Spin−Orbit Coupling and Conical Intersections. IV. A Perturbative Determination of the Electronic Energies, Derivative Couplings, and a Rigorous Diabatic Representation near a Conical Intersection. The General Case†

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Conical intersections play an essential role in electronically nonadiabatic processes. For molecules with an odd number of electrons the spin−orbit interaction produces essential changes in the topography and connectivity of points of conical intersection. In the nonrelativistic case, or when the molecule has an even number of electrons, η, the dimension of the branching space, the space in which the conical topography is evinced, is 2. By contrast, for molecules with an odd number of electrons the branching space is 5 dimensional ($\eta = 5$) in general, or 3-dimensional ($\eta = 3$) when C_s symmetry is present. Recently, we have used degenerate perturbation theory to obtain analytic representations of the energy, and of the derivative couplings, and a "rigorous" diabatic basis in the vicinity of a conical intersection for the $\eta = 3$ case. Here, we extend this analysis to the general, no symmetry, $\eta = 5$, case. The perturbative results provide valuable insights into the nature of this singular point.

I. Introduction

Conical intersections are known to play a key role in nonrelativistic, spin-conserving, electronically nonadiabatic processes.[1−8] In this case η, the dimension of the branching space,[9] is 2. The distinquishing property of the branching space is that, independent of the number of internal coordinates, the η internal coordinates spanning this space are responsible for the double cone topography of the intersecting adiabatic potential energy surfaces. In other words, the difference of the energies of the two adiabatic potential energy surfaces is lifted in a linear manner in each of these coordinates. When the spin−orbit interaction is included the situation remains unchanged, provided the molecule has an even number of electrons. However, for molecules with an odd number of electrons, odd-electron molecules, including the spin−orbit interaction changes the situation qualitatively. In this case, η is 5 in general, or 3 when C_s symmetry can be imposed.[10]

Previously, in the nonrelativistic case,[11] we used an analytic representation of the energy and derivative couplings in the vicinity of a conical intersection obtained from degenerate perturbation theory[12] to understand the effects of conical intersections on nuclear dynamics. (See also ref 9.) Extending that analysis to the $\eta = 3$ case[13] provided both, insight into this class of conical intersections, and computational tools for treating them. For example, while most treatments of nuclear motion in the presence of the spin−orbit interaction use formulations based on approximate diabatic states whose residual derivative couplings are unknown,[14] our analysis provided a transformation to a basis that is, in a well-defined approximation, rigorously diabatic in the vicinity of the conical intersection.

Here, this analysis is extended to the general, $\eta = 5$, case. As such the presentation is strictly formal, with numerical applications reserved for future publications. Section II presents the analysis of the vicinity of the conical intersection. The perturbative expressions for the electronic energies, the derivative couplings and the transformation to a locally diabatic basis are derived. The phase of the electronic wave function and its relation to Berry's classic geometric phase theorem,[15] is discussed. Section III summarizes and discusses directions for future research.

II. Theory

A. Electronic Hamiltonian. In this work relativistic effects are included in the no-pair or large component only approximation.[16] The total electronic Hamiltonian $H^e(\mathbf{r};\mathbf{R}) = H^0(\mathbf{r};\mathbf{R}) + H^{so}(\mathbf{r};\mathbf{R})$ where $H^0(\mathbf{r};\mathbf{R})$ is the nonrelativistic Coulomb Hamiltonian, $H^{so}(\mathbf{r};\mathbf{R})$ is a spin−orbit Hamiltonian, $\mathbf{R}$ denotes the coordinates of the N^{nuc} nuclei, and $\mathbf{r}$ denotes the coordinates of the N^{el} electrons. The relativistic[nonrelativistic] eigenstates, Ψ^e_i [Ψ^0_I], are eigenfunctions of $H^e(\mathbf{r};\mathbf{R})$ [$H^0(\mathbf{r};\mathbf{R})$]. Lower (upper) case letters will be used to denote eigenfunctions of H^e (H^0). A point of conical intersection of states i,j of H^e [I, J of H^0] will be denoted $\mathbf{R}^{x,ij}$ [$\mathbf{R}^{x,IJ}$].

B. Time Reversal Symmetry and Conical Intersections. In the Introduction, it was observed that conical intersections with different η were possible. The origin of these differences[10] is the behavior of the wave functions under the time reversal operator.[17] The time reversal operator, T, is an anti-unitary operator, that is, for ϕ and ψ arbitrary functions, $\langle\phi|\psi\rangle^* = \langle T\phi|T\psi\rangle$, with $T^2 = +I(-I)$ if the number of electrons is even (odd). For a molecule with an odd number of electrons

$$\langle\phi|T\phi\rangle^* = \langle T\phi|T^2\phi\rangle = -\langle T\phi|\phi\rangle = -\langle\phi|T\phi\rangle^*$$

so that

$$\langle\phi|T\phi\rangle = 0 \tag{1a}$$

that is ϕ and $T\phi$ are orthogonal. Further, because T commutes with H^e, ψ and $T\psi$ are degenerate and

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$$\langle\phi|H^e\psi\rangle^* = \langle T\phi|TH^e\psi\rangle = \langle T\phi|H^eT\psi\rangle \quad (1b)$$

The degeneracy of Ψ^e_i and $T\Psi^e_i$ is referred to as Kramers' degeneracy.[18] For a molecule with an even number of electrons, ϕ and $T\phi$ are linearly dependent and with the choice $\phi = T\phi$

$$\langle\phi|H^e\psi\rangle^* = \langle T\phi|TH^e\psi\rangle = \langle T\phi|H^eT\psi\rangle = \langle\phi|H^e\psi\rangle \quad (1c)$$

Thus, in this case, compared to eq 1b, $\langle\phi|H^e\psi\rangle$ is real-valued. A set of functions will be referred to as time-reversal adapted, provided for each ϕ in the set $T\phi$ is also in the set.

To summarize, for an even-electron molecule, the pairs, Ψ and $T\Psi$, are linearly dependent so that a conical intersection involves two intersecting states. All matrix elements of the Hamiltonian may be chosen real-valued. However, for an odd-electron molecule the wave functions come in linearly independent pairs, Ψ and $T\Psi$. At a conical intersection *four*, rather than two, states must become degenerate. The nonvanishing interactions among these states will in general be complex-valued. With these observations we are in a position to explain the changes in the dimension of the branching space noted in the Introduction. To accomplish this, perturbation theory is used to rigorously reduce the, in general, infinite dimensional Hilbert space describing the electronic states to one of minimal dimension.

C. Perturbation Theory and Conical Intersections. The restriction in the dimension of the electronic space is accomplished by the judicious choice of basis states. Assume that initially each Ψ^e_k is expanded in a basis of time-reversal adapted configuration state functions (TRA-CSFs[19] ψ^e)

$$\Psi^e_k(\mathbf{r};\mathbf{R}) = \sum_{\alpha=1}^{N^{CSF}} d^k_\alpha(\mathbf{R})\psi^e_\alpha(\mathbf{r};\mathbf{R}) \quad (2a)$$

where N^{CSF} is large and $\mathbf{d}^k$, which is complex-valued, can be written in terms of its real and imaginary parts as $\mathbf{d}^k \equiv \mathbf{d}^{r,k} + i\,\mathbf{d}^{i,k}$. The $\mathbf{d}^k$ are the solutions of the electronic Schrödinger equation in the TRA-CSF basis

$$[\mathbf{H}^{e,r}(\mathbf{R}) + i\mathbf{H}^{e,i}(\mathbf{R}) - E^e_k(\mathbf{R})]\mathbf{d}^k(\mathbf{R}) = 0 \quad (2b)$$

where

$$\langle\psi^e_\alpha(\mathbf{r};\mathbf{R})|H^e(\mathbf{r};\mathbf{R})|\psi^e_\beta(\mathbf{r};\mathbf{R})\rangle_{\mathbf{r}} \equiv H^e_{\alpha\beta}(\mathbf{R}) = \mathrm{Re}H^e_{\alpha\beta}(\mathbf{R}) + i\mathrm{Im}H^e_{\alpha\beta}(\mathbf{R}) \equiv H^{e,r}_{\alpha\beta}(\mathbf{R}) + iH^{e,i}_{\alpha\beta}(\mathbf{R}) \quad (2c)$$

Here, and throughout this work the matrix element $M_{i,j}$ will, for simplicity, be written M_{ij} when no confusion will result.

The desired reduction in dimension can be obtained with the use of a time-reversal adapted crude adiabatic basis defined by

$$\Psi^c_k(\mathbf{r};\mathbf{R}) = \sum_{\alpha=1}^{N^{CSF}} d^k_\alpha(\mathbf{R}^{x,ij})\psi^e_\alpha(\mathbf{r};\mathbf{R}) \quad (3)$$

Note that each point of conical intersection requires a distinct crude adiabatic basis. To describe $E^e_k(\mathbf{R})$ near an $\mathbf{R}^{x,ij,}$ we expand $\mathbf{H}^e(\mathbf{R})$ to second-order giving

$$\mathbf{H}^e(\mathbf{R}) = \mathbf{H}^e(\mathbf{R}^{x,ij}) + \nabla\mathbf{H}^e(\mathbf{R}^{x,ij})\cdot\delta\mathbf{R} + (1/2)\delta\mathbf{R}\cdot\nabla\nabla\mathbf{H}^e(\mathbf{R}^{x,ij})\cdot\delta\mathbf{R} \quad (4)$$

where $\delta\mathbf{R} = \mathbf{R} - \mathbf{R}^{x,ij}$. Re-expressing $\mathbf{H}^e$ in the crude adiabatic basis gives

$$\tilde{\mathbf{H}}^e(\mathbf{R}) \equiv \mathbf{d}^\dagger(\mathbf{R}^{x,ij})\mathbf{H}^e(\mathbf{R})\mathbf{d}(\mathbf{R}^{x,ij}) \quad (5a)$$

$$\approx \mathbf{d}(\mathbf{R}^{x,ij})^\dagger[\mathbf{H}^e(\mathbf{R}^{x,ij}) + \nabla\mathbf{H}^e(\mathbf{R}^{x,ij})\cdot\delta\mathbf{R} + (1/2)\delta\mathbf{R}\cdot\nabla\nabla\mathbf{H}^e(\mathbf{R}^{x,ij})\cdot\delta\mathbf{R}]\mathbf{d}(\mathbf{R}^{x,ij}) \quad (5b)$$

$$\equiv \mathbf{E}^e(\mathbf{R}^{x,ij}) + \underline{\tilde{\mathbf{H}}}^{[1]}\cdot\delta\mathbf{R} + (1/2)\delta\mathbf{R}\cdot\underline{\underline{\tilde{\mathbf{H}}}}^{[2]}\cdot\delta\mathbf{R} \quad (5c)$$

where the matrix elements of $\mathbf{E}^e(\mathbf{R}^{x,ij})$, are $\mathrm{E}^e(\mathbf{R}^{x,ij})_{kl} = \delta_{kl}E^e_l(\mathbf{R}^{x,ij})$, $\mathbf{d}$ is a matrix composed of columns $\mathbf{d}^k$, † denotes the complex conjugate transpose, a single (double) bar under a quantity denotes a vector (matrix) of matrices, so that

$$\underline{\tilde{\mathbf{H}}}^{[1]} = (\tilde{\mathbf{H}}^{(1),1}, \tilde{\mathbf{H}}^{(1),2}, ..., \tilde{\mathbf{H}}^{(1),N^{int}}) \quad (6a)$$

$$\underline{\underline{\tilde{\mathbf{H}}}}^{[2]} = (\tilde{\mathbf{H}}^{(2),11}, \tilde{\mathbf{H}}^{(2),21}, \tilde{\mathbf{H}}^{(2),31}, ..., \tilde{\mathbf{H}}^{(2),N^{int}N^{int}}) \quad (6b)$$

with

$$\tilde{H}^{(1),\kappa}_{mn}(\mathbf{R}) = \mathbf{d}^m(\mathbf{R}^{x,ij})^\dagger\left[\frac{\partial}{\partial R_\kappa}\mathbf{H}^e(\mathbf{R})\right]\mathbf{d}^n(\mathbf{R}^{x,ij}) \quad (7a)$$

$$\equiv h^{mn}_\kappa(\mathbf{R}) \text{ if } m \neq n \text{ and} \equiv g^m_\kappa(\mathbf{R}) \text{ if } m = n \quad (7b)$$

and finally

$$\tilde{H}^{(2),\kappa\kappa'}_{mn}(\mathbf{R}) = \mathbf{d}^m(\mathbf{R}^{x,ij})^\dagger\left[\frac{\partial}{\partial R_\kappa\partial R_{\kappa'}}\mathbf{H}^e(\mathbf{R})\right]\mathbf{d}^n(\mathbf{R}^{x,ij}) \quad (7c)$$

The eigenstates are expanded in the crude adiabatic basis

$$\Psi^e_k(\mathbf{r};\mathbf{R}) = \sum_{l\in Q}\xi^k_l(\mathbf{R})\Psi^c_l(\mathbf{r};\mathbf{R}) + \sum_{l\in P}\Xi^k_l(\mathbf{R})\Psi^c_l(\mathbf{r};\mathbf{R}) \quad (8)$$

where Q is spanned by the functions degenerate at $\mathbf{R}^{x,ij}$ and P is its orthogonal complement. Thus Q has dimension 4(2) for the case of an odd (even) electron molecule.

To describe the vicinity of a conical intersection we require the contributions linear in $\delta\mathbf{R}$ to eq 2b. To accomplish this we expand $\xi(\mathbf{R})$, $\Xi(\mathbf{R})$, and $E^e_i(\mathbf{R})$

$$\xi^k(\mathbf{R}) = \xi^{(0),k}(\mathbf{R}^{x,ij}) + \xi^{(1),k}(\mathbf{R}) + \xi^{(2),k}(\mathbf{R}) \quad (9a)$$

$$\Xi^k(\mathbf{R}) = \qquad \Xi^{(1),k}(\mathbf{R}) + \Xi^{(2),k}(\mathbf{R}) \quad (9b)$$

$$E^e_k(\mathbf{R}) = E^e_k(\mathbf{R}^{x,ij}) + E^{e,(1)}_k(\mathbf{R}) + E^{e,(2)}_k(\mathbf{R}) \quad (9c)$$

where the superscript (n) indicates the order of contribution from $\delta\mathbf{R}$. In eq 9b, we observed that since the crude adiabatic basis is used $\Xi^{(0),k} = 0$ for $k \in Q$. With this observation partitioning theory[20] can be used to show that the degeneracy is lifted at first order, that is linearly, in the Q-space only, which will therefore be used to define the branching space. Equation 2b can be rewritten as

$$\begin{pmatrix} {}^{QQ}\mathbf{H}^e - E^e_k\mathbf{I} & {}^{QP}\mathbf{H}^e \\ {}^{PQ}\mathbf{H}^e & {}^{PP}\mathbf{H}^e - E^e_k\mathbf{I}\end{pmatrix}\begin{pmatrix}\boldsymbol{\xi}^k \\ \boldsymbol{\Xi}^k\end{pmatrix} = \begin{pmatrix}\mathbf{0}\\ \mathbf{0}\end{pmatrix} \quad \begin{matrix}(10a)\\(10b)\end{matrix}$$

where ${}^{AB}H^e_{ij} = \tilde{H}^e_{ij}$ provided $i \in$ A and $j \in$ B with $A, B \in Q, P$. Then solving eq 10b for $\boldsymbol{\Xi}^k$ and inserting the result in eq 10a gives

$$({}^{QQ}\mathbf{H}^{e} + {}^{QP}\mathbf{H}^{e}\,(E_k^{e}\mathbf{I} - {}^{PP}\mathbf{H}^{e})^{-1}\,{}^{PQ}\mathbf{H}^{e} - E_k^{e}\mathbf{I})\boldsymbol{\xi}^{k} = \mathbf{0} \quad (10c)$$

Because ${}^{QP}H_{ik}^{e}(\mathbf{R}^{x,ij}) = 0 = \Xi_i^{(0),k}$, the second term in eq 10c does not contribute until second order. Thus, the first-order result is

$$(\underline{\tilde{\mathbf{H}}}^{[1]} \cdot \delta\mathbf{R} - E_k^{e,(1)}(\mathbf{R}))\boldsymbol{\xi}^{(0),k}(\mathbf{R}^{x,ij}) = \mathbf{0} \quad (11)$$

These equations are valid whether the system has an even or odd number of electrons. The analytic solution of eq 11 with its qualifying equalities eqs 7−9, is the lynchpin for the remainder of this work.

D. Branching Space. Using eqs 1a, 7b and the *four* function Q-space spanned by Ψ^{e}_i, Ψ^{e}_j and $T\Psi^{e}_i \equiv \Psi^{e}_{Ti}$, $T\Psi^{e}_j \equiv \Psi^{e}_{Tj}$, the Hamiltonian in eq 11 becomes

$$\underline{\tilde{\mathbf{H}}}^{[1]} \cdot \delta\mathbf{R} = (\mathbf{s}^{ij} \cdot \delta\mathbf{R})\mathbf{I} + \begin{pmatrix} -\mathbf{g}^{ij} & \mathbf{h}^{ij} & 0 & \mathbf{h}^{iTj} \\ \mathbf{h}^{ij*} & \mathbf{g}^{ij} & -\mathbf{h}^{iTj} & 0 \\ 0 & -\mathbf{h}^{iTj*} & -\mathbf{g}^{ij} & \mathbf{h}^{ij*} \\ \mathbf{h}^{iTj*} & 0 & \mathbf{h}^{ij} & \mathbf{g}^{ij} \end{pmatrix} \cdot \delta\mathbf{R} \quad (12a)$$

where $\mathbf{R} = \mathbf{R}^{x,ij} + \delta\mathbf{R}$, $2\mathbf{g}^{ij} = \mathbf{g}^{i} - \mathbf{g}^{j}$ and $2\mathbf{s}^{ij} = \mathbf{g}^{i} + \mathbf{g}^{j}$ and all matrix elements are evaluated at $\mathbf{R}^{x,ij}$. In appendix A, it is shown that the four eigenvalues of $\underline{\tilde{\mathbf{H}}}^{[1]} \cdot \delta\mathbf{R}$ are

$$E_{\pm}^{e}(\mathbf{R}) = (\mathbf{s}^{ij} \cdot \delta\mathbf{R}) \pm \sqrt{([\mathbf{g}^{ij} \cdot \delta\mathbf{R}]^2 + |\mathbf{h}^{ij} \cdot \delta\mathbf{R}|^2 + |\mathbf{h}^{iTj} \cdot \mathbf{R}|^2)} \quad (13)$$

where $E^{e}_{-} = E_i^{e,(1)}$, $E^{e}_{+} = E_j^{e,(1)}$ and each is doubly degenerate. To proceed further, it is necessary to distinguish between even and odd-electron systems. For odd-electron systems in the absence of spatial symmetry, eq 12a is applicable in its full generality. When C_s or higher symmetry exists $\mathbf{h}^{iTj} = 0$ (ref 10) so that eq 12a becomes

$$\underline{\tilde{\mathbf{H}}}^{[1]} \cdot \delta\mathbf{R} = (\mathbf{s}^{ij} \cdot \delta\mathbf{R})\mathbf{I} + \begin{pmatrix} -\mathbf{g}^{ij} & \mathbf{h}^{ij} & 0 & 0 \\ \mathbf{h}^{ij*} & \mathbf{g}^{ij} & 0 & 0 \\ 0 & 0 & -\mathbf{g}^{ij} & \mathbf{h}^{ij*} \\ 0 & 0 & \mathbf{h}^{ij} & \mathbf{g}^{ij} \end{pmatrix} \cdot \delta\mathbf{R} \quad (12b)$$

For even-electron systems there are only two independent, degenerate functions at $\mathbf{R}^{x,ij}$, Ψ^{e}_i and Ψ^{e}_j and the Hamiltonian matrix is symmetric. Equation 12a reduces to

$$\underline{\tilde{\mathbf{H}}}^{[1]} \cdot \delta\mathbf{R} = (\mathbf{s}^{ij} \cdot \delta\mathbf{R})\mathbf{I} + \begin{pmatrix} -\mathbf{g}^{ij} & \mathbf{h}^{ij} \\ \mathbf{h}^{ij} & \mathbf{g}^{ij} \end{pmatrix} \cdot \delta\mathbf{R} \quad (12c)$$

When only $\mathbf{H}^0$ is used, the Hamiltonian matrix is symmetric and $\mathbf{h}^{iTj} = 0$ for all $\mathbf{R}$, regardless of the number of electrons. Then for odd-electron molecules eq 12b reduces to the direct sum of two copies of eq 12c. From eq 13, the linearly independent, nonvanishing, members of the five vectors $\mathbf{g}^{ij}(\mathbf{R}^{x,ij})$, $\mathbf{Re}\mathbf{h}^{ij}(\mathbf{R}^{x,ij}) \equiv \mathbf{h}^{r,ij}(\mathbf{R}^{x,ij})$, $\mathrm{Im}\mathbf{h}^{ij}(\mathbf{R}^{x,ij}) \equiv \mathbf{h}^{i,ij}(\mathbf{R}^{x,ij})$, and $\mathrm{Re}\mathbf{h}^{iTj}(\mathbf{R}^{x,ij}) \equiv \mathbf{h}^{r,iTj}(\mathbf{R}^{x,ij})$, $\mathbf{Im}\mathbf{h}^{iTj}(\mathbf{R}^{x,ij}) \equiv \mathbf{h}^{i,iTj}(\mathbf{R}^{x,ij})$, lift the degeneracy in a linear manner and therefore constitute the branching space. Thus $\eta = 5$, 3 and 2 for eqs 12a, 12b, and 12c and $\eta = 2$ always for H^0, as noted in the Introduction.

E. Intersection-Adapted Coordinates. $\underline{\tilde{\mathbf{H}}}^{[1]} \cdot \delta\mathbf{R}$ is most conveniently expressed in terms of z, x, y, v, w, displacements along the intersection-adapted coordinates,[9] $\mathbf{z} = \mathbf{g}^{ij}(\mathbf{R}^{x,ij})/g$, $\mathbf{x} = \mathbf{h}^{r,ij}(\mathbf{R}^{x,ij})/h^{r}$, $\mathbf{y} = \mathbf{h}^{i,ij}(\mathbf{R}^{x,ij})/h^{i}$, $\mathbf{v} = \mathbf{h}^{r,iTj}(\mathbf{R}^{x,i})/t^{r}$, $\mathbf{w} = \mathbf{h}^{i,iTj}(\mathbf{R}^{x,i})/t^{i}$ where $g = ||\mathbf{g}^{ij}(\mathbf{R}^{x,ij})||$, $h^{r} = ||\mathbf{h}^{r,ij}(\mathbf{R}^{x,ij})||$, $h^{i} = ||\mathbf{h}^{i,ij}(\mathbf{R}^{x,ij})||$, $t^{r} = ||\mathbf{h}^{r,iTj}(\mathbf{R}^{x,ij})||$, $t^{i} = ||\mathbf{h}^{i,iTj}(\mathbf{R}^{x,ij})||$. With these definitions

$$\underline{\tilde{\mathbf{H}}}^{[1]} \cdot \delta\mathbf{R} = (\mathbf{s}^{ij} \cdot \delta\mathbf{R})\mathbf{I} + \mathbf{H}^{(1)}(x, y, z, v, w) \quad (14a)$$

$$\mathbf{H}^{(1)}(x, y, z, v, w) = \begin{pmatrix} -gz & h^{r}x + ih^{i}y & 0 & t^{r}v + it^{i}w \\ h^{r}x - ih^{i}y & gz & -(t^{r}v + it^{i}w) & 0 \\ 0 & -(t^{r}v - it^{i}w) & -gz & h^{r}x - ih^{i}y \\ t^{r}v - it^{i}w & 0 & h^{r}x + ih^{i}y & gz \end{pmatrix} \quad (14b)$$

where

$$gz = \mathbf{g}^{ij}(\mathbf{R}^{x,ij}) \cdot \delta\mathbf{R} \quad (15a)$$

$$h^{r}x + ih^{i}y = \mathbf{h}^{ij}(\mathbf{R}^{x,ij}) \cdot \delta\mathbf{R} \quad (15b)$$

$$t^{r}v + it^{i}w = \mathbf{h}^{iTj}(\mathbf{R}^{x,ij}) \cdot \delta\mathbf{R} \quad (15c)$$

It will be convenient to replace these Cartesian coordinates with the spherical polar coordinates $\rho^{(1)}$, $\theta^{(1)}$, $\phi^{(1)}$, for the $\mathbf{z}$, $\mathbf{x}$, $\mathbf{y}$ ($\mathbf{g}^{ij}$, $\mathbf{h}^{r,ij}$, $\mathbf{h}^{i,ij}$) axes and polar coordinates ρ', $\phi^{(2)}$ for the $\mathbf{v}$, $\mathbf{w}$ ($\mathbf{h}^{r,iTj}$, $\mathbf{h}^{i,iTj}$) axes. These coordinates are defined in Appendix B as

$$z = \rho^{(1)}\cos\theta^{(1)} \quad x = \rho^{(1)}\sin\theta^{(1)}\cos\phi^{(1)} \quad y = \rho^{(1)}\sin\theta^{(1)}\sin\phi^{(1)} \quad (B.1)$$

and

$$v = \rho'\cos\phi^{(2)} \quad w = \rho'\sin\phi^{(2)} \quad (B.2)$$

Because the $\mathbf{d}^{k}$, $k = i, j, Ti, Tj$ are defined only up to a unitary transformation among themselves only the branching space, rather than the individual vectors, is well defined. This flexibility can be put to advantage. The basis vectors defined above are most useful if they are mutually orthogonal. In the $\eta = 2$ (ref 21) and $\eta = 3$ (ref 22) cases, we have shown that the vectors defining the branching space can indeed be chosen orthogonal, without altering the form of eq 14. In Appendix C, a dimensionality argument is used to show that this may also be accomplished for the vectors $\mathbf{g}^{ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{r,ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{i,ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{r,iTj}(\mathbf{R}^{x,ij})$, and $\mathbf{h}^{i,iTj}(\mathbf{R}^{x,ij})$.

F. Eigenvectors. A key goal of this work is the characterization of the singularity in the derivative couplings. To achieve this goal, an analytic expression for the eigenvectors of $\mathbf{H}^{(1)}$ is required. This result will also enable a discussion of the geometric phase effect and determination of an approximate diabatic basis that eliminates the singular part of the derivative coupling. In Appendix B, the eigenvectors of $\mathbf{H}^{(1)}$ are derived. The result is expressed as a transformation $\mathbf{U}^{(p)}$ from Ψ^{c}_k, to $\Psi^{e}_{k'}$, $k = i, j, Ti, Tj$, and $k' = i, Tj, j, Ti$

$$\Psi^{e\dagger} = \Psi^{c\dagger}\mathbf{U}^{(p)}(\rho^{(1)}, \theta^{(1)}, \phi^{(1)}, \rho', \phi^{(2)}) \quad (16a)$$

where

$$\mathbf{U}^{(\mathrm{p})} = \begin{pmatrix} \cos\Theta^{(1)}\cos\Theta^{(2)} & \cos\Theta^{(1)}e^{i\gamma^{(2)}}\sin\Theta^{(2)} & e^{i\gamma^{(1)}}\sin\Theta^{(1)}\cos\Theta^{(2)} & e^{i\gamma^{(1)}}\sin\Theta^{(1)}e^{i\gamma^{(2)}}\sin\Theta^{(2)} \\ -e^{-i\gamma^{(1)}}\sin\Theta^{(1)}\cos\Theta^{(2)} & -e^{-i\gamma^{(1)}}\sin\Theta^{(1)}e^{i\gamma^{(2)}}\sin\Theta^{(2)} & \cos\Theta^{(1)}\cos\Theta^{(2)} & \cos\Theta^{(1)}e^{i\gamma^{(2)}}\sin\Theta^{(2)} \\ -e^{-i\gamma^{(1)}}\sin\Theta^{(1)}e^{-i\gamma^{(2)}}\sin\Theta^{(2)} & e^{-i\gamma^{(1)}}\sin\Theta^{(1)}\cos\Theta^{(2)} & -\cos\Theta^{(1)}e^{-i\gamma^{(2)}}\sin\Theta^{(2)} & \cos\Theta^{(1)}\cos\Theta^{(2)} \\ -\cos\Theta^{(1)}e^{-i\gamma^{(2)}}\sin\Theta^{(2)} & \cos\Theta^{(1)}\cos\Theta^{(2)} & e^{i\gamma^{(1)}}\sin\Theta^{(1)}e^{-i\gamma^{(2)}}\sin\Theta^{(2)} & -e^{i\gamma^{(1)}}\sin\Theta^{(1)}\cos\Theta^{(2)} \end{pmatrix} \quad (16b)$$

The $\Theta^{(i)}$, $\gamma^{(i)}$ $i = 1, 2$, are functions of $\rho^{(1)}$, $\theta^{(1)}$, $\phi^{(1)}$, and ρ', $\phi^{(2)}$ as discussed in Appendix B.

G. Derivative Couplings and Diabatic States. According to eq 8 at an arbitrary **R** the adiabatic states can be expanded in a basis of crude adiabatic states

$$\Psi^{\mathrm{e}}_{\kappa}(\mathbf{r};\mathbf{R}) = \sum_{w\in Q,P} \Psi^{c}_{w}(\mathbf{r};\mathbf{R})U_{wk}(\mathbf{R}) \quad (17)$$

The derivative coupling $\mathbf{f}^{kl}(\mathbf{R})$ is given by

$$\mathbf{f}^{kl}(\mathbf{R}) = \langle\Psi^{\mathrm{e}}_{k}(\mathbf{r};\mathbf{R})|\nabla\Psi^{\mathrm{e}}_{l}(\mathbf{r};\mathbf{R})\rangle = {}^{\mathrm{CI}}\mathbf{f}^{kl} + {}^{\mathrm{CSF}}\mathbf{f}^{kl} \quad (18a)$$

where

$${}^{\mathrm{CI}}\mathbf{f}^{kl} = \sum_{w} U^{\dagger}_{kw}(\mathbf{R})\nabla U_{wl}(\mathbf{R}) \quad (18b)$$

$${}^{\mathrm{CSF}}\mathbf{f}^{kl} = \sum_{w,w'} U^{\dagger}_{kw}(\mathbf{R})\mathbf{f}^{ww'}U_{w'l}(\mathbf{R}) \text{ and}$$

$$\mathbf{f}^{ww'} = \langle\Psi^{\mathrm{c}}_{w}(\mathbf{r};\mathbf{R})|\nabla\Psi^{\mathrm{c}}_{w'}(\mathbf{r};\mathbf{R})\rangle_{\mathbf{r}} \quad (18c)$$

Note that because the $\mathbf{f}^{kl}$ are complex-valued $\mathbf{f}^{kk}$ is nonzero. Further since the $\Psi^{\mathrm{e}}{}_{k}$ are determined only up to a phase

$$\langle e^{i\Omega_k(\mathbf{R})}\Psi^{\mathrm{e}}_{k}(\mathbf{r};\mathbf{R})|\nabla e^{i\Omega_l(\mathbf{R})}\Psi^{\mathrm{e}}_{l}(\mathbf{r};\mathbf{R})\rangle = e^{-i(\Omega_k-\Omega_l)}\mathbf{f}^{kl}(\mathbf{R}) + i\delta_{kl}\nabla\Omega_l \quad (19)$$

and the diagonal derivative coupling, $\mathbf{f}^{kk}$, is only determined once that phase is specified.

Near the conical intersection the derivative coupling is singular. The singularity in the derivative coupling is contained in the term ${}^{\mathrm{CI}}\mathbf{f}^{kl}$. The contribution from ${}^{\mathrm{CSF}}\mathbf{f}^{kl}$ is non singular. Indeed it is quite modest, arising from the limited geometry dependence of the TRA-CSFs. Near $\mathbf{R}^{x,ij}$, **U** can be approximated by $\mathbf{U}^{(\mathrm{p})}$, that is $U_{wk} \cong U^{(p)}{}_{wk} = \xi^{k(0)}_{w}$ for w, $k \in Q$, and $U_{wk} = 0$ otherwise. From this observation and eq 16a, the *inverse* transformation $\mathbf{U}^{-1}$ applied to the "exact" adiabatic states (that is the solution to eq 2b) produces states that approach the crude adiabatic states as $\mathbf{R} \rightarrow \mathbf{R}^{x,ij}$ which because of their limited geometry dependence are approximate diabatic states. Alternatively, replacing the unknown $\mathbf{U}(\mathbf{R})$ by the known $\mathbf{U}^{(\mathrm{p})}(\mathbf{R}^{x,ij})$ yields approximate diabatic states which rigorously remove the singularity in the derivative coupling at the conical intersection and generally improve in quality as $\mathbf{R}^{x,ij}$ is approached. In the nonrelativistic case, this class of approximate diabatic states has been used in studies of nuclear dynamics with promising results.[23]

As in the $\eta = 2$(ref 24) and $\eta = 3$ (ref 13) cases, determination of **U** for higher order displacements is possible and will be the subject of a future work.

Explicit expressions for the singular components of the derivative coupling can be obtained from the definition of ${}^{\mathrm{CI}}\mathbf{f}^{kl}$ in eq 18b, with $U_{wk} = U^{(p)}{}_{wk}$ that is

$${}^{\mathrm{CI}}\mathbf{f}^{kl} = \sum_{w\in Q} U^{(p)*}_{wk}\nabla U^{(p)}_{wl} \quad (20)$$

We find, suppressing (here and below) the superscript CI and replacing *Tjk* with *Tj,k* for clarity

$$\mathbf{f}^{Tj,i} = e^{-i\gamma^{(2)}}(-\nabla\Theta^{(2)} + i\nabla\gamma^{(2)}/2\,\sin 2\Theta^{(2)}) \quad (21a)$$

$$\mathbf{f}^{ji} = e^{-i\gamma^{(1)}}(-\cos 2\Theta^{(2)}\nabla\Theta^{(1)} + i[\sin 2\Theta^{(1)}\cos 2\Theta^{(2)}\nabla\gamma^{(1)}/2]) \quad (21b)$$

$$\mathbf{f}^{Ti,i} = e^{-i(\gamma^{(1)}+\gamma^{(2)})}(-\sin 2\Theta^{(2)}\nabla\Theta^{(1)} + i[\sin 2\Theta^{(1)}\sin 2\Theta^{(2)}\nabla\gamma^{(1)}/2]) \quad (21c)$$

$$\mathbf{f}^{ii} = -i(\nabla\gamma^{(1)}\sin^{2}\Theta^{(1)} + \nabla\gamma^{(2)}\sin^{2}\Theta^{(2)}) \quad (21d)$$

$$\mathbf{f}^{jj} = i(\nabla\gamma^{(1)}\sin^{2}\Theta^{(1)} - \nabla\gamma^{(2)}\sin^{2}\Theta^{(2)}) \quad (21e)$$

$$\mathbf{f}^{Tj,j} = e^{i(\gamma^{(1)}-\gamma^{(2)})}(\sin 2\Theta^{(2)}\nabla\Theta^{(1)} + i[\sin 2\Theta^{(1)}\sin 2\Theta^{(2)}\nabla\gamma^{(1)}/2]) \quad (21f)$$

In eqs 21a−21f, for notational simplicity, ∇ indicates differentiations with respect to a general set the independent variables, including $\rho^{(2)}$, $\Theta^{(i)}$, $\gamma^{(i)}$, $i = 1, 2$. The previously reported[13] $\eta = 3$ results are obtained from eqs 21a−21e by setting $\Theta^{(2)} = \gamma^{(2)} = 0$. In the $\eta = 3$ case $\mathbf{f}^{Tj,i}$ vanishes, as expected, because in this case the Ψ and $\mathrm{T}\Psi$ blocks are not coupled. As $f^{kl}_{\rho^{(2)}} = 0$, $k, l \in i, j$ (at this order) the singularity in the derivative couplings can only arise from the $\eta - 1 = 4$ angular coordinates. A similar result is obtained in the $\eta = 3$ (ref 13) and 2 (ref 24) cases where the singular derivative couplings are restricted derivatives with respect to $\eta - 1$ angular coordinates.

In practical applications, the $\mathbf{f}^{kl}$ are required in terms of the original Cartesian intersection-adapted coordinates, *x*, *y*, *z*, *υ*, *w*. Expressing the components of $\mathbf{f}^{kl}$ in these coordinates will also make the nature of the divergence in $\mathbf{f}^{kl}$ clear. This change of variables is accomplished using the chain rule. The details are presented in Appendix D and yield (note $f^{kl}_{\rho^{(2)}} = 0$) for $s =$ *x*, *y*, or *z*

$$f^{k,l}_{s} = \left(\frac{\partial\theta^{(1)}}{\partial s}\frac{[h^{(1)}g]}{q^{(1)^2}} + \frac{\partial\phi^{(1)}}{\partial s}\frac{[h^{\mathrm{i}^2} - h^{\mathrm{r}^2}]}{2h^{(1)}}\sin 2\phi^{(1)}\frac{g\sin 2\theta^{(1)}}{2q^{(1)^2}}\right)\frac{f^{k,l}_{\Theta^{(1)}}}{2} + \frac{\partial\phi^{(1)}}{\partial s}\frac{[h^{\mathrm{i}}h^{\mathrm{r}}]}{h^{(1)^2}}f^{k,l}_{\gamma^{(1)}} + \frac{\rho^{(1)}\rho_q{}'}{\rho^{(2)^2}}\left(\frac{\partial\theta^{(1)}}{\partial s}\frac{[g^2 - h^{(1)^2}]}{2q^{(1)}}\sin 2\theta^{(1)} - \frac{\partial\phi^{(1)}}{\partial s}\frac{[h^{\mathrm{i}^2} - h^{\mathrm{r}^2}]}{2q^{(1)}}\sin 2\phi^{(1)}\sin^{2}\theta^{(1)} - \frac{\partial\rho^{(1)}}{\partial s}\frac{q^{(1)}}{\rho^{(1)}}\right)\frac{f^{k,l}_{\Theta^{(2)}}}{2} \quad (22)$$

for $s = \upsilon$ or w

$$f^{kl}_{s} = \frac{\rho_q{}^{(1)}}{\rho_q{}'^2 + \rho_q{}^{(1)^2}}\left(\frac{\partial\phi^{(2)}}{\partial s}\rho'\frac{[t^{\mathrm{i}^2} - t^{\mathrm{r}^2}]}{2q^{(2)}}\sin 2\phi^{(2)} + \frac{\partial\rho'}{\partial s}q^{(2)}\right)\frac{f^{k,l}_{\Theta^{(2)}}}{2} + \frac{\partial\phi^{(2)}}{\partial s}\frac{t^{\mathrm{i}}t^{\mathrm{r}}}{q^{(2)^2}}f^{k,l}_{\gamma^{(2)}} \quad (23)$$

Here and in eq 24, below $k, l \in i, j, Ti, Tj$ and the f^{kl}_{ω}, $\omega = \Theta^{(i)}$, $\gamma^{(i)}$, $i = 1, 2$, are given in eqs 21a−21f. Note that when they do not vanish, $(\partial\phi^{(1)}/\partial s)$, $(\partial\theta^{(1)}/\partial s) \approx 1/\rho^{(1)}$, $(\partial\phi^{(2)}/\partial s) \approx 1/\rho'$, whereas $(\partial\rho/\partial s) \approx \rho^0$, for $\rho = \rho^{(1)}$ or ρ'. Then, because the conical intersection is located at $\rho^{(1)} = \rho' = 0$ from eqs 22 and 23 the singularities in the derivative couplings are seen to be of the form

$$\frac{1}{\rho'} f^{kl}_{\gamma^{(2)}}, \frac{\rho'}{\rho^{(2)^2}} f^{kl}_{\Theta^{(2)}} \text{ or } \frac{\rho^{(1)}}{\rho^{(2)^2}} f^{kl}_{\Theta^{(2)}}, \frac{1}{\rho^{(1)}} f^{kl}_{\Theta^{(1)}}, \frac{1}{\rho^{(1)}} f^{kl}_{\gamma^{(1)}} \qquad (24)$$

H. Geometric Phase. Although somewhat tangential to this work we comment briefly on the geometric phase effect, reserving a more complete treatment for a future work. The geometric phase was first introduced by Longuet-Higgins[25] to treat the Jahn−Teller problem, subsequently used by Mead and Truhlar[26] in the single electronic state nuclear motion problem, and ultimately generalized to arbitrary adiabatic processes in the highly influential work of Berry.[15] Both Longuet-Higgins, and Mead and Truhlar, employed a Hamiltonian of the form in eq 12c, whereas Berry essentially considered eq 12b which contained the work of Mead and Truhlar as a special case. Here we consider the more general Hamiltonian in eq 12a which has also been discussed in refs 37−39.

The scaled coordinates defined in eqs B.1 and B.2 will be used. This is equivalent to taking $g = h^r = h^i = t^r = t^i = 1$ in eqs B9a−B9c, in which case in eq 16b $\gamma^{(i)} = \phi^{(i)}$ and $2\Theta^{(i)} = \theta^{(i)}$, for $i = 1, 2$. A series of values of $(\rho^{(1)}, \theta^{(1)}, \phi^{(1)}, \rho', \phi^{(2)})$ defines a path in nuclear coordinate space. Along such a path $\Theta^{(1)}$ increases by π when $\theta^{(1)}$ increases by 2π. See eq D.4. However this does not happen for $\Theta^{(2)}$. Because $\rho^{(1)}$ and ρ' are strictly positive $\Theta^{(2)}$ returns to itself along any closed path (see eq B.4). Then from the $\Theta^{(i)}$ dependence of $\mathbf{U}^{(p)}$ in eq 16b, $\mathbf{U}^{(p)}$ should be multiplied by $e^{i\Theta^{(1)}}$ to make the adiabatic wave functions single-valued. These single-valued adiabatic electronic wave functions form an appropriate basis for the solution of the nuclear Schrödinger equation using single-valued nuclear wave functions.[26] Here, the analytic representation of the eigenfunctions make it straightforward to guarantee single-valued wave functions. In numerical examples, to be considered in future work, the situation is more complicated since the two Kramers' doublets may become mixed when traversing a closed path.

Because the Hamiltonian we consider is more general than that of Berry it is interesting to ask under what circumstances the geometric phase of Berry will be recovered. From eq 21d for $\mathbf{f}^{ii}$, Berry's result will be obtained provided there is no contribution from the second term. This will occur when the path has no component along $\nabla\xi^{(2)}$. To illustrate consider two paths, path1 [path2] with only $\phi^{(1)}$ [$\phi^{(2)}$] increasing from 0 to 2π. In these cases

$$\mathrm{Im}\oint \mathbf{f}^{ii} \cdot d\mathbf{R} = -\oint \sin^2\Theta^{(I)} \nabla\gamma^{(I)} \cdot d\mathbf{R} = -\int_0^{2\pi} \sin^2\Theta^{(I)} d\phi = -2\pi \sin^2\Theta^{(I)} = -\pi(1 - \cos\theta^{(I)}) \qquad (25)$$

where $I = 1$ (2) for path1 (path2). For path 1, eq 25 is Berry's result as for example shown in eq 29c of ref 13. This occurs despite the fact that ρ' and hence $\mathbf{h}^{Tji}$, the coupling to the full 5 dimensional branching space, does not vanish. Path2 is not included in Berry's treatment. See, however, ref 38.

III. Summary and Conclusions

In recent years, considerable insight into nonrelativistic, nonadiabatic processes has been gained by focusing on conical intersections. As a result of the present work, the formalism required for an analogous treatment of relativistic, nonadiabatic processes, in molecules with an odd number of electrons, is now largely complete. Previously, we reported a perturbative description of the vicinity of an $\eta = 3$ conical intersection.[13,22,27] That analysis provided valuable insights into the nature of that class of conical intersections. The singularity in the derivative coupling was analyzed and a transformation to approximate diabatic states that eliminates that singularity derived. This work extends that analysis to the $\eta = 5$ case largely completing our formal perturbative analysis of conical intersections in molecules with an odd number of electrons.

In the nonrelativistic, $\eta = 2$, case, time-dependent wave packet methods have been used to great advantage in the study of nonadiabatic dynamics involving conical intersections.[4,28−35] Recently, we used time-dependent wave packets to analyze nuclear motion near conical intersections in the adiabatic representation for the nonrelativistic Hamiltonian.[11] The present analysis will enable us to extend these time-dependent nuclear dynamics studies to the $\eta = 3$ and $\eta = 5$ cases, complementing previous two dimensional studies of $\eta = 2$ model systems.[36] These capabilites together with our algorithm for locating $\eta = 3$ and 5 conical intersections[19] will enable us to determine the prevalence, and significance for nuclear dynamics, of these classes of conical intersections in practical systems.

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Appendix A: *Eigenvalues and Eigenvectors of* $\boldsymbol{H}^{(1)}(x, y, z, \upsilon, w)$. Equation 14b. In this Appendix analytic expressions for the eigenvectors and eigenvalues of the Hamiltonian in eq 14b

$$\mathbf{M} \equiv \mathbf{H}^{(1)}(x, y, z, \upsilon, w) \equiv \begin{pmatrix} \mathbf{h}^{(1)} & \mathbf{v} \\ \mathbf{v}^\dagger & \mathbf{h}^{(1)*} \end{pmatrix} \qquad (A.1a)$$

where

$$\mathbf{h}^{(1)} = \begin{pmatrix} -gz & h^r x + ih^i y \\ h^r x - ih^i y & gz \end{pmatrix}$$
$$\mathbf{v} = \begin{pmatrix} 0 & t^r\upsilon + it^i w \\ -(t^r\upsilon + it^i w) & 0 \end{pmatrix} \equiv \begin{pmatrix} 0 & a \\ -a & 0 \end{pmatrix} \qquad (A.1b)$$

are derived. Diagonalization of $\mathbf{M}$ is accomplished in three steps. Let

$$\mathbf{U}^{(1)} = \begin{pmatrix} \mathbf{u}^{(1)} & \mathbf{0} \\ \mathbf{0} & \mathbf{u}^{(1)*} \end{pmatrix} \text{ where } \mathbf{u}^{(1)\dagger}\mathbf{h}^{(1)}\mathbf{u}^{(1)} = \boldsymbol{\epsilon}^{(1)} \qquad (A.2a)$$

and

$$\boldsymbol{\epsilon}^{(1)} = \begin{pmatrix} -[(gz)^2 + (h^r x)^2 + (h^i y)^2]^{1/2} & 0 \\ 0 & [(gz)^2 + (h^r x)^2 + (h^i y)^2]^{1/2} \end{pmatrix} \qquad (A.2b)$$

then

$$\mathbf{M}^{(1)} \equiv \mathbf{U}^{(1)\dagger}\mathbf{M}\mathbf{U}^{(1)} = \begin{pmatrix} \mathbf{u}^{(1)\dagger} & \mathbf{0} \\ \mathbf{0} & \mathbf{u}^{(1)*\dagger} \end{pmatrix}\begin{pmatrix} \mathbf{h}^{(1)} & \mathbf{v} \\ \mathbf{v}^{\dagger} & \mathbf{h}^{(1)*} \end{pmatrix}\begin{pmatrix} \mathbf{u}^{(1)} & \mathbf{0} \\ \mathbf{0} & \mathbf{u}^{(1)*} \end{pmatrix} = \begin{pmatrix} \mathbf{u}^{(1)\dagger}\mathbf{h}^{(1)}\mathbf{u}^{(1)} & \mathbf{u}^{(1)\dagger}\mathbf{v}\mathbf{u}^{(1)*} \\ \mathbf{u}^{(1)*\dagger}\mathbf{v}^{\dagger}\mathbf{u}^{(1)} & \mathbf{u}^{(1)*\dagger}\mathbf{h}^{(1)*}\mathbf{u}^{(1)*} \end{pmatrix} = \begin{pmatrix} \epsilon_1 & 0 & 0 & a \\ 0 & \epsilon_2 & -a & 0 \\ 0 & -a^* & \epsilon_1 & 0 \\ a^* & 0 & 0 & \epsilon_2 \end{pmatrix} \quad \text{(A.3)}$$

where we have noted that $\mathbf{u}^{(1)\dagger}\mathbf{v}\mathbf{u}^{(1)*} = \mathbf{v}$.

Next reorder the transformed functions using the permutation matrix

$$\mathbf{P} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} \quad \text{(A.4)}$$

which puts them in the order 1, 4, 2, 3

$$\mathbf{M}^{(2)} = \mathbf{P}^{\dagger}\mathbf{M}^{(1)}\mathbf{P} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}\begin{pmatrix} \epsilon_1 & 0 & 0 & a \\ 0 & \epsilon_2 & -a & 0 \\ 0 & -a^* & \epsilon_1 & 0 \\ a^* & 0 & 0 & \epsilon_2 \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \epsilon_1 & a & 0 & 0 \\ a^* & \epsilon_2 & 0 & 0 \\ 0 & 0 & \epsilon_2 & -a \\ 0 & 0 & -a^* & \epsilon_1 \end{pmatrix} \equiv (\epsilon_1 + \epsilon_2)/2\ \mathbf{I} + \begin{pmatrix} \mathbf{h}^{(2)} & \mathbf{0} \\ \mathbf{0} & -\mathbf{h}^{(2)} \end{pmatrix} \quad \text{(A.5)}$$

where $\epsilon_1 + \epsilon_2 = 0$ because $\mathbf{M}$ is traceless and

$$\mathbf{h}^{(2)} = \begin{pmatrix} \Delta\epsilon & a \\ a^* & -\Delta\epsilon \end{pmatrix}$$
$$\Delta\epsilon = (\epsilon_1 - \epsilon_2)/2 = -[(gz)^2 + (h^{\mathrm{r}}x)^2 + (h^{\mathrm{i}}y)^2]^{1/2} \quad \text{(A.6)}$$

Finally define $\mathbf{u}^{(2)}$ such that

$$\epsilon^{(2)} = \mathbf{u}^{(2)\dagger}\,\mathbf{h}^{(2)}\mathbf{u}^{(2)} = \begin{pmatrix} -(\Delta\epsilon^2 + |a|^2)^{1/2} & 0 \\ 0 & (\Delta\epsilon^2 + |a|^2)^{1/2} \end{pmatrix} \quad \text{(A.7a)}$$

where

$$\Delta\epsilon^2 + |a|^2 = (gz)^2 + (h^{\mathrm{r}}x)^2 + (h^{\mathrm{i}}y)^2 + (t^{\mathrm{r}}v)^2 + (t^{\mathrm{i}}w)^2 \quad \text{(A.7b)}$$

Then

$$\mathbf{M}^{(3)} = \mathbf{U}^{(2)\dagger}\mathbf{M}^{(2)}\mathbf{U}^{(2)} = \begin{pmatrix} \epsilon^{(2)} & \mathbf{0} \\ \mathbf{0} & -\epsilon^{(2)} \end{pmatrix} \quad \text{(A.8a)}$$

where

$$\mathbf{U}^{(2)} = \begin{pmatrix} \mathbf{u}^{(2)} & \mathbf{0} \\ \mathbf{0} & \mathbf{u}^{(2)} \end{pmatrix} \quad \text{(A.8b)}$$

From eqs A.7a and A.8 the Kramers' degenerate pairs are roots (1, 4) and roots (2,3). The overall transformation $\mathbf{U}^{(\mathrm{p})}$ is given by

$$\mathbf{U}^{(\mathrm{p})} = \begin{pmatrix} u_{11}^{(1)} & u_{12}^{(1)} & 0 & 0 \\ u_{21}^{(1)} & u_{22}^{(1)} & 0 & 0 \\ 0 & 0 & u_{11}^{(1)*} & u_{12}^{(1)*} \\ 0 & 0 & u_{21}^{(1)*} & u_{22}^{(1)*} \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} u_{11}^{(2)} & u_{12}^{(2)} & 0 & 0 \\ u_{21}^{(2)} & u_{22}^{(2)} & 0 & 0 \\ 0 & 0 & u_{11}^{(2)} & u_{12}^{(2)} \\ 0 & 0 & u_{21}^{(2)} & u_{22}^{(2)} \end{pmatrix} \quad \text{(A.9a)}$$

$$= \begin{pmatrix} u_{11}^{(1)} & 0 & u_{12}^{(1)} & 0 \\ u_{21}^{(1)} & 0 & u_{22}^{(1)} & 0 \\ 0 & u_{12}^{(1)*} & 0 & u_{11}^{(1)*} \\ 0 & u_{22}^{(1)*} & 0 & u_{21}^{(1)*} \end{pmatrix} \times \begin{pmatrix} u_{11}^{(2)} & u_{12}^{(2)} & 0 & 0 \\ u_{21}^{(2)} & u_{22}^{(2)} & 0 & 0 \\ 0 & 0 & u_{11}^{(2)} & u_{12}^{(2)} \\ 0 & 0 & u_{21}^{(2)} & u_{22}^{(2)} \end{pmatrix}$$
$$= \begin{pmatrix} u_{11}^{(1)}u_{11}^{(2)} & u_{11}^{(1)}u_{12}^{(2)} & u_{12}^{(1)}u_{11}^{(2)} & u_{12}^{(1)}u_{12}^{(2)} \\ u_{21}^{(1)}u_{11}^{(2)} & u_{21}^{(1)}u_{12}^{(2)} & u_{22}^{(1)}u_{11}^{(2)} & u_{22}^{(1)}u_{12}^{(2)} \\ u_{12}^{(1)*}u_{21}^{(2)} & u_{12}^{(1)*}u_{22}^{(2)} & u_{11}^{(1)*}u_{21}^{(2)} & u_{11}^{(1)*}u_{22}^{(2)} \\ u_{22}^{(1)*}u_{21}^{(2)} & u_{22}^{(1)*}u_{22}^{(2)} & u_{21}^{(1)*}u_{21}^{(2)} & u_{21}^{(1)*}u_{22}^{(2)} \end{pmatrix} \quad \text{(A.9b)}$$

Appendix B: *Representations of $U^{(p)}$.* To obtain explicit expressions for the $\mathbf{u}^{(\mathrm{i})}$ it is convenient to introduce spherical polar coordinates ($\rho^{(1)}$, $\theta^{(1)}$, $\phi^{(1)}$), polar (ρ', $\phi^{(2)}$) and hyperspherical coordinates ($\rho^{(2)}$,$\theta^{(2)}$) as follows. Let

$$z' = gz = \rho^{(1)}\cos\theta^{(1)} \quad x' = h^{\mathrm{r}}x = \rho^{(1)}\sin\theta^{(1)}\cos\phi^{(1)}$$
$$y' = h^{\mathrm{i}}y = \rho^{(1)}\sin\theta^{(1)}\sin\phi^{(1)} \quad \text{(B.1)}$$

and

$$v' = t^{\mathrm{r}}v = \rho'\cos\phi^{(2)} \qquad w' = t^{\mathrm{i}}w = \rho'\sin\phi^{(2)} \quad \text{(B.2)}$$

so that

$$\mathbf{h}^{(1)} = \rho^{(1)}\begin{pmatrix} -\cos\theta^{(1)} & e^{i\phi^{(1)}}\sin\theta^{(1)} \\ e^{-i\phi^{(1)}}\sin\theta^{(1)} & \cos\theta^{(1)} \end{pmatrix} \text{and}$$
$$\mathbf{h}^{(2)} = \begin{pmatrix} -\rho^{(1)} & \rho' e^{i\phi^{(2)}} \\ \rho' e^{-i\phi^{(2)}} & \rho^{(1)} \end{pmatrix} \quad \text{(B.3)}$$

Note that the underlying coordinate axes are linearly independent but not necessarily orthogonal. See, however, Appendix C. Introducing the hyper polar coordinates $\rho^{(2)}$, $\theta^{(2)}$ by

$$\rho^{(1)} = \rho^{(2)}\cos\theta^{(2)} \text{ and } \rho' = \rho^{(2)}\sin\theta^{(2)} \quad \text{(B.4)}$$

then

$$\mathbf{h}^{(2)} = \rho^{(2)}\begin{pmatrix} -\cos\theta^{(2)} & \sin\theta^{(2)}e^{i\phi^{(2)}} \\ \sin\theta^{(2)}e^{-i\phi^{(2)}} & \cos\theta^{(2)} \end{pmatrix} \quad \text{(B.5)}$$

In these coordinates $\rho^{(1)^2} = (gz)^2 + (h^{\mathrm{r}}x)^2 + (h^{\mathrm{i}}y)^2$ and $\rho^{(2)^2} = (gz)^2 + (h^{\mathrm{r}}x)^2 + (h^{\mathrm{i}}y)^2 + (t^{\mathrm{r}}v)^2 + (t^{\mathrm{i}}w)^2$. Further $\mathbf{h}^{(1)}$ and $\mathbf{h}^{(2)}$

have the same form

$$\mathbf{h}^{(i)} = \rho^{(i)}\begin{pmatrix} -\cos\theta^{(i)} & e^{i\phi^{(i)}}\sin\theta^{(i)} \\ e^{-i\phi^{(i)}}\sin\theta^{(i)} & \cos\theta^{(i)} \end{pmatrix} \tag{B.6}$$

and can be diagonalized by the transformation

$$\mathbf{u}^{(i)} = \begin{pmatrix} \cos\Theta^{(i)} & e^{i\gamma^{(i)}}\sin\Theta^{(i)} \\ -e^{-i\gamma^{(i)}}\sin\Theta^{(i)} & \cos\Theta^{(i)} \end{pmatrix} \tag{B.7}$$

where $\Theta^{(i)} = \theta^{(i)}/2$, γ and $\gamma^{(i)} = \phi^{(i)}$, $i = 1, 2$.

The simple relation between the parameters of $\mathbf{h}^{(i)}$ and those of $\mathbf{u}^{(i)}$ comes from the use of scaled coordinates to define the polar and spherical polar coordinates in eqs B.1 and B.2. Alternatively, one can choose unscaled coordinates as follows. Let

$$z = \rho^{(1)}\cos\theta^{(1)} \quad x = \rho^{(1)}\sin\theta^{(1)}\cos\phi^{(1)}$$
$$y = \rho^{(1)}\sin\theta^{(1)}\sin\phi^{(1)} \tag{B.8a}$$

and

$$v = \rho'\cos\phi^{(2)} \quad w = \rho'\sin\phi^{(2)} \tag{B.8b}$$

Then define

$$h^{(1)}(\phi^{(1)})\cos\xi^{(1)} = h^{r}\cos\phi^{(1)} \quad h^{(1)}(\phi^{(1)})\sin\xi^{(1)} = h^{i}\sin\phi^{(1)} \tag{B.9a}$$

and

$$q^{(1)}(\theta^{(1)}, \phi^{(1)})\cos\lambda^{(1)} = g\cos\theta^{(1)}$$
$$q^{(1)}(\theta^{(1)}, \phi^{(1)})\sin\lambda^{(1)} = h^{(1)}(\phi^{(1)})\sin\theta^{(1)} \tag{B.9b}$$

$$q^{(2)}(\phi^{(2)})\cos\xi^{(2)} = t^{r}\cos\phi^{(2)} \quad q^{(2)}(\phi^{(2)})\sin\xi^{(2)} = t^{i}\sin\phi^{(2)} \tag{B.9c}$$

$$\mathbf{h}^{(1)} = \rho^{(1)}q^{(1)}\begin{pmatrix} -\cos\lambda^{(1)} & e^{i\xi^{(1)}}\sin\lambda^{(1)} \\ e^{-i\xi^{(1)}}\sin\lambda^{(1)} & \cos\lambda^{(1)} \end{pmatrix}$$
$$\mathbf{h}^{(2)} = \begin{pmatrix} -\rho^{(1)}q^{(1)} & \rho' q^{(2)}e^{i\xi^{(2)}} \\ \rho' q^{(2)}e^{-i\xi^{(2)}} & \rho^{(1)}q^{(1)} \end{pmatrix} \tag{B.10}$$

Introducing the hyper polar coordinates

$$\rho^{(2)}\cos\lambda^{(2)} = \rho^{(1)}q^{(1)} \text{ and } \rho^{(2)}\sin\lambda^{(2)} = \rho' q^{(2)} \tag{B.11}$$

$\mathbf{h}^{(2)}$ becomes

$$\mathbf{h}^{(2)} = \rho^{(2)}\begin{pmatrix} -\cos\lambda^{(2)} & \sin\lambda^{(2)}e^{i\xi^{(2)}} \\ \sin\lambda^{(2)}e^{-i\xi^{(2)}} & \cos\lambda^{(2)} \end{pmatrix} \tag{B.12}$$

$\mathbf{h}^{(1)}$ and $\mathbf{h}^{(2)}$ have the form of eq B.6 and can be diagonalized by the transformation in eq B.7 with $\Theta^{(1)} = \lambda^{(1)}/2$, $\gamma^{(1)} = \xi^{(1)}$ and $\Theta^{(2)} = \lambda^{(2)}/2$, $\gamma^{(2)} = \xi^{(2)}$. Therefore $\mathbf{U}^{(p)}$ (eq A.9b) is given by

$$\begin{pmatrix} \cos\Theta^{(1)}\cos\Theta^{(2)} & \cos\Theta^{(1)}e^{i\gamma^{(2)}}\sin\Theta^{(2)} & e^{i\gamma^{(1)}}\sin\Theta^{(1)}\cos\Theta^{(2)} & e^{i\gamma^{(1)}}\sin\Theta^{(1)}e^{i\gamma^{(2)}}\sin\Theta^{(2)} \\ -e^{-i\gamma^{(1)}}\sin\Theta^{(1)}\cos\Theta^{(2)} & -e^{-i\gamma^{(1)}}\sin\Theta^{(1)}e^{i\gamma^{(2)}}\sin\Theta^{(2)} & \cos\Theta^{(1)}\cos\Theta^{(2)} & \cos\Theta^{(1)}e^{i\gamma^{(2)}}\sin\Theta^{(2)} \\ -e^{-i\gamma^{(1)}}\sin\Theta^{(1)}e^{-i\gamma^{(2)}}\sin\Theta^{(2)} & e^{-i\gamma^{(1)}}\sin\Theta^{(1)}\cos\Theta^{(2)} & -\cos\Theta^{(1)}e^{-i\gamma^{(2)}}\sin\Theta^{(2)} & \cos\Theta^{(1)}\cos\Theta^{(2)} \\ -\cos\Theta^{(1)}e^{-i\gamma^{(2)}}\sin\Theta^{(2)} & \cos\Theta^{(1)}\cos\Theta^{(2)} & e^{i\gamma^{(1)}}\sin\Theta^{(1)}e^{-i\gamma^{(2)}}\sin\Theta^{(2)} & -e^{i\gamma^{(1)}}\sin\Theta^{(1)}\cos\Theta^{(2)} \end{pmatrix} \tag{B.13}$$

The C_s symmetry result is obtained by substituting $\Theta^{(2)} = 0$ into (B.13) giving

$$\mathbf{U}^{Cs} = \begin{pmatrix} \cos\Theta^{(1)} & 0 & e^{i\gamma^{(1)}}\sin\Theta^{(1)} & 0 \\ -e^{-i\gamma^{(1)}}\sin\Theta^{(1)} & 0 & \cos\Theta^{(1)} & 0 \\ 0 & e^{-i\gamma^{(1)}}\sin\Theta^{(1)} & 0 & \cos\Theta^{(1)} \\ 0 & \cos\Theta^{(1)} & 0 & e^{i\gamma^{(1)}}\sin\Theta^{(1)} \end{pmatrix} \tag{B.14}$$

Recall that for this transformation in the time-reversal adapted crude adiabatic state basis, the Kramers' degenerate pairs are (1,3) and (2,4). Thus, the $\mathbf{U}^{Cs}$ evinces the requisite Kramers' degeneracy for the pairs (1,4) and (2,3). Equation B.14 was derived previously in ref 13.

Appendix C: *Orthogonal Intersection-Adapted Coordinates.* In this appendix, it is shown that the conditions requiring the vectors defining the branching space to be orthogonal, define a unique, up to trivial interchanges, unitary transformation of the electronic wave functions consistent with time reversal symmetry. In a future work a generalization of the well known[40] homomorphism between the full three dimensional rotation group and the group of 2×2 unitary matrices with determinant 1 will be used to give an explicit solution to this problem.[41] Note that straightforward orthogonalization of $\mathbf{g}^{ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{r,ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{i,ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{r,iTj}(\mathbf{R}^{x,ij})$, and $\mathbf{h}^{i,iTj}(\mathbf{R}^{x,ij})$ changes the form of the Hamiltonian in eq 12a and is not what is considered here. Instead the orthogonalization must be accomplished by a unitary transformation, $\mathbf{V}$, of the electronic states. Let

$$(\tilde{\Psi}^{e}_{i}\ \tilde{\Psi}^{e}_{j}\ \tilde{\Psi}^{e}_{Ti}\ \tilde{\Psi}^{e}_{Tj}) = (\Psi^{e}_{i}\ \Psi^{e}_{j}\ \Psi^{e}_{Ti}\ \Psi^{e}_{Tj})\mathbf{V} \text{ with } V_{kl} = \langle\Psi^{e}_{k}|\tilde{\Psi}^{e}_{l}\rangle \tag{C.1}$$

define the transformation from the "nascent" electronic wave functions Ψ^{e}_{k}, $k = i, j, Ti$ and Tj to the $\tilde{\Psi}^{e}_{k}$, $k = i, j, Ti$ and Tj for which the $\mathbf{g}^{ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{r,ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{i,ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{r,iTj}(\mathbf{R}^{x,ij})$ and $\mathbf{h}^{i,iTj}(\mathbf{R}^{x,ij})$ are orthogonal.

A general unitary matrix $\mathbf{V}$ consists of N^2 complex-valued matrix elements, that is $2N^2$ parameters. Viewed as column constraints, the requirement $\mathbf{V}^{\dagger}\mathbf{V} = \mathbf{I}$ constitutes $N(N-1)/2$ orthogonality equations, $O(k, l) = O^{r}(k, l) + iO^{i}(k, l) = 0$ for $1 = k < l = N$ defining $N(N-1)$ parameters and N normalization equations, $N(k)=1$, $1 = k = N$ defining N parameters, for a total of N^2 parameters and leaving N^2 parameters undefined or free. Pairwise orthogonality of $\mathbf{g}^{ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{r,ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{i,ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{r,iTj}(\mathbf{R}^{x,ij})$ and $\mathbf{h}^{i,iTj}(\mathbf{R}^{x,ij})$ constitutes $5!/((5-2)!2!) = 10$ equations. Because $N = 4$, the problem appears under determined. However this is not the case because $\mathbf{V}$ is not an arbitrary unitary

matrix but connects two pairs of time-reversal adapted states. Taking matrix elements of eq C.1 and using eq 1a gives

$$V_{kl}^{*} = \langle T\Psi_k^e | T\tilde{\Psi}_l^e \rangle = \langle \Psi_{Tk}^e | \tilde{\Psi}_{Tl}^e \rangle = V_{TkTl},$$

$$V_{kTl}^{*} = \langle T\Psi_k^e | T\tilde{\Psi}_{Tl}^e \rangle = -\langle \Psi_{Tk}^e | \tilde{\Psi}_l^e \rangle = -V_{Tkl} \quad \text{(C.2a)}$$

$$V_{Tkl}^{*} = \langle T\Psi_{Tk}^e | T\tilde{\Psi}_l^e \rangle = -\langle \Psi_k^e | \tilde{\Psi}_{Tl}^e \rangle = -V_{kTl} \quad \text{(C.2b)}$$

so that

$$\mathbf{V} = \begin{pmatrix} V_{ii} & V_{ij} & V_{iTi} & V_{iTj} \\ V_{ji} & V_{jj} & V_{jTi} & V_{jTj} \\ V_{Tii} & V_{Tij} & V_{TiTi} & V_{TiTj} \\ V_{Tji} & V_{Tjj} & V_{TjTi} & V_{TjTj} \end{pmatrix} = \begin{pmatrix} V_{ii} & V_{ij} & V_{iTi} & V_{iTj} \\ V_{ji} & V_{jj} & V_{jTi} & V_{jTj} \\ -V_{iTi}^{*} & -V_{iTj}^{*} & V_{ii}^{*} & V_{ij}^{*} \\ -V_{jTi}^{*} & -V_{jTj}^{*} & V_{ji}^{*} & V_{jj}^{*} \end{pmatrix} \quad \text{(C.3)}$$

which has $8 \times 2 = 16$ parameters. Because $N(1) = N(3)$ and $N(2) = N(4)$, there are 2 *unique* normalization equations, $N(k) = 1$ $k = 1, 2$

$$N(1) = |V_{ii}|^2 + |V_{ji}|^2 + |V_{Tii}|^2 + |V_{Tji}|^2 = 1 \quad \text{(C.4a)}$$

$$N(2) = |V_{ij}|^2 + |V_{jj}|^2 + |V_{Tij}|^2 + |V_{Tjj}|^2 = 1 \quad \text{(C.4b)}$$

determining 2 parameters. There are 2 unique orthogonality equations

$$O(1,2) = V_{ii}^{*}V_{ij} + V_{ji}^{*}V_{jj} + V_{iTi}V_{iTj}^{*} + V_{jTi}V_{jTj}^{*} = 0 \quad \text{(C.5a)}$$

$$O(3,2) = V_{iTi}^{*}V_{ij} + V_{jTi}^{*}V_{jj} - V_{ii}V_{iTj}^{*} - V_{ji}V_{jTj}^{*} = 0 \quad \text{(C.5b)}$$

determining 4 parameters. The remaining 4 orthogonality constraints are redundant because $O(3,4) = O(1,2)^*$, $-O(1,4) = O(3,2)$ and the equations $O(1,3) = 0$, $O(2,4) = 0$ are identities. Thus, including time reversal symmetry, unitarity leaves 10 parameters free- precisely the number required to orthogonalize the vectors $\mathbf{g}^{ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{r,ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{i,ij}(\mathbf{R}^{x,ij})$, $\mathbf{h}^{r,iTj}(\mathbf{R}^{x,ij})$ and $\mathbf{h}^{i,iTj}(\mathbf{R}^{x,ij})$.

The 10 vector orthogonality equations follow from $\tilde{\mathbf{d}}^i = \sum_{k=1}^{4} \mathbf{d}^k V_{ki}$ and definitions (7b). They can be solved using the Newton−Raphson approach employed in ref 22 for the $\eta = 3$ case.

Appendix D: *Evaluation of* f_s^{kl} $s = x,y,z$ v,w. *eqs 22−23.* Before assembling the chain rule for evaluation of f_s^{kl} it is useful to begin by summarizing the relationships among the myriad of variables

$$\rho', \phi^{(2)}: v,w \qquad \rho^{(1)}, \theta^{(1)}, \phi^{(1)}: x, y, z \qquad \lambda^{(1)}, q^{(1)}: \theta^{(1)}, \phi^{(1)}$$

$$\lambda^{(2)}, \rho^{(2)}: \rho', \rho^{(1)}, \theta^{(1)}, \phi^{(1)}, \phi^{(2)} \qquad \xi^{(1)}: \phi^{(1)} \qquad \xi^{(2)}: \phi^{(2)}$$

$$\Theta^{(i)} = \lambda^{(i)}/2 \qquad \gamma^{(i)} = \xi^{(i)}$$

where the colon is read (here and only here) as "depends on". Using these dependencies, the chain rule becomes

$$\frac{\partial}{\partial s} = \left(\frac{\partial\theta^{(1)}}{\partial s}\frac{\partial\lambda^{(1)}}{\partial\theta^{(1)}} + \frac{\partial\phi^{(1)}}{\partial s}\frac{\partial\lambda^{(1)}}{\partial\phi^{(1)}}\right)\frac{\partial\Theta^{(1)}}{\partial\lambda^{(1)}}\frac{\partial}{\partial\Theta^{(1)}}$$

$$+ \frac{\partial\phi^{(1)}}{\partial s}\frac{\partial\xi^{(1)}}{\partial\phi^{(1)}}\frac{\partial\gamma^{(1)}}{\partial\xi^{(1)}}\frac{\partial}{\partial\gamma^{(1)}}$$

$$+ \left(\frac{\partial\theta^{(1)}}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\theta^{(1)}} + \frac{\partial\phi^{(2)}}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\phi^{(2)}} + \frac{\partial\phi^{(1)}}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\phi^{(1)}} + \frac{\partial\rho^{(1)}}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\rho^{(1)}}\right.$$

$$\left. + \frac{\partial\rho'}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\rho'}\right)\frac{\partial\Theta^{(2)}}{\partial\lambda^{(2)}}\frac{\partial}{\partial\Theta^{(2)}} + \frac{\partial\phi^{(2)}}{\partial s}\frac{\partial\xi^{(2)}}{\partial\phi^{(2)}}\frac{\partial\gamma^{(2)}}{\partial\xi^{(2)}}\frac{\partial}{\partial\gamma^{(2)}} \quad \text{(D.1)}$$

and f_s^{kl} is given by

$$f_s^{kl} = \left(\frac{\partial\theta^{(1)}}{\partial s}\frac{\partial\lambda^{(1)}}{\partial\theta^{(1)}} + \frac{\partial\phi^{(1)}}{\partial s}\frac{\partial\lambda^{(1)}}{\partial\phi^{(1)}}\right)\frac{\partial\Theta^{(1)}}{\partial\lambda^{(1)}}f^{kl}_{\Theta^{(1)}} + \frac{\partial\phi^{(1)}}{\partial s}\frac{\partial\xi^{(1)}}{\partial\phi^{(1)}}\frac{\partial\gamma^{(1)}}{\partial\xi^{(1)}}f^{kl}_{\gamma^{(1)}}$$

$$+ \left(\frac{\partial\theta^{(1)}}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\theta^{(1)}} + \frac{\partial\phi^{(2)}}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\phi^{(2)}} + \frac{\partial\phi^{(1)}}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\phi^{(1)}} + \frac{\partial\rho^{(1)}}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\rho^{(1)}}\right.$$

$$\left. + \frac{\partial\rho'}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\rho'}\right)\frac{\partial\Theta^{(2)}}{\partial\lambda^{(2)}}f^{kl}_{\Theta^{(2)}}$$

$$+ \frac{\partial\phi^{(2)}}{\partial s}\frac{\partial\xi^{(2)}}{\partial\phi^{(2)}}\frac{\partial\gamma^{(2)}}{\partial\xi^{(2)}}f^{kl}_{\gamma^{(2)}} \quad \text{(D.2)}$$

Using the above dependencies, eq D.2 becomes for $s = x, y, z$

$$f_s^{kl} = \left(\frac{\partial\theta^{(1)}}{\partial s}\frac{\partial\lambda^{(1)}}{\partial\theta^{(1)}} + \frac{\partial\phi^{(1)}}{\partial s}\frac{\partial\lambda^{(1)}}{\partial\phi^{(1)}}\right)\frac{f^{kl}_{\Theta^{(1)}}}{2} + \frac{\partial\phi^{(1)}}{\partial s}\frac{\partial\xi^{(1)}}{\partial\phi^{(1)}}f^{kl}_{\gamma^{(1)}}$$

$$+ \left(\frac{\partial\theta^{(1)}}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\theta^{(1)}} + \frac{\partial\phi^{(1)}}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\phi^{(1)}} + \frac{\partial\rho^{(1)}}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\rho^{(1)}}\right)\frac{f^{kl}_{\Theta^{(2)}}}{2} \quad \text{(D.3a)}$$

and for $s = v, w$

$$f_s^{kl} = \left(\frac{\partial\phi^{(2)}}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\phi^{(2)}} + \frac{\partial\rho'}{\partial s}\frac{\partial\lambda^{(2)}}{\partial\rho'}\right)\frac{f^{kl}_{\Theta^{(2)}}}{2} + \frac{\partial\phi^{(2)}}{\partial s}\frac{\partial\xi^{(2)}}{\partial\phi^{(2)}}f^{kl}_{\gamma^{(2)}} \quad \text{(D.3b)}$$

To proceed further specific relations among the variables are required. From definitions B.1 and B.2 of Appendix B, we deduce

$$\tan\xi^{(1)} = (h^i/h^r)\tan\phi^{(1)}$$

$$h^{(1)}(\phi^{(1)})^2 = (h^i\sin\phi^{(1)})^2 + (h^r\cos\phi^{(1)})^2 \quad \text{(D.4a)}$$

$$\tan\xi^{(2)} = t^i/t^r\tan\phi^{(2)}$$

$$q^{(2)}(\phi^{(2)})^2 = (t^i\sin\phi^{(2)})^2 + (t^r\cos\phi^{(2)})^2 \quad \text{(D.4b)}$$

$$\tan\lambda^{(1)} = (h^{(1)}(\phi^{(1)})/g)\tan\theta^{(1)}$$

$$q^{(1)}(\theta^{(1)}, \phi^{(1)})^2 = (g\cos\theta^{(1)})^2 + (h^1(\phi^{(1)})\sin\theta^{(1)})^2 \quad \text{(D.4c)}$$

$$\rho^{(2)} = [(\rho^{(1)}q^{(1)})^2 + (\rho' q^{(2)})^2]^{1/2}$$

$$\text{and } \tan\lambda^{(2)} = \rho' q^{(2)}/[\rho^{(1)}q^{(1)}] \equiv \rho'_q/\rho_q^{(1)} \quad \text{(D.4d)}$$

It is convenient to begin by evaluating the s independent contributions

$$\frac{\partial\lambda^{(1)}}{\partial\theta^{(1)}}, \frac{\partial\lambda^{(1)}}{\partial\phi^{(1)}}, \frac{\partial\xi^{(1)}}{\partial\phi^{(1)}}, \frac{\partial\lambda^{(2)}}{\partial\theta^{(1)}}, \frac{\partial\lambda^{(2)}}{\partial\phi^{(2)}}, \frac{\partial\lambda^{(2)}}{\partial\phi^{(1)}}, \frac{\partial\lambda^{(2)}}{\partial\rho^{(1)}}, \frac{\partial\lambda^{(2)}}{\partial\rho'}, \frac{\partial\xi^{(2)}}{\partial\phi^{(2)}}$$

which follow from straightforward, albeit tedious, differentiation of eqs D4.a−D4.d

$$\frac{\partial\lambda^{(1)}}{\partial\theta^{(1)}}=\frac{[h^{(1)}g]}{q^{(1)^2}} \qquad \frac{\partial\lambda^{(1)}}{\partial\phi^{(1)}}=\frac{[h^{i^2}-h^{r^2}]}{2h^{(1)}}\sin 2\phi^{(1)}\frac{g\sin 2\theta^{(1)}}{2q^{(1)^2}}$$

$$\frac{\partial\xi^{(1)}}{\partial\phi^{(1)}}=\frac{[h^{i}h^{r}]}{h^{(1)^2}} \qquad \frac{\partial\lambda^{(2)}}{\partial\theta^{(1)}}=\frac{-\rho^{(1)}\rho'q^{(2)}}{\rho_q'^2+\rho_q^{(1)^2}}\frac{[h^{(1)}-g^2]}{2q^{(1)}}\sin 2\theta^{(1)}$$

$$\frac{\partial\lambda^{(2)}}{\partial\phi^{(2)}}=\frac{\rho'\rho^{(1)}}{\rho_q'^2+\rho_q^{(1)^2}}q^{(1)}\frac{[t^{i^2}-t^{r^2}]}{2q^{(2)}}\sin 2\phi^{(2)}$$

$$\frac{\partial\lambda^{(2)}}{\partial\phi^{(1)}}=\frac{-\rho'\rho^{(1)}}{\rho_q'^2+\rho_q^{(1)^2}}\frac{q^{(2)}}{q^{(1)}}\frac{[h^{i^2}-h^{r^2}]}{2}\sin 2\phi^{(1)}\sin^2\theta^{(1)}$$

$$\frac{\partial\lambda^{(2)}}{\partial\rho^{(1)}}=\frac{-\rho'}{\rho_q'^2+\rho_q^{(1)^2}}q^{(2)}q^{(1)}$$

$$\frac{\partial\lambda^{(2)}}{\partial\rho'}=\frac{\rho^{(1)}}{\rho_q'^2+\rho_q^{(1)^2}}q^{(2)}q^{(1)} \qquad \frac{\partial\xi^{(2)}}{\partial\phi^{(2)}}=\frac{t^{i}t^{r}}{q^{(2)^2}} \quad \text{(D.5)}$$

Using eq D.5 in eq D.3a gives for $s = x, y, z$

$$f_s^{kl}=\left(\frac{\partial\theta^{(1)}}{\partial s}\frac{[h^{(1)}g]}{q^{(1)^2}}+\frac{\partial\phi^{(1)}}{\partial s}\frac{[h^{i^2}-h^{r^2}]}{2h^{(1)}}\sin 2\phi^{(1)}\frac{g\sin 2\theta^{(1)}}{2q^{(1)^2}}\right)\frac{f^{kl}_{\Theta^{(1)}}}{2}+$$
$$\frac{\partial\phi^{(1)}}{\partial s}\frac{[h^{i}h^{r}]}{h^{(1)}}f^{kl}_{\gamma^{(1)}}+\frac{\rho^{(1)}\rho_q'}{\rho_q'^2+\rho_q^{(1)^2}}\left(\frac{\partial\theta^{(1)}}{\partial s}\frac{[g^2-h^{(1)2}]}{2q^{(1)}}\sin 2\theta^{(1)}-\right.$$
$$\left.\frac{\partial\phi^{(1)}}{\partial s}\frac{[h^{i^2}-h^{r^2}]}{2q^{(1)}}\sin 2\phi^{(1)}\sin^2\theta^{(1)}-\frac{\partial\rho^{(1)}}{\partial s}\frac{q^{(1)}}{\rho^{(1)}}\right)\frac{f^{kl}_{\Theta^{(2)}}}{2} \quad \text{(D.6)}$$

whereas using eq D.5 in eq D.3b gives for s = υ, w

$$f_s^{kl}=\frac{\rho_q^{(1)}}{\rho_q'^2+\rho_q^{(1)^2}}\left(\frac{\partial\phi^{(2)}}{\partial s}\rho'\frac{[t^{i^2}-t^{r^2}]}{2q^{(2)}}\sin 2\phi^{(2)}+\frac{\partial\rho'}{\partial s}q^{(2)}\right)\frac{f^{kl}_{\Theta^{(2)}}}{2}$$
$$+\frac{\partial\phi^{(2)}}{\partial s}\frac{[t^{i}t^{r}]}{q^{(2)^2}}f^{kl}_{\gamma^{(2)}} \quad \text{(D.7)}$$

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