly coupled.

We let x^m, $m = 1; \ldots; 3N - 6$ be coordinates on a section S, which we break up as $x^m = (y^I; z^i)$, where $I = 1; \ldots; \dim D$ and $i = 1; \ldots; \mathrm{codim} D$, making y^I coordinates along the degeneracy manifold, and z^i coordinates transverse to it. We let $z^i = 0$ on D, and we use the summation convention on coordinate indices I and i. See Fig. 2. This is merely a coordinate description of a neighbor-hood of D. The whole construction takes place in S, a subset of the nuclear configuration space which in general is curved; and D as a subset of S is generally a curved manifold.

These coordinates draw attention to the manifolds $y = y_0 = \text{const}$: illustrated in the figure which are transverse to D and upon which z^i are coordinates. These manifolds correspond roughly to what has been called the "branching space" by Yarkony (2004); there is one such manifold for each point on D. We propose to establish a diabatic basis in a neighborhood of D by parallel transporting along radial lines in the transverse spaces away from D. We will denote this basis by

$|Dx;k\rangle$; it is like the basis $|px;k\rangle$ except that the reference point for the parallel transport, instead of being fixed, moves along D as x moves. That is, if $x = (y;z)$, then for the basis $|Dx;k\rangle$ the reference point for the parallel transport is $x_0 = (y;0)$.

This construction requires that a diabatic basis be established on D, before being propagated along the transverse spaces. This can be done by any convenient means, for example, the singular-value method or by parallel transport. Once this is done, not only do we have frames for points $x_0 = (y;0) \in D$, but the y^l-components of the connection, that is,

$$F^{aa}_{l;kl}(x_0) = \langle Dx_0;k|\P_l|Dx_0;l\rangle; \tag{95}$$

where $\P_l = \P/\P y^l$, become known at points $x_0 \in D$.

Once the basis $|Dx_0;k\rangle$ is established for $x_0 = (y;0) \in D$, we use parallel transport along radial lines in the transverse spaces to create $|Dx;k\rangle$ in a neighborhood of D, that is, for $x = (y;z)$. The radial line is $x(l) = (y;lz)$, which interpolates between $(y;0)$ and $(y;z)$ as l goes from 0 to 1. The radial component of the connection in this basis vanishes, for example, for $k;l \in A$ we have

$$z^i\langle Dx;k|\P_i|Dx;l\rangle = z^iF^{aa}_{i;kl}(y;z) = 0; \tag{96}$$

which is like (71) and proved in the same way.

D. Connection and Curvature in a Neighborhood of D

To find the connection and curvature in the basis $|Dx;k\rangle$ we begin with the curvature. Since the curvature is a tensor, the numerical values of its components at a point x, say, $G^{aa}_{mn;kl}(x)$, depend on the the coordinates and the basis at x. We wish to find these components in the basis $|Dx;k\rangle$ where $x = (y;z)$. But the basis $|Dx;k\rangle$ is the same as the parallel-transported basis $|px;k\rangle$ if the reference point for the latter is taken to be $x_0 = (y;0)$. So with that understanding about the reference point, our expressions for the curvature in the basis $|px;k\rangle$ are valid also in the basis $|Dx;k\rangle$. We will, however, want to break the coordinate indices up into their y- and z-parts, by replacing indices m, etc., by I or i, etc. For example, we can rewrite (88) as

$$G^{aa}_{ij}(y;z) = (P^{ab}_iP^{ba}_j \quad h.c.) + (P^{ab}_iP^{ba}_{jk} + P^{ab}_{ik}P^{ba}_j \quad h.c.)z^k + \cdots; \tag{97}$$

and similarly for the (iI), (Ii) and (IJ) components of G. Here we have replaced x^m by $(0;z^i)$, since the parallel transport is taking place only in the transverse manifold (at constant y). Also,

all derivatives of the projection operator in (97) are understood to be evaluated on the degeneracy manifold at point $(y;0)$. As for (93), it can be expressed in the basis $|Dx;k\rangle$, whereupon it becomes

$$G_{ij}^{aa}(y;z) = [H_i^{ab}R(e_0)^2H_j^{ba} \quad h.c.] + \dots; \tag{98}$$

and similarly for the other components (iI), (Ii) and (IJ), where now the derivatives of H are evaluated at $(y;0)$.

To obtain the connection in a neighborhood of D we begin with the components F_i. These are related to the components G_{ij} of the curvature by an integral formula like (73), that is,

$$F_i^{aa}(y;z) = \int_0^1 d\lambda\, \lambda z^j G_{ji}(y;\lambda z). \tag{99}$$

This is really a special case of (73), which applies to any parameter space that the Hamiltonian depends on, upon which the coordinates are x^m; by interpreting that parameter space as the transverse space $y = $ const. and by replacing x^m with z^i, we obtain (99). One can also repeat the derivation of (73) with a changed notation. This then implies a version of (79),

$$F_i^{aa} = 0; \tag{100a}$$

$$\partial_j F_i^{aa} = \frac{1}{2}G_{ji}^{aa}; \tag{100b}$$

$$\partial_j\partial_k F_i^{aa} = \frac{1}{3}[\partial_k G_{ji}^{aa} + \partial_j G_{ki}^{aa}]; \tag{100c}$$

etc., where both sides are understood to be evaluated at $(y;0)$. Now expressing the curvature in terms of the Hamiltonian, we obtain a Taylor series for F_i in terms of the coordinates z^i,

$$F_i^{aa}(y;z) = \frac{1}{2}[H_j^{ab}R(e_0)^2H_i^{ba} \quad h.c.]z^j + \dots; \tag{101}$$

a version of (94). Here we omit the second order term (which is available) as it is rather lengthy, and the derivatives on the right hand side are understood to be evaluated at $(y;0)$.

As for the components F_I, we use the integral formula,

$$F_I^{aa}(y;z) = F_I^{aa}(y;0) + \int_0^1 d\lambda\, z^j G_{jI}^{aa}(y;\lambda z); \tag{102}$$

which may be compared with (73). In this formula it is understood that components of the connection and curvature are taken with respect to the basis $|Dx;k\rangle$ (while the basis $|px;k\rangle$ was used in (73)). To prove (102) we express G in terms of F so that the integral becomes

$$\int_0^1 d\lambda\, z^j f(\partial_j F_I^{aa})(y;\lambda z) \quad (\partial_I F_j^{aa})(y;\lambda z) + [F_j^{aa}(y;\lambda z); F_I^{aa}(y;\lambda z)]g; \tag{103}$$

and we use (96), which causes the commutator and the second term to vanish. As for the first term, it is

$$\int_0^1 d\lambda \, \frac{d}{d\lambda} F_\lambda^{aa}(y;\lambda z) = F_1^{aa}(y;z) - F_0^{aa}(y;0); \tag{104}$$

which proves (102).

Now we expand the integrand in (102) in powers of λ and do the integral to obtain

$$F_\lambda^{aa}(y;z) = F_\lambda^{aa}(y;0) + z^j G_{j\lambda}^{aa}(y;0) + \frac{1}{2} z^j z^k (\partial_k G_{j\lambda}^{aa})(y;0) + \cdots \tag{105}$$

This implies

$$\partial_i F_\lambda^{aa} = G_{i\lambda}^{aa}; \tag{106a}$$

$$\partial_i \partial_j F_\lambda^{aa} = \frac{1}{2}[\partial_j G_{i\lambda}^{aa} + \partial_i G_{j\lambda}^{aa}]; \tag{106b}$$

where everything is evaluated at $(y;0)$. Finally, we may express the connection in terms of the Hamiltonian and its derivatives,

$$F_\lambda^{aa}(y;z) = F_\lambda^{aa}(y;0) + [H_i^{ab} R(e_0)^2 H_\lambda^{ba} - \text{h.c.}] z^i + \cdots; \tag{107}$$

where again we omit the available second order term due to its length. Taken with (101) this provides an expansion of the connection in a neighborhood of D. We see that the components along D and those transverse to D can both be expressed in terms of the curvature, but the expansions are different. Again, the bb-block is obtained by swapping $a \leftrightarrow b$.

We make one final comment. In the case of triatomic molecules in the electrostatic model the degeneracy manifold D is a one-dimensional curve inside the section S, as noted. Thus if we use parallel transport along D to create frame on D, the component of F along D will vanish. That is, $F^{aa}(y;0) = 0$, where there is only one index λ since D is one-dimensional. But then (101) shows that the transverse components F^{aa} also vanish on D. Thus we have shown that in the 3-body problem with the electrostatic model for the electronic Hamiltonian, there exists a diabatic basis such that the derivative couplings vanish on the degeneracy manifold. This construction only works when the degeneracy manifold is one-dimensional.

VI. CONCLUSIONS

In this article we have given two versions of a parallel-transported diabatic basis, one valid in a neighborhood of a point (which is allowed to lie on a degeneracy manifold or seam), and

another which is valid in a neighborhood of a degeneracy manifold of possibly global extent. In both cases we have given Taylor series expansions of the basis vectors, the derivative couplings and the curvature. We have demonstrated the close relationship between the parallel-transported basis and the singular-value basis, showing that they agree to second order in a Taylor series expansion about a point. Our expansion of the singular-value basis seems to be new. We have promoted a method of carrying out these expansions that relies on the projection operator and that avoids small or vanishing energy denominators or other singularities. This approach seems to be new in the literature on diabatic bases. We have also exploited integral relationships that hold between the connection and curvature in the parallel-transported basis, which are generalizations of Poincaré gauge to a non-Abelian context and which provide a convenient means for computing the derivative couplings. Our goal is to give analytic treatments of connection and curvature in the neighborhood of degeneracy manifolds that will be useful for future work, including multi-dimensional Landau-Zener normal forms.

ACKNOWLEDGMENTS

One of us (R.L.) would like to thank Alden Mead for his kind hospitality and many stimulating and memorable conversations during the spring of 1993, as well as his support of the present work. The authors would also like to acknowledge many stimulating conversations and much good advice from Enzo Aquilanti, Tucker Carrington, Eric Heller and David Yarkony. JES was supported by the National Science Foundation under Grant No. CHE-2102402.

Appendix A: Mathematical Arguments and Proofs

1. P(x) Is Smooth

To show that the projection operator P(x), defined by (3), is a smooth function of x we may show that it is a smooth function of the electronic Hamiltonian H(x), which we assume is smooth. In this discussion we assume that x is restricted to a region of the nuclear configuration space in which no degeneracies cross the boundaries of the set A, as in the main body of the paper. This region need not be simply connected or contractible or otherwise topologically simple.

We follow Kato (1949); Bloch (1958) in writing $P(x)$ in terms of $H(x)$,

$$P(x) = \frac{1}{2\pi i} \int_C \frac{dz}{z - H(x)}; \tag{A1}$$

where C is a contour that surrounds the discrete energy eigenvalues $e_k(x)$ for $k \in A$ and no others (that is, none for $k \notin A$). Since the energy eigenvalues move about as x changes, the contour C must be a function of x and we must specify it. We let e_l and e_h be low and high energy values, respectively. If k_0 (see (1)) is the ground state we let e_l be any fixed energy less than the lower bound of $e_0(x)$ in the region in question, otherwise we let $e_l = (1/2)(e_{k_0 - 1} + e_{k_0})$. Likewise we let $e_h = (1/2)(e_{k_0+N_1 - 1} + e_{k_0+N_l})$. Then we let $C(x)$ be a rectangular contour in the complex energy plane bounded on the left and right by e_l and e_h that encircles the eigenvalues for $k \in A$. Now small changes in x produce small changes in both $C(x)$ and $H(x)$, of which the former do not change $P(x)$ and the latter induce small changes in $P(x)$. Therefore $P(x)$ is a smooth function of x.

2. Identities and Differential Equations Involving $y(x)$, $P(x)$ and $Q(x)$

Identities involving the projection operators $P(x)$ and $Q(x)$ include $P + Q = 1$, $P^2 = P$, $Q^2 = Q$, $QP = PQ = 0$, $P' = P'P + PP'$ and $PP'P = 0$, where prime means differentiation with respect to a parameter l.

To prove (42) we assume (41) is true so that the left hand side of (42) can be written

$$\begin{aligned} &\frac{d}{dl} + P' \quad [(1 - P)y] = - P'y + (1 - P)y' + P'(1 - P)y \\ &= [- P' + (1 - P)P' + P'(1 - P)]y \\ &= (P_0 - P'P - PP')y = 0: \end{aligned} \tag{A2}$$

A similar proof is to show that if y satisfies (44) then Qy satisfies (42). We have

$$\begin{aligned} &\frac{d}{dl} + P' \quad [(1 - P)y] \\ &= [- P' + (1 - P)(P'P - PP') + P'(1 - P)]y = 0: \end{aligned} \tag{A3}$$

Next we show that if y satisfies (44) and $Qy = 0$ then $y' = P'y$. First, $Qy = 0$ implies $y = Py$. Next, we are given $y' = P'Py - PP'y$, of which the first term is $P'y$ and the second is $-PP'Py = 0$. Thus, $y' = P'y$.

3. Proof of Eq. (62)

We work in any basis for which the derivatives are defined, which we denote simply by $|x;k\rangle$. We are carrying out parallel transport along a curve $x(\lambda)$ according to (44), where the prime means $d/d\lambda$.

First we define

$$F_{\lambda;kl} = \langle x;k|\frac{d}{d\lambda}|x;l\rangle = F_{m;kl}\frac{dx^m}{d\lambda} = \frac{d}{d\lambda}\langle x;k|\quad|x;l\rangle. \tag{A4}$$

Next we note that $P|x;k\rangle = |x;k\rangle$ if $k \in A$ and 0 otherwise. This implies $\langle x;k|P|x;l\rangle = \delta_{kl}$ if $k;l \in A$, and 0 otherwise. Then by differentiating this we obtain

$$\langle x;k|P^0|x;l\rangle = \begin{cases} F_{\lambda;kl} & \text{if } k \in A \text{ and } l \notin A, \\ +F_{\lambda;kl} & \text{if } k \notin A \text{ and } l \in A, \\ 0 & \text{otherwise.} \end{cases} \tag{A5}$$

This then implies

$$\langle x;k|[P^0;P]|x;l\rangle = \begin{cases} F_{\lambda;kl} & \text{if } k \in A \text{ and } l \notin A \text{ or } k \notin A \text{ and } l \in A, \\ 0 & \text{otherwise.} \end{cases} \tag{A6}$$

Now we differentiate (61) and substitute into (44), obtaining

$$\frac{d|y\rangle}{d\lambda} = \sum_{all\,k}\frac{d}{d\lambda}|x;k\rangle y_k + |x;k\rangle\frac{dy_k}{d\lambda} = \sum_{all\,k}[P^0;P]|x;k\rangle y_k; \tag{A7}$$

or,

$$\frac{dy_k}{d\lambda} = \sum_{all\,l}\langle x;k|[P^0;P]|x;l\rangle\quad F_{\lambda;kl}y_l: \tag{A8}$$

Taking now the cases $k \in A$ and $k \notin A$, we find

$$\frac{dy_k}{d\lambda}\frac{1}{y_l} = \begin{cases} \sum_{l\notin A} F_{\lambda;kl} & \text{if } k \in A, \\ \sum_{l\in A} F_{\lambda;kl}\dfrac{y_l}{y_l} & \text{if } k \notin A. \end{cases} \tag{A9}$$

Comparing this with (60) we obtain (62).

4. Proof of (67)

In this section we write simply $|x;k\rangle$ for the basis that was denoted $|bx;k\rangle$ in Sec. IV E. It is a basis that is smooth and block-diagonalizes the Hamiltonian but is otherwise arbitrary. All

matrices in this section are taken with respect to this basis. To begin we have

$$\partial_m F^{aa}_{n;kl} = \langle x;k|\partial_m|x;l\rangle + \langle x;k|\partial_n|x;l\rangle; \tag{A10}$$

so that

$$\partial_m F^{aa}_{n;kl} - \partial_n F^{aa}_{m;kl} = \langle x;k|[\partial_m,\partial_n]|x;l\rangle \qquad (m \neq n): \tag{A11}$$

We also have

$$\begin{aligned}(F^{aa}_m F^{aa}_n)_{kl} &= \sum_{m\in A}\langle x;k|\partial_m|x;m\rangle\langle x;m|\partial_n|x;l\rangle = \sum_{m\in A}\partial_m\langle x;k|x;m\rangle\langle x;m|\partial_n|x;l\rangle \\ &= \langle x;k|\partial_m P\,\partial_n|x;l\rangle : \end{aligned} \tag{A12}$$

Combining (A11) and (A12) we find

$$G^{aa}_{mn;kl} = \partial_m F^{aa}_{n;kl} - \partial_n F^{aa}_{m;kl} + [F^{aa}_m, F^{aa}_n]_{kl} = \langle x;k|\partial_m Q\,\partial_n|x;l\rangle \qquad (m \neq n); \tag{A13}$$

where we use $P + Q = 1$. Similarly we find, for $k;l \in A$,

$$G^{bb}_{mn;kl} = \langle x;k|\partial_m P\,\partial_n|s;l\rangle \qquad (m \neq n): \tag{A14}$$

The calculation so far has a history going back at least to Baer (1975).

Now by expanding $\partial_m\langle x;k|P|x;l\rangle = 0$ we find that the matrix of P_r in the basis $|x;k\rangle$ is given by

$$P_r = \begin{pmatrix} 0 & F^{ab}_r \\ F^{ba}_r & 0 \end{pmatrix}. \tag{A15}$$

so that the product matrix is

$$P_m P_n = \begin{pmatrix} F^{ab}_m F^{ba}_n & 0 \\ 0 & F^{ba}_m F^{ab}_n \end{pmatrix}. \tag{A16}$$

This shows immediately that the off-diagonal blocks of the matrix of $[P_m, P_n]$ vanish, confirming these blocks of (67). As for the diagonal blocks, first let $k;l \in A$, so that

$$\begin{aligned}\langle x;k|P_m P_n|x;l\rangle &= \sum_{m\notin A}\langle x;k|\partial_m|x;m\rangle\langle x;m|\partial_n|x;l\rangle \\ &= -\sum_{m\notin A}\partial_m\langle x;k|x;m\rangle\langle x;m|\partial_n|x;l\rangle \\ &= \langle x;k|\partial_m Q\,\partial_n|x;l\rangle : \end{aligned} \tag{A17}$$

Antisymmetrizing this in $(m;n)$ and combining with (A13) we obtain the aa-block of (67). We derive the bb-block similarly.

REFERENCES

Aquilanti, V. and Cavalli, S., "Coordinates for molecular dynamics: Orthogonal local systems," J. Chem. Phys. 85, 1355 (1986).

Baer, M., "Adiabatic and diabatic representations for atom-molecule collisions: treatment of the collinear arrangement," Chem. Phys. Lett. 35, 112 (1975).

Baer, M., "Adiabatic and diabatic representations for atom-diatom collisions: Treatment of the three-dimensional case," Chem. Phys. 15, 49 (1976).

Baer, M., "Electronic non-adiabatic transitions. Derivation of the general adiabatic-diabatic transformation matrix," Mol. Phys. 40, 1011 (1980).

Baer, M., "Topological effects in molecular systems: an attempt towards a complete theory," Chem. Phys. 259, 123 (2000a).

Baer, M., "The topological spin as a new assignment of electronic manifolds in molecular systems," Chem. Phys. Lett. 329, 450 (2000b).

Baer, M., "The electronic adiabatic-to-diabatic transformation matrix and the Wigner rotation matrix," Chem. Phys. Lett. 347, 149 (2001).

Baer, M., "The electronic non-adiabatic coupling term in molecular systems: A theoretical approach," Adv. Chem. Phys. 124, 39 (2002).

Baer, M. and Alijah, A., "Quantized non-adiabatic coupling terms to ensure diabatic potentials," Chem. Phys. Lett. 319, 489 (2000).

Baer, M. and Englman, R., "A study of the diabatic electronic representation within the Born-Oppenheimer approximation," Mol. Phys. 75, 293 (1992).

Berry, M. V., "Quantal phase factors accompanying adiabatic changes," Proc. R. Soc. Lond. A 392 (1984).

Berry, M. V. and Robbins, J. M., "Chaotic classical and half-classical adiabatic reactions: geometric magnetism and deterministic friction," Proc. R. Soc. Lond. A 442 (1993).

Bian, X., Wu, Y., Teh, H.-H., Zhou, Z., Chen, H.-T., and Subotnik, J. E., "Modeling nonadiabatic dynamics with degenerate electronic states, intersystem crossing, and spin separation: A key goal for chemical physics," J. Chem. Phys. 154, 110901 (2021).

Bloch, C., "Sur la théorie des perturbations des états liés," Nucl. Phys. 6, 320 (1958).

Bohm, A., Boya, L. J., and Kendrick, B., "Derivation of the geometric phase," Phys. Rev. A 43, 1206 (1991).

Bohm, A., Kendrick, B., and Loewe, M. E., "The Berry phase in molecular physics," Int. J. Quantum Chem. 41, 53 (1992).

Bohm, A., Kendrick, B., Loewe, M. E., and Boya, L. J., "The Berry connection and Born-Oppenheimer method," J. Math. Phys. 33, 977 (1992).

Cave, R. J. and Newton, M. D., "Generalization of the Mullikan-Hush treatment for the calculation of electron transfer matrix elements," Chem. Phys. Lett. 249, 15 (1996).

Cave, R. J. and Newton, M. D., "Calculation of electronic coupling matrix elements for ground and excited state electron transfer reactions: Comparison of the generalized Mulliken-Hush and block diagonalization methods," J. Chem. Phys. 106, 9213 (1997).

Cederbaum, L. S., "Born-Oppenheimer approximation and beyond," in Conical Intersections: Electronic Structure, Dynamics and Spectroscopy, edited by W. Domcke, D. R. Yarkony, and H. Köppel (World Scientific, Singapore, 2004) p. 3.

Choi, S. and Vaníček, J., "How important are the residual nonadiabatic couplings for an accurate simulation of nonadiabatic quantum dynamics in a quasiadiabatic representation?" J. Chem. Phys. 154, 124119 (2021).

Cimiraglia, R., Malrieu, J.-P., Persico, M., and Spiegelmann, F., "Quasi-diabatic states and dynamical couplings from ab initio CI calculations: a new proposal," J. Phys. B 18, 3073 (1985).

des Cloizeaux, J., "Extension d'une formule de Lagrange à des problèmes de valeurs propres," Nucl. Phys. 20, 321 (1960).

Cohen-Tannoudji, C., Dupont-Roc, J., and Grynberg, G., Photons and Atoms (John Wiley & Sons, New York, 1989).

Faraji, S., Gómez-Carrasco, S., and Köppel, H., "Multistate vibronic dynamics and multiple conical intersections," in Conical Intersections, Theory, Computation and Experiment, edited by W. Domcke, D. R. Yarkony, and H. Köppel (World Scientific, Singapore, 2012) p. 249.

Herzberg, G. and Longuet-Higgins, H. C., "Intersection of potential energy surfaces in polyatomic molecules," Discuss. Faraday Soc. 35, 77 (1963).

Kato, T., "On the convergence of the perturbation method. I." Prog. Theor. Phys. 4, 514 (1949).

Kendrick, B. and Mead, C. A., "The geometric vector potential in molecular systems with arbitrarily many identical nuclei," J. Chem. Phys. 102, 4160 (1995).

Kendrick, B. K., "Geometric phase effects in chemical reaction dynamics," in Conical Intersections: Electronic Structure, Dynamics and Spectroscopy, edited by W. Domcke, D. R. Yarkony, and H. Köppel (World Scientific, Singapore, 2004) p. 521.

Kendrick, B. K., Mead, C. A., and Truhlar, D. G., "Properties of nonadiabatic couplings and the generalized Born-Oppenheimer approximation," Chem. Phys. 277, 31 (2002).

Klein, D. J., "Degenerate perturbation theory," J. Chem. Phys. 61, 786 (1974).

Kobayashi, S. and Nomizu, K., Foundations of Differential Geometry (John Wiley & Sons, Inc, New York, 1963).

Köppel, H., "Diabatic representation: Methods for the construction of diabatic electronic states," in Conical Intersections: Electronic Structure, Dynamics and Spectroscopy, edited by W. Domcke, D. R. Yarkony, and H. Köppel (World Scientific, Singapore, 2004) p. 175.

Littlejohn, R. G. and Flynn, W. G., "Geometric phases in the asymptotic theory of coupled wave equations," Phys. Rev. A 44, 5239 (1991).

Littlejohn, R. G. and Flynn, W. G., "Phase integral theory, coupled wave equations, and mode conversion," Chaos 2, 149 (1992).

Littlejohn, R. G. and Reinsch, M., "Gauge fields in the separation of rotations and internal motions in the n-body problem," Rev. Mod. Phys. 69, 213 (1997).

Longuet-Higgins, H. C., "The intersection of potential energy surfaces in polyatomic molecules," Proc. Roy. Soc. Lond. A 344, 147 (1975).

Matsunaga, N. and Yarkony, D. R., "Energies and derivative couplings in the vicinity of a conical intersection 3. The 'most' diabatic basis," Mol. Phys. 93, 79 (1998).

Mead, C. A., "Electronic spin-orbit interaction and the molecular Aharanov-Bohm effect," Chem. Phys. 49, 33 (1980a).

Mead, C. A., "The molecular Aharanov-Bohm effect in bound states," Chem. Phys. 49, 23 (1980b).

Mead, C. A., "Electronic Hamiltonian, wave functions, and energies, and derivative coupling between Born-Oppenheimer states in the vicinity of a conical intersection," J. Chem. Phys. 78, 807 (1983).

Mead, C. A., "Molecular Kramers degeneracy and non-Abelian adiabatic phase factors," Phys. Rev. Lett. 59, 161 (1987).

Mead, C. A., "The Born-Oppenheimer approximation in molecular quantum mechanics," in Mathematical Frontiers in Computational Chemical Physics, edited by D. G. Truhlar (Springer-Verlag, New York, 1988) p. 1.

Mead, C. A., "The geometric phase in molecular systems," Rev. Mod. Phys. 64, 51 (1992).

Mead, C. A. and Truhlar, D. G., "On the determination of Born-Oppenheimer nuclear motion wave functions including complications due to conical intersections and identical nuclei," J.

Chem. Phys. 70, 2284 (1979).

Mead, C. A. and Truhlar, D. G., "Conditions for the definition of a strictly diabatic electronic basis for molecular systems," J. Chem. Phys. 77, 6090 (1982).

Nakahara, M., Geometry, Topology and Physics, 2nd ed. (Taylor & Francis, New York, 2003).

von Neumann, J. and Wigner, E. P., "Über das Verhalten von Eigenwerten bei adiabatischen Prozessen," Phys. Zeit. 30, 467 (1929).

Pacher, T., Cederbaum, L. S., and Köppel, H., "Approximately diabatic states from block diagonalization of the electronic Hamiltonian," J. Chem. Phys. 89, 7367 (1988).

Pacher, T., Cederbaum, L. S., and Köppel, H., "Adiabatic and quasidiabatic states in a gauge theoretical framework," Adv. Chem. Phys. 84, 293 (1993).

Pacher, T., Mead, C. A., Cederbaum, L. S., and Köppel, H., "Gauge theory and quasiadiabatic states in molecular physics," J. Chem. Phys. 91, 7057 (1989).

Panati, G., Spohn, H., and Teufel, S., "Space-adiabatic perturbation theory in quantum dynamics," Phys. Rev. Lett. 88, 250405 (2002).

Richings, G. W. and Habershon, S., "A new diabatization scheme for direct quantum dynamics: Procrustes diabatization," J. Chem. Phys. 152, 154108 (2020).

Richings, G. W. and Worth, G. A., "A practical diabatisation scheme for use with direct-dynamics variational multi-configuration Gaussian method," J. Phys. Chem. A 119, 12457–12470 (2015).

Rosso, K. M. and Dupuis, M., "Electron transfer in environmental systems: A frontier for theoretical chemistry," Theor. Chem. Acc. 116, 124 (2006).

Simon, B., "Holonomy, the quantum adiabatic theorem, and Berry's phase," Phys. Rev. Lett. 51, 2167 (1983).

Smirnov, Y. F. and Shitikova, K. V., "Method of K harmonics and the shell model," Sov. J. Particles Nucl. 8, 344 (1977).

Smith, F. T., "Diabatic and adiabatic representations for atomic collision problems," Phys. Rev. 179, 111 (1969).

Subotnik, J. E., Cave, R. J., Steele, R. P., and Shenvi, N., "The initial and final states of electron and energy transfer processes: Diabatization as motivated by system-solvent interactions," J. Chem. Phys. 130, 234102 (2009).

Subotnik, J. E., Yeganeh, S., Cave, R. J., and Ratner, M. A., "Constructing diabatic states from adiabatic states: Extending generalized Mulliken-Hush to multiple charge centers with Boys localization," J. Chem. Phys. 129, 244101 (2008).

Teufel, S., Adiabatic Perturbation Theory in Quantum Dynamics (Springer-Verlag, Berlin, 2003).

Thompson, T. C. and Mead, C. A., "Adiabatic electronic energies and nonadiabatic couplings to all orders for system of three identical muclei with conical intersection," J. Chem. Phys. 82, 2408 (1985).

Venghaus, F. and Eisfeld, W., "Block-diagonalization as a tool for the robust diabatization of high-dimensional potential energy surfaces," J. Chem. Phys. 144, 114110 (2016).

Wang, X.-G. and Tucker Carrington, J., "A simple method for deriving kinetic energy operators," J. Chem. Phys. 113, 7097 (2000).

Weigert, S. and Littlejohn, R. G., "Diagonalization of multicomponent wave equations with a Born-Oppenehimer example," Phys. Rev. A 47, 3506 (1993).

Werner, H.-J. and Meyer, W., "MCSCF study of the avoided curve crossing of the two lowest $1S^+$ states of LiF," J. Chem. Phys. 74, 5802 (1981).

Wittig, C., "Geometric phase and gauge connection in polyatomic molecules," Phys. Chem. Chem. Phys. 14, 6409 (2012).

Wu, Y., Miao, G., and Subotnik, J. E., "Chemical reaction rates for systems with spin-orbit coupling and an odd number of electrons: Does Berry's phase lead to meaningful spin-dependent nuclear dynamics for a two state crossing?" J. Phys. Chem. A 124, 7355 (2020).

Xu, D. and Schulten, K., "Coupling of protein motion to electron transfer in a photosynthetic reaction center: Investigating the low temperature behavior in the framework of the spin-boson model," Chem. Phys. 182, 91 (1994).

Yarkony, D. R., "Diabolical conical intersections," Rev. Mod. Phys. 68, 985 (1996).

Yarkony, D. R., "Energies and derivative couplings in the vicinity of a conical intersection using degenerate perturbation theory and analytic gradient techniques. 1," J. Phys. Chem. A 101, 4263 (1997).

Yarkony, D. R., "On the adiabatic to diabatic states transformation near intersections of conical intersections," J. Chem. Phys. 112, 2111 (2000).

Yarkony, D. R., "Conical intersections: The new conventional wisdom," J. Phys. Chem. A 105, 6277 (2001).

Yarkony, D. R., "Conical intersections: Their description and consequences," in Conical Intersections: Electronic Structure, Dynamics and Spectroscopy, edited by W. Domcke, D. R. Yarkony, and H. Köppel (World Scientific, Singapore, 2004) p. 41.

Yarkony, D. R., "Nonadiabatic quantum chemistry—past, present and future," Chem. Rev. 112,

481 (2012).

Zhu, X. and Yarkony, D. R., “Non-adiabaticity: the importance of conical intersections,” Mol. Phys. 114, 1983 (2016).