On the properties of the seam and branching spaces of conical intersections in molecules with an odd number of electrons: A group homomorphism approach

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The properties of the branching and seam spaces of conical intersections in a molecule with an odd number of electrons are explored for the general case, where the molecule has no spatial symmetry and the Hamiltonian explicitly includes the spin–orbit interaction. A realization of the homomorphism connecting the symplectic group of order 4, Sp(4), and the group of proper rotations in five dimensions SO(5) is used to find an orthogonal representation of the branching space that preserves the standard form of the electronic Hamiltonian near a conical intersection. An invariant property of the branching space is also identified. These findings extend previous results for the nonrelativistic Hamiltonian and the relativistic Hamiltonian with C_s symmetry. A model Hamiltonian representing a tetra-atomic molecule with three coupled doublet electronic states is used to demonstrate the efficacy of the approach and illustrate possible seam loci. The seam of conical intersection is shown to have two distinct branches, one bounded and one infinite in extent. The branching spaces of these seams are characterized.
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I. INTRODUCTION

In the vicinity of a conical intersection the difference of the energies of the two adiabatic potential energy surfaces is lifted in a linear manner if the displacement includes a component of the branching space,[1] a vector space of dimension η. In other words the distinguishing property of the branching space is that, regardless of the number of internal coordinates, the η internal coordinates spanning this space alone are responsible for the double cone topography of the intersecting adiabatic potential energy surfaces. The orthogonal complement of the branching space is the seam space. For the nonrelativistic Hamiltonian, which describes spin-conserving, electronically nonadiabatic processes,[2–9] $\eta=2$. 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]

It is highly desirable to describe the branching space in terms of an orthogonal set of nuclear displacements (vectors). This requires a particular choice, unitary transformation, of the degenerate electronic states at the conical intersection. Previously we have determined this transformation in the nonrelativistic case, where $\eta=2$,[11] and in the relativistic case with C_s symmetry, where $\eta=3$,[12] and suggested that a similar result is also possible for the $\eta=5$ case.[13] For $\eta=2$ and 3, the $\eta(\eta-1)/2$ equations defining the orthogonal representation of the branching space can be readily expressed in terms of the parameters defining the unitary transformation of the electronic states. For $\eta=5$ this approach is impractical and an alternative approach is required.

Near a conical intersection the electronic Hamiltonian, including the spin–orbit interaction, of a system with an odd number of electrons, can be expanded in terms of five basic 4×4 Hermitian matrices. The use of these basic matrices greatly simplifies the treatment of such systems. For example, this representation was used by Mead to describe the Jahn–Teller effect in tetrahedral CH_4^+ with the spin–orbit interaction explicitly included.[14] Here we show how these matrices can be used to determine the unitary transformation of the electronic states that produces the orthogonal representation of the $\eta=5$ branching space. Using Weyl's well-known[15] method for demonstrating the homomorphism of SU(2) onto SO(3), we generate an explicit representation of homomorphism of Sp(4)[16,17] onto SO(5), in the space spanned by five basic matrices. Here SU(N) is the group of $N\times N$ unitary matrices with determinant +1, and SO(M) is the group of proper rotations in M dimensions. Sp($2n$) is the sympletic group of order $2n$, here a subgroup of SU(N),[17] for $2n=N$. This homomorphism associates with a rotation of the branching space vectors, an element of SO(5), a unitary transformation of the electronic states, an element of Sp(4). The explicit form for this homomorphism deduced here obviates the construction of the $\eta(\eta-1)/2$ orthogonality equations and is the key to the present approach.

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While this unitary transformation changes the overlap of the branching space vectors, in the $\eta=2$ and 3 cases a quantity was found that is invariant under this transformation. In the nonrelativistic case this invariant proved useful in locating the special set of nuclear configurations referred to as confluences where two branches of the same seam of conical intersections intersect.[18,19] Nuclear dynamics near a confluence of seam branches is expected to differ significantly from that near a true conical intersection since the potential energy surface topography is dramatically different in these two regions.[19]

In Sec. II we describe the homomorphism and how it can be used to determine the transformation of the electronic states and the associated invariant for the $\eta=5$ case. In Sec. III, the efficacy of this approach is established, branching spaces are characterized, and possible connectivities of conical intersection seams illustrated in the $\eta=5$ and 3 cases using a model Hamiltonian corresponding to three coupled doublet states in a tetra-atomic molecule. Section IV summarizes and discusses directions for future study.

II. THEORY

For a molecule with an odd number of electrons all electronic eigenstates come in degenerate pairs $\Psi_i(\mathbf{q};\mathbf{Q})$ and $\hat{T}\Psi_i(\mathbf{q};\mathbf{Q})\equiv\Psi_{Ti}(\mathbf{q};\mathbf{Q})$. Here $\hat{T}$ is the time reversal operator and $\mathbf{q}[\mathbf{Q}]$ denote the electronic [nuclear] coordinates. See Refs. 10, 13, and 20 for a discussion of time reversal and electronic states. In this work the electronic states are assumed to be expanded to a basis of time reversal adapted configuration state functions (CSFs):[20]

$$\Psi_k(\mathbf{q};\mathbf{Q})=\sum_{\alpha=1}^{N^{\mathrm{CSF}}} c_\alpha^k(\mathbf{Q})\psi_\alpha(\mathbf{q};\mathbf{Q}). \tag{1}$$

In a time reversal adapted basis the CSFs come in pairs ψ_α and $\hat{T}\psi_\alpha$. The basis is referred to as an ordered time reversal adapted (OTRA) basis provided the functions are ordered, $\psi_\alpha,\psi_\beta,\psi_\gamma,\ldots,\hat{T}\psi_\alpha,\hat{T}\psi_\beta,\hat{T}\psi_\gamma,\ldots$. The construction of a time reversal adapted CSF basis is described in Ref. 20.

As a consequence of time reversal symmetry, a conical interaction of potential energy surfaces i and j, at $\mathbf{Q}^{x,ij}$, represents an intersection of two pairs of degenerate states, $(\Psi_i,\hat{T}\Psi_i)$ and $(\Psi_j,\hat{T}\Psi_j)$. Then, as discussed in detail in Ref. 13, near $\mathbf{Q}^{x,ij}$, with the states in the order, Ψ_i, Ψ_j, Ψ_{Ti}, Ψ_{Tj}, the electronic Hamiltonian $\mathbf{H}^e$ and its traceless part $\mathbf{H}$ can be written to first order in displacements from $\mathbf{Q}^{x,ij}$ [see Eq. (12a) in Ref. 13] as

$$\mathbf{H}(\mathbf{Q})\equiv\mathbf{H}^e(\mathbf{Q})-(\mathbf{s}^{ij}\cdot\delta\mathbf{Q})\mathbf{I}$$
$$=\begin{pmatrix} \mathbf{g}^{ij} & \mathbf{h}^{ij} & 0 & \mathbf{h}^{iTj} \\ \mathbf{h}^{ij*} & -\mathbf{g}^{ij} & -\mathbf{h}^{iTj} & 0 \\ 0 & -\mathbf{h}^{iTj*} & \mathbf{g}^{ij} & \mathbf{h}^{ij*} \\ \mathbf{h}^{iTj*} & 0 & \mathbf{h}^{ij} & -\mathbf{g}^{ij} \end{pmatrix}\cdot\delta\mathbf{Q}, \tag{2a}$$

where $\mathbf{Q}=\mathbf{Q}^{x,ij}+\delta\mathbf{Q}$, $2\mathbf{s}^{ij}=\mathbf{h}^{ii}+\mathbf{h}^{jj}$, $2\mathbf{g}^{ij}=\mathbf{h}^{ii}-\mathbf{h}^{jj}$,

$$\mathbf{h}^{ij}(\mathbf{Q})=\mathbf{c}^i(\mathbf{Q}^{x,ij})^\dagger\nabla\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{Q})\mathbf{c}^j(\mathbf{Q}^{x,ij}). \tag{2b}$$

Here $\nabla\mathbf{H}^{e,\mathrm{CSF}}$ is the gradient of the electronic Hamiltonian matrix in the CSF basis. It is important to recall that the $\mathbf{h}^{ij}$ are readily evaluated using analytic gradient techniques.[20]

$\mathbf{H}$ is a specific example of a matrix $\mathbf{M}$ composed of two independent square submatrices, $\mathbf{a}$ and $\mathbf{b}$,

$$\mathbf{M}=\begin{pmatrix} \mathbf{a} & \mathbf{b} \\ -\mathbf{b}^* & \mathbf{a}^* \end{pmatrix}\equiv[\mathbf{a};\mathbf{b}]. \tag{3a}$$

This form for $\mathbf{M}$ reflects the use of an OTRA basis, the fact that $\hat{T}$ is antiunitary, that is

$$\langle\psi|\phi\rangle^*=\langle\hat{T}\psi|\hat{T}\phi\rangle, \tag{3b}$$

and that $\hat{T}^2=-I$ for an odd electron system.[10] In an OTRA basis the matrix of any linear operator that commutes with $\hat{T}$, has the form of $\mathbf{M}$, will be referred to as a *T-type* matrix and will be denoted $[\mathbf{a};\mathbf{b}]$. Note that if $\mathbf{M}$ is Hermitian $\mathbf{a}$ too is Hermitian, but $\mathbf{b}$ is antisymmetric.

Equation (2a) is the starting point for present analysis. The five real vectors, $\mathbf{v}^{(1)},\ldots,\mathbf{v}^{(5)}$, with

$$\mathbf{h}^{ii}-\mathbf{h}^{jj}=2\mathbf{v}^{(3)},$$
$$\mathbf{h}^{ij}=\mathbf{v}^{(1)}-i\mathbf{v}^{(2)}, \tag{4}$$
$$\mathbf{h}^{i,Tj}=\mathbf{v}^{(4)}-i\mathbf{v}^{(5)},$$

form the basis for the branching space at $\mathbf{Q}^{x,ij}$. These vectors are in general linearly independent but need not be orthogonal. Indeed they are not even continuous as a function of $\mathbf{Q}^{x,ij}$. This is a consequence of the fact that at $\mathbf{Q}^{x,ij}$ the Ψ_k, $k=i$, Ti, j and Tj, are defined only up to a T-type unitary transformation, $\mathbf{U}$. In the following we demonstrate how this unitary transformation can be chosen so that the $\mathbf{v}^{(l)}$ become orthogonal and consequently continuous. In addition this choice of $\mathbf{U}$ provides a valuable tool for analyzing a conical intersection.

A. A compact representation of the electronic Hamiltonian near a conical intersection

The $\mathbf{v}^{(i)}$ provide a convenient coordinate system for describing the vicinity of a conical intersection. For $\mathbf{\Delta}^t=(x,y,z,v,w)$, where the subscript t denotes the transpose, a displacement in these scaled intersection adapted coordinates,[1] Eq. (2a) becomes

$$\mathbf{H}(\mathbf{Q})=\begin{pmatrix} z & x-iy & 0 & v-iw \\ x+iy & -z & -(v-iw) & 0 \\ 0 & -(v+iw) & z & x+iy \\ v+iw & 0 & x-iy & -z \end{pmatrix}$$
$$\equiv(\mathbf{\Gamma}_x,\mathbf{\Gamma}_y,\mathbf{\Gamma}_z,\mathbf{\Gamma}_v,\mathbf{\Gamma}_w)\cdot\mathbf{\Delta}. \tag{5a}$$

Here the 4×4 matrices $\mathbf{\Gamma}_k$, $k=x,y,z,v,w$ are T-type, specifically (see also Ref. 14)

$$\mathbf{\Gamma}_k=[\sigma_k;\mathbf{0}] \quad \text{for } k=x,y,z,$$
$$\mathbf{\Gamma}_v=[\mathbf{0};i\sigma_y], \tag{5b}$$
$$\mathbf{\Gamma}_w=[\mathbf{0};\sigma_y],$$

where the $\boldsymbol{\sigma}$ are the Pauli matrices.[21]

B. Unitary transformations, rotations, and the Sp(4)→SO(5) homomorphism

In this section we describe the general relation between a T-type unitary transformation of the electronic states and a rotation of the five-component vector $\mathbf{\Delta}$. This relation is given by the homomorphism of Sp(4), the T-type subset of SU(4), onto SO(5).[16,17] These results, which are known,[16,17] are presented here since they provide the foundation for the realization of the homomorphism derived in Secs. II C and II E.

Observe that a unitary transformation of $\mathbf{H}$ that preserves time reversal symmetry must produce an $\mathbf{H}'$ which has the same form as in Eq. (5a) except with different entries, that is

$$\begin{aligned}\mathbf{H}' &= \mathbf{U}\mathbf{H}\mathbf{U}^\dagger\\ &= (\mathbf{\Gamma}_x, \mathbf{\Gamma}_y, \mathbf{\Gamma}_z, \mathbf{\Gamma}_v, \mathbf{\Gamma}_w)\cdot\mathbf{\Delta}'\\ &\equiv (\mathbf{\Gamma}_x, \mathbf{\Gamma}_y, \mathbf{\Gamma}_z, \mathbf{\Gamma}_v, \mathbf{\Gamma}_w)\cdot\mathbf{R}(\mathbf{U})\mathbf{\Delta}\end{aligned} \tag{6a}$$

with $\mathbf{R}(\mathbf{U})$ obtained by comparing coefficients of the $\mathbf{\Gamma}$. Thus the (4×4) unitary transformation of the electronic states $\mathbf{U}$ induces a (5×5) transformation $\mathbf{R}(\mathbf{U})$ of $\mathbf{\Delta}$,

$$\mathbf{\Delta}' = \mathbf{R}(\mathbf{U})\mathbf{\Delta}. \tag{6b}$$

Since[13] $(x'^2+y'^2+z'^2+v'^2+w'^2)^2 = \det \mathbf{H}' = \det \mathbf{H} = (x^2+y^2+z^2+v^2+w^2)^2$, $\mathbf{R}(\mathbf{U})$ is norm preserving. For this reason we will refer to $\mathbf{R}(\mathbf{U})$ as a rotation. A more general treatment of the invariants of groups such as SO(5), one of the classical continuous groups, is given by Weyl.[16]

The transformations in Eqs. (6a) and (6b) are more familiar with the 2×2 case for the Hermitian matrix $\mathbf{a} = x\sigma_x + y\sigma_y + z\sigma_z \equiv (\sigma_x, \sigma_y, \sigma_z)\cdot\boldsymbol{\delta}$ with $\boldsymbol{\delta} = (x,y,z)^t$, $\mathbf{a}' = \mathbf{u}\mathbf{a}\mathbf{u}^\dagger = (\sigma_x, \sigma_y, \sigma_z)\cdot\boldsymbol{\delta}'$ defines $\mathbf{r}(\mathbf{u})$ by $\boldsymbol{\delta}' = \mathbf{r}(\mathbf{u})\boldsymbol{\delta}$. $\mathbf{r}(\mathbf{u})$ is the homomorphism of SU(2) onto SO(3) noted in Sec. I.

We now show that like $\mathbf{r}$, the rotation $\mathbf{R}$ is a group homomorphism. It will be convenient to denote 2×2 unitary matrices and the induced orthogonal 3×3 matrices by lower case letters and 4×4 and the induced 5×5 matrices by upper case letters. $\mathbf{R}$ preserves the multiplication rule since, from Eqs. (6a) and 6(b) if

$$\mathbf{U} = \mathbf{U}^{(2)}\mathbf{U}^{(1)}$$

then

$$\mathbf{R}(\mathbf{U}) = \mathbf{R}(\mathbf{U}^{(2)})\mathbf{R}(\mathbf{U}^{(1)}). \tag{6c}$$

It is readily shown that the product of two T-type matrices is again T-type. $\mathbf{R}$ is a 2-to-1 mapping, as is $\mathbf{r}$, since the matrices $-\mathbf{U}$ and $\mathbf{U}$ have the same image.

We now consider the domain of $\mathbf{R}$ in more detail. Note that SU(4) is a $4^2-1=15$ parameter group while SO(5) is only a ${}_5C_2=10$ parameter group. However we are only concerned with the subset of the 4×4 unitary matrices that are consistent with time reversal symmetry, T-type $\mathbf{U}$. This subgroup of SU(4) is indeed determined by 10 independent parameters, as we now explain.

A general $N\times N$ complex-valued matrix has $2N^2$ independent parameters (the real and imaginary part of each matrix element). However here $\mathbf{U}$ has fewer parameters since it must (i) be consistent with time reversal symmetry and (ii) be unitary, that is $\mathbf{U}\mathbf{U}^\dagger = \mathbf{U}^\dagger\mathbf{U} = \mathbf{I}$. Since $\mathbf{U}$ is a T-type matrix it must have the form of $\mathbf{M}$ in Eq. (3a). Thus for $N=2n$, time reversal symmetry limits $\mathbf{U}$ to $2n^2+2n^2=4n^2$ independent matrix elements. Also $\mathbf{U}\mathbf{U}^\dagger$, a Hermitian matrix, is again T-type with $\mathbf{a}$ Hermitian and $\mathbf{b}$ antisymmetric. Further if the $\mathbf{U}$ is to be unitary then $\mathbf{a}=\mathbf{1}$ and $\mathbf{b}=\mathbf{0}$. Since $\mathbf{a}=\mathbf{1}$ gives $n+2\times n(n-1)/2$ independent equations and $\mathbf{b}=\mathbf{0}$ gives $2\times n(n-1)/2$ independent equations, the number of undefined parameters $D_U(n)$ is given by

$$\begin{aligned}D_U(n) &= 4n^2 - [n + 2\times\tfrac{1}{2}n(n-1)] - 2\times\tfrac{1}{2}n(n-1)\\ &= n(2n+1).\end{aligned} \tag{7}$$

For $n=2$, $D_U(n)=10$, as required.

$D_U(n)$ is precisely the number of parameters determining the sympletic group of order $2n$, Sp$(2n)$. This is not a coincidence. We now show that the T-type elements of SU(N) are indeed Sp$(2n)$, for $2n=N$. Sp$(2n)$ can be defined[17] as the subgroup of SU$(2n)$, which leaves a given skew-symmetry bilinear form [see Eq. (8a)] invariant. This should be contrasted with SO(M), which leaves a symmetric bilinear form (scalar product) invariant.[16] In the present notation a unitary $\mathbf{U}$ is an element of Sp(4) provided[17]

$$\mathbf{U}^t\mathbf{G}\mathbf{U} = \mathbf{G} \tag{8a}$$

or equivalently since $\mathbf{G}\mathbf{G}^t = \mathbf{U}^\dagger\mathbf{U} = \mathbf{I}$,

$$\mathbf{G}\mathbf{U}\mathbf{G}^t = \mathbf{U}^*, \tag{8b}$$

where $\mathbf{G} = [\mathbf{0};\mathbf{1}]$ and $\mathbf{1}$ is an $n\times n$ unit matrix. It is readily verified by direct substitution that if $\mathbf{U}$ is T-type, Eq. (8a) holds. Conversely, if $\mathbf{U}\in$ Sp$(2n)$ so that Eq. (8a) and hence Eq. (8b) hold then for a general $2n\times2n$ unitary $\mathbf{U}$ given by

$$\mathbf{U} = \begin{pmatrix}\mathbf{a} & \mathbf{b}\\ \mathbf{c} & \mathbf{d}\end{pmatrix}, \tag{9a}$$

where $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, $\mathbf{d}$ are $n\times n$ matrices

$$\begin{pmatrix}\mathbf{0} & \mathbf{1}\\ -\mathbf{1} & \mathbf{0}\end{pmatrix}\begin{pmatrix}\mathbf{a} & \mathbf{b}\\ \mathbf{c} & \mathbf{d}\end{pmatrix}\begin{pmatrix}\mathbf{0} & -\mathbf{1}\\ \mathbf{1} & \mathbf{0}\end{pmatrix} = \begin{pmatrix}\mathbf{d} & -\mathbf{c}\\ -\mathbf{b} & \mathbf{a}\end{pmatrix} = \begin{pmatrix}\mathbf{a}^* & \mathbf{b}^*\\ \mathbf{c}^* & \mathbf{d}^*\end{pmatrix} \tag{9b}$$

so that $\mathbf{U}$ is required to be T-type. Thus the T-type subset of SU(4) is Sp(4) and the homomorphism $\mathbf{R}$ is a mapping from Sp(4) onto SO(5). This homomorphism of Sp(4) onto SO(5) is elegantly expressed in Judd's classic work[17] in terms of root figure diagrams. The relation between Sp(4) and SU(4) has also been discussed by Judd[17] in the context of tensor operators.

C. Elementary U and their images R(U)

We now turn to the construction of specific ''elementary'' $\mathbf{U}$ and the rotations $\mathbf{R}(\mathbf{U})$. Here Eq. (6c) is particularly useful. Since from Refs. 15 and 22

$$\mathbf{u}^{(xy)}(\phi/2) = \begin{pmatrix} e^{i\phi/2} & 0\\ 0 & e^{-i\phi/2}\end{pmatrix}:$$

$$\mathbf{r}(\mathbf{u}^{(xy)}(\phi/2)) = \begin{pmatrix}\cos\phi & \sin\phi & 0\\ -\sin\phi & \cos\phi & 0\\ 0 & 0 & 1\end{pmatrix} \tag{10a}$$

TABLE I. Elementary 4×4 unitary matrices and 5×5 rotation matrices.

$\mathbf{U}^{(xy)}(\phi)$	$\mathbf{U}^{(zx)}(\theta)$	$\mathbf{U}^{(vw)}(\phi)$	$\mathbf{U}^{(zv)}(\theta)$
$[\mathbf{u}^{(xy)}(\phi/2);\mathbf{0}]$	$[\mathbf{u}^{(zx)}(\theta/2);\mathbf{0}]$	$[e^{i\phi/2}\mathbf{1};\mathbf{0}]$	$[(\cos\,\theta/2)\mathbf{1};(\sin\,\theta/2)\sigma_x]$
$\begin{pmatrix} \mathbf{u}^{(xy)} & \mathbf{0} \\ \mathbf{0} & \mathbf{u}^{(xy)*} \end{pmatrix}$	$\begin{pmatrix} \mathbf{u}^{(zx)} & \mathbf{0} \\ \mathbf{0} & \mathbf{u}^{(zx)*} \end{pmatrix}$	$\begin{pmatrix} e^{i\phi/2}\mathbf{1} & \mathbf{0} \\ \mathbf{0} & e^{-i\phi/2}\mathbf{1} \end{pmatrix}$	$\begin{pmatrix} \cos\,\theta/2 & 0 & 0 & \sin\,\theta/2 \\ 0 & \cos\,\theta/2 & \sin\,\theta/2 & 0 \\ 0 & -\sin\,\theta/2 & \cos\,\theta/2 & 0 \\ -\sin\,\theta/2 & 0 & 0 & \cos\,\theta/2 \end{pmatrix}$
$\mathbf{R}^{(xy)}(\phi)$	$\mathbf{R}^{(zx)}(\theta)$	$\mathbf{R}^{(vw)}(\phi)$	$\mathbf{R}^{(zv)}(\theta)$
$\begin{pmatrix} \cos\,\phi & \sin\,\phi & 0 & 0 & 0 \\ -\sin\,\phi & \cos\,\phi & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \cos\,\theta & 0 & -\sin\,\theta & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ \sin\,\theta & 0 & \cos\,\theta & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & \cos\,\phi & \sin\,\phi \\ 0 & 0 & 0 & -\sin\,\phi & \cos\,\phi \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & \cos\,\theta & \sin\,\theta & 0 \\ 0 & 0 & -\sin\,\theta & \cos\,\theta & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$

and

$$\mathbf{u}^{(zx)}(\theta/2)=\begin{pmatrix} \cos\,\theta/2 & \sin\,\theta/2 \\ -\sin\,\theta/2 & \cos\,\theta/2 \end{pmatrix}:$$

$$\mathbf{r}(\mathbf{u}^{(zx)}(\theta/2))=\begin{pmatrix} \cos\,\theta & 0 & -\sin\,\theta \\ 0 & 1 & 0 \\ \sin\,\theta & 0 & \cos\,\theta \end{pmatrix} \tag{11a}$$

using the block matrix multiplication we find

$$\mathbf{U}^{(xy)}(\phi/2)\equiv[\mathbf{u}^{(xy)};\mathbf{0}]:\mathbf{R}(\mathbf{U}^{(xy)}(\phi/2))\equiv\mathbf{R}^{(xy)}(\phi), \tag{10b}$$

$$\mathbf{U}^{(zx)}(\theta/2)\equiv[\mathbf{u}^{(zx)};\mathbf{0}]:\mathbf{R}(\mathbf{U}^{(zx)}(\theta/2))\equiv\mathbf{R}^{(zx)}(\phi), \tag{11b}$$

where $\mathbf{R}^{(xy)}(\phi)$ and $\mathbf{R}^{(zx)}(\theta)$ and their preimages are given in Table I. To mix the state and time reversed state blocks we introduce the permutation matrix

$$\mathbf{P}=\left[\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix};\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}\right]:$$

$$\mathbf{R}(\mathbf{P})\equiv\mathbf{R}^{(P)}=\begin{pmatrix} 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \end{pmatrix}, \tag{12}$$

so that $\mathbf{P}^2[\mathbf{R}^{(P)^2}]$ is a diagonal matrix with diagonal elements $(1,-1,1,-1)$ $[(-1,-1,1,-1,-1)]$. Thus $\mathbf{P}^4[\mathbf{R}^{(P)^4}]$ is a unit matrix and $\mathbf{P}^{-1}=\mathbf{P}^3$. Further we define two additional transformations and induced rotations:

$$\mathbf{U}^{(vw)}(\theta/2)\equiv\mathbf{P}^{-1}\mathbf{U}^{(xy)}(\phi/2)\mathbf{P}=[e^{i\phi/2}\mathbf{1};\mathbf{0}]:$$

$$\mathbf{R}(\mathbf{U}^{(vw)}(\phi/2))\equiv\mathbf{R}^{(vw)}(\phi) \tag{13a}$$

and

$$\mathbf{U}^{(zv)}(\theta/2)\equiv\mathbf{P}^{-1}\mathbf{U}^{(zx)}(\phi/2)\mathbf{P}=[(\cos\,\theta/2)\mathbf{1};(\sin\,\theta/2)\sigma_x]:$$

$$\mathbf{R}(\mathbf{U}^{(zv)}(\theta/2))\equiv\mathbf{R}^{(zv)}(\theta). \tag{14a}$$

$\mathbf{R}^{(vw)}(\phi)$, $\mathbf{R}^{(zv)}(\theta)$, and their preimages are tabulated in Table I. $\mathbf{U}^{(xy)}$, $\mathbf{U}^{(zx)}$, $\mathbf{U}^{(vw)}$, and $\mathbf{U}^{(zv)}$ are the four ''elementary'' matrices which will be used in Sec. II E to construct the requisite T-type $\mathbf{U}$.

In Sec. II E the following relations, readily confirmed by matrix multiplication, will be used:

$$\mathbf{P}\mathbf{U}^{(xy)}(\phi/2)\mathbf{P}^{-1}=\mathbf{U}^{(vw)}(\phi/2), \tag{13b}$$

$$\mathbf{P}\mathbf{U}^{(zx)}(\theta/2)\mathbf{P}^{-1}=\mathbf{U}^{(zv)}(-\theta/2). \tag{14b}$$

For use in that section we also define:

$$\mathbf{U}^{(2)}(\phi,\theta)=\mathbf{U}^{(zx)}(\theta/2)\mathbf{U}^{(xy)}(\phi/2), \tag{15a}$$

$$\tilde{\mathbf{U}}^{(2)}(\phi,\theta)=\mathbf{U}^{(zv)}(\theta/2)\mathbf{U}^{(vw)}(\phi/2), \tag{15b}$$

$$\mathbf{U}^{(3)}(\phi,\theta,\gamma)=\mathbf{U}^{(xy)}(\gamma/2)\mathbf{U}^{(zx)}(\theta/2)\mathbf{U}^{(xy)}(\phi/2), \tag{15c}$$

$$\tilde{\mathbf{U}}^{(3)}(\phi,\theta,\gamma)=\mathbf{U}^{(vw)}(\gamma/2)\mathbf{U}^{(zv)}(\theta/2)\mathbf{U}^{(vw)}(\phi/2) \tag{15d}$$

and their induced rotations: $\mathbf{R}^{(2)}(\phi,\theta)$, $\tilde{\mathbf{R}}^{(2)}(\phi,\theta)$, $\mathbf{R}^{(3)}(\phi,\theta,\gamma)$, and $\tilde{\mathbf{R}}^{(3)}(\phi,\theta,\gamma)$. Combining Eqs. (13a), (14a), and (15a) gives

$$\mathbf{P}^{-1}\mathbf{U}^{(2)}(\phi,\theta)\mathbf{P}=\mathbf{P}^{-1}\mathbf{U}^{(zx)}(\theta/2)\mathbf{P}\mathbf{P}^{-1}\mathbf{U}^{(xy)}(\phi/2)\mathbf{P}$$
$$=\mathbf{U}^{(zv)}(\theta/2)\mathbf{U}^{(vw)}(\phi/2)=\tilde{\mathbf{U}}^{(2)}(\phi,\theta) \tag{16a}$$

and combining Eqs. (13b), (14b), and (15a) gives

$$\mathbf{P}\mathbf{U}^{(2)}(\phi,\theta)\mathbf{P}^{-1}=\tilde{\mathbf{U}}^{(2)}(\phi,-\theta). \tag{16b}$$

Finally since $\mathbf{P}^2=\mathbf{P}^{-2}$ using Eqs. (16a) and (16b) gives

$$\mathbf{P}^2\mathbf{U}^{(2)}(\phi,\theta)\mathbf{P}^2=\mathbf{U}^{(2)}(\phi,-\theta). \tag{16c}$$

D. Rotating the branching space

By way of summary, observe that near a conical intersection $\mathbf{H}$ can be written as

$$\mathbf{H}=\sum_{i=1}^{5}\mathbf{\Gamma}_i(\mathbf{v}^{(i)}\cdot\delta\mathbf{Q}) \tag{17}$$

so that Eq. (6b) becomes, in component form for clarity,

$$\mathbf{v}'^{(k)}\cdot\delta\mathbf{Q}=\sum_j \mathbf{R}(\mathbf{U})_{kj}(\mathbf{v}^{(j)}\cdot\delta\mathbf{Q}) \tag{18a}$$

or since $\delta\mathbf{Q}$ is arbitrary

$$\mathbf{v}'^{(k)}=\sum_j \mathbf{R}(\mathbf{U})_{kj}\mathbf{v}^{(j)}. \tag{18b}$$

Thus the unitary transform $\mathbf{U}$ of the electronic states induces a transformation, $\mathbf{R}(\mathbf{U})$, of precisely the vectors we wish to orthogonalize. In the following we show how $\mathbf{U}$, constructed from a product of the $\mathbf{U}^{(l)}$ introduced in this section, can be used to construct $\mathbf{v}'^{(k)}$ that are mutually orthogonal.

Note from Eq. (6) that the functional form of $\mathbf{H}$ [see Eq. (5a)] is invariant under the orthogonalization in Eq. (18b). An orthogonalization that does not originate from a unitary transformation of the electronic states, e.g., a symmetric orthogonalization of the $\mathbf{v}^{(j)}$, would require the original matrix elements in Eq. (5a) to be re-expressed in the new basis, producing more general, albeit still linear, expressions for the individual matrix elements. The present approach provides the advantages of an orthogonal set without complicating the form of $\mathbf{H}$.

E. A representative of U

In this section $\mathbf{U}$ is constructed as a product of the "elementary" $\mathbf{U}$ in Sec. II C. The number of such elementary transformations reflects the number of free parameters available to T-type $\mathbf{U}$, that is 10, which is precisely the number of equations that arise from the requirement that five vectors be mutually orthogonal.

Thus, here $\mathbf{U}$ will be a product of $\mathbf{U}^{(l)}$ and $\mathbf{P}$ involving ten angles. Consider

$$\mathbf{U}^{(10)}=\mathbf{U}^{(2)}(\phi_5,\theta_5)\mathbf{P}\mathbf{U}^{(2)}(\phi_4,\theta_4)\mathbf{P}\mathbf{U}^{(2)}(\phi_3,\theta_3)\times\mathbf{P}\mathbf{U}^{(2)}(\phi_2,\theta_2)\mathbf{P}\mathbf{U}^{(2)}(\phi_1,\theta_1). \tag{19}$$

The associated rotation, $\mathbf{R}^{(10)}\equiv\mathbf{R}(\mathbf{U}^{(10)})$, which is readily constructed from Eq. (6c), is given by

$$\mathbf{R}^{(10)}=\mathbf{R}^{(2)}(\phi_5,\theta_5)\mathbf{R}^{(P)}\mathbf{R}^{(2)}(\phi_4,\theta_4)\mathbf{R}^{(P)}\times\mathbf{R}^{(2)}(\phi_3,\theta_3)\mathbf{R}^{(P)}\mathbf{R}^{(2)}(\phi_2,\theta_2)\mathbf{R}^{(P)}\mathbf{R}^{(2)}(\phi_1,\theta_1). \tag{20a}$$

The following partial products $\mathbf{R}^{(l)}$ will be required:

$$\mathbf{R}^{(2)}\equiv\mathbf{R}^{(2)}(\phi_5,\theta_5), \tag{20b}$$

$$\mathbf{R}^{(2n+2)}\equiv\mathbf{R}^{(2n)}\mathbf{R}^{(P)}\mathbf{R}^{(2)}(\phi_{5-n},\theta_{5-n}),\quad n=1,2,3. \tag{20c}$$

For $\mathbf{R}^{(10)}$ to provide a solution to Eq. (18b), it must be invertible. In the following the recursion relation, Eq. (20), will be used to demonstrate this property analytically.

When an odd electron molecule has C_s symmetry $\mathbf{v}^{(4)}$ and $\mathbf{v}^{(5)}$ vanish identically. In this case there are only three orthogonality equations. The three parameter unitary transformation that accomplishes the orthogonalization is[12]

$$\mathbf{U}^{(\eta=3)}=[\mathbf{u}^{(3)};\mathbf{0}] \tag{21}$$

with $\mathbf{u}^{(3)}$ given in terms of the Eular angles α,β,γ, by $\mathbf{u}^{(3)}(\alpha,\beta,\gamma)\equiv\mathbf{u}^{(xy)}(\gamma/2)\mathbf{u}^{(zx)}(\beta/2)\mathbf{u}^{(xy)}(\alpha/2)$,

$$\mathbf{u}^{(3)}(\alpha,\beta,\gamma)=\begin{pmatrix} e^{i(\gamma+\alpha)/2}\cos\beta/2 & e^{i(\gamma-\alpha)/2}\sin\beta/2 \\ -e^{-i(\gamma-\alpha)/2}\sin\beta/2 & e^{-i(\gamma+\alpha)/2}\cos\beta/2 \end{pmatrix}. \tag{22}$$

The induced Euler rotation is

$$\mathbf{r}(\mathbf{u}^{(3)})=\begin{pmatrix} \cos\gamma\cos\beta\cos\alpha-\sin\gamma\sin\alpha & \cos\gamma\cos\beta\sin\alpha+\sin\gamma\cos\alpha & -\cos\gamma\sin\beta \\ -\sin\gamma\cos\beta\cos\alpha-\cos\gamma\sin\alpha & -\sin\gamma\cos\beta\sin\alpha+\cos\gamma\cos\alpha & \sin\gamma\sin\beta \\ \sin\beta\cos\alpha & \sin\beta\sin\alpha & \cos\beta \end{pmatrix}. \tag{23}$$

In order to make the connection with the present result we rearrange $\mathbf{U}^{(10)}$ as follows. Inserting $\mathbf{P}^4$, the identity matrix, into Eq. (19) as indicated in the following yields

$$\mathbf{U}^{(10)}=\mathbf{U}^{(2)}(\phi_5,\theta_5)\mathbf{P}\mathbf{U}^{(2)}(\phi_4,\theta_4)\mathbf{P}^3\mathbf{P}^2\times\mathbf{U}^{(2)}(\phi_3,\theta_3)\mathbf{P}^2\mathbf{P}^3\mathbf{U}^{(2)}(\phi_2,\theta_2)\mathbf{P}\mathbf{U}^{(2)}(\phi_1,\theta_1), \tag{24a}$$

which using Eqs. (16a)–(16c) gives

$$\mathbf{U}^{(10)}=\mathbf{U}^{(2)}(\phi_5,\theta_5)\mathbf{P}\mathbf{U}^{(2)}(\phi_4,\theta_4)\mathbf{P}^{-1}\mathbf{P}^2\times\mathbf{U}^{(2)}(\phi_3,\theta_3)\mathbf{P}^2\mathbf{P}^{-1}\mathbf{U}^{(2)}(\phi_2,\theta_2)\mathbf{P}\mathbf{U}^{(2)}(\phi_1,\theta_1) \tag{24b}$$

$$=\mathbf{U}^{(2)}(\phi_5,\theta_5)\tilde{\mathbf{U}}^{(2)}(\phi_4,-\theta_4)\mathbf{P}^2\mathbf{U}^{(2)}(\phi_3,\theta_3)\mathbf{P}^2\times\tilde{\mathbf{U}}^{(2)}(\phi_2,\theta_2)\mathbf{U}^{(2)}(\phi_1,\theta_1) \tag{24c}$$

$$=\mathbf{U}^{(2)}(\phi_5,\theta_5)\tilde{\mathbf{U}}^{(2)}(\phi_4-\theta_4)\mathbf{U}^{(2)}(\phi_3,-\theta_3)\times\tilde{\mathbf{U}}^{(2)}(\phi_2,\theta_2)\mathbf{U}^{(2)}(\phi_1,\theta_1) \tag{24d}$$

and since (see Table I) $\mathbf{U}^{(xy)}(\phi_3)$ commutes with $\tilde{\mathbf{U}}^{(2)}(\phi_2,\theta_2)$, $\mathbf{U}^{(10)}$ becomes

$$\mathbf{U}^{(10)}=\mathbf{U}^{(2)}(\phi_5,\theta_5)\tilde{\mathbf{U}}^{(2)}(\phi_4,-\theta_4)\mathbf{U}^{(zx)}(-\theta_3)\times\tilde{\mathbf{U}}^{(2)}(\phi_2,\theta_2)\mathbf{U}^{(3)}(\phi_1,\theta_1,\phi_3). \tag{24e}$$

From Eqs. (10a), (11a), and (15c) $\mathbf{U}^{(3)}$ in Eq. (24e) has the form of $\mathbf{U}^{(\eta=3)}$ so that $\mathbf{U}^{(10)}$ with only ϕ_1,θ_1,ϕ_3 nonzero is precisely $\mathbf{U}^{(\eta=3)}$.

F. An orthogonal representation of the branching space

Equation (18b), $\mathbf{v}'^{(k)}=\Sigma_j\mathbf{R}(\mathbf{U})_{kj}\mathbf{v}^{(j)}$, is the key to the present analysis as it connects $\mathbf{U}$ with $\mathbf{R}(\mathbf{U})$, the orthogonal transformation of $\mathbf{v}^{(j)}$. Let $\mathbf{O}$ be the orthogonal transformation with determinant $+1$ that diagonalizes $D(\mathbf{v}^{(1)},\mathbf{v}^{(2)},\mathbf{v}^{(3)},\mathbf{v}^{(4)},\mathbf{v}^{(5)})$, the overlap matrix of the $\mathbf{v}^{(j)}$, $j=1-5$, that is

$$D(\mathbf{v}'^{(1)},\mathbf{v}'^{(2)},\mathbf{v}'^{(3)},\mathbf{v}'^{4},\mathbf{v}'^{(5)})_{kl} =[\mathbf{O}D(\mathbf{v}^{(1)},\mathbf{v}^{(2)},\mathbf{v}^{(3)},\mathbf{v}^{(4)},\mathbf{v}^{(5)})\mathbf{O}^t]_{kl}=\delta_{kl}[v'^{(k)}]^2, \tag{25}$$

where $v'^{(k)}$ is the norm of $\mathbf{v}'^{(k)}$ and

$$D(\mathbf{v}^{(1)},\mathbf{v}^{(2)},\mathbf{v}^{(3)},\mathbf{v}^{(4)},\mathbf{v}^{(5)})_{kl}=\mathbf{v}^{(k)^t}\cdot\mathbf{v}^{(l)}. \tag{26}$$

Then it suffices to show that $\mathbf{O}=\mathbf{R}(\mathbf{U})$, that is $\mathbf{O}$ can be written as the image of a $\mathbf{U}$ under $\mathbf{R}$. This is accomplished using Eqs. (20a)–(20c) since from these equations it follows that

$$(R_{51}^{(10)},R_{52}^{(10)},R_{53}^{(10)}) =\sin\phi_4\sin\theta_2(\sin\theta_1\cos\phi_1,\ \sin\theta_1\sin\phi_1,\cos\theta_1), \tag{27a}$$

$$(R_{21}^{(8)},R_{22}^{(8)},R_{23}^{(8)}) =-\sin\phi_5\sin\theta_3(\sin\theta_2\cos\phi_2,\sin\theta_2\sin\phi_2,\cos\theta_2), \tag{27b}$$

$$(R_{41}^{(6)},R_{42}^{(6)},R_{43}^{(6)}) =\sin\theta_4(\sin\theta_3\cos\phi_3,\sin\theta_3\sin\phi_3,\cos\theta_3), \tag{27c}$$

$$(R_{11}^{(4)},R_{12}^{(4)},R_{13}^{(4)}) =-\sin\theta_5(\sin\theta_4\cos\phi_4,\sin\theta_4\sin\phi_4,\cos\theta_4), \tag{27d}$$

$$(R_{31}^{(2)},R_{32}^{(2)},R_{33}^{(2)})=(\sin\theta_5\cos\phi_5,\sin\theta_5\sin\phi_5,\cos\theta_5). \tag{27e}$$

The ten angles are determined in the ranges of $0\leqslant\phi_i<2\pi$ and $0\leqslant\theta_i\leqslant\pi$. This choice of angles allows $\mathbf{U}$ to be determined from $\mathbf{R}(\mathbf{U})$. In the solution of Eq. (27) the sign of each of $\sin\phi_4$ and $\sin\phi_5$ is determined self-consistently. The details of obtaining these equations are presented in the Appendix.

G. An R-invariant quantity

The above-described orthogonalization procedure has been carried out using alternative approaches in the $\eta=2$ and $\eta=3$ cases. In the $\eta=2$ case the branching plane is spanned by $\mathbf{v}^{(1)}$ and $\mathbf{v}^{(3)}$. It was found that the cross product $\mathbf{v}^{(1)}\times\mathbf{v}^{(3)}$ is invariant under the rotation of the two degenerate eigenstates that orthogonalizes $\mathbf{v}^{(1)}$ and $\mathbf{v}^{(3)}$.[23] In the $\eta=3$ case the branching space is spanned by $\mathbf{v}^{(1)}$, $\mathbf{v}^{(2)}$, and $\mathbf{v}^{(3)}$. It was found that the scalar triple product $\mathbf{v}^{(1)}\times\mathbf{v}^{(2)}\cdot\mathbf{v}^{(3)}$ is invariant under the rotation of the degenerate eigenstates that orthogonalizes $\mathbf{v}^{(1)}$, $\mathbf{v}^{(2)}$, and $\mathbf{v}^{(3)}$.[24] Here the cross product and scalar triple product are evaluated in the branching space. This invariant can be used to identify regions of coordinate space where two branches of the same seam intersect.[18]

The generalization of these results to the $\eta=5$ case follows from the observations that for $\eta=2$:

$$\mathbf{v}^{(1)}\times\mathbf{v}^{(3)}=\det\begin{pmatrix} v_1^{(1)} & v_2^{(1)} \\ v_1^{(3)} & v_2^{(3)} \end{pmatrix}=\pm v'^{(1)}v'^{(3)}, \tag{28a}$$

and for $\eta=3$:

$$\mathbf{v}^{(1)}\times\mathbf{v}^{(2)}\cdot\mathbf{v}^{(3)}=\det\begin{pmatrix} v_1^{(1)} & v_2^{(1)} & v_3^{(1)} \\ v_1^{(2)} & v_2^{(2)} & v_3^{(2)} \\ v_1^{(3)} & v_2^{(3)} & v_3^{(3)} \end{pmatrix}=\pm v'^{(1)}v'^{(2)}v'^{(3)}, \tag{28b}$$

where the $\mathbf{v}^{(k)}$ are expanded in a basis for the branching space. The choice of basis determines sign in Eqs. (28a) and (28b). The observation in Sec. II C that $\mathbf{R}(\mathbf{U})$ is norm preserving demonstrates that for $\eta=5$ the invariant, $I(\mathbf{v}^{(1)},\mathbf{v}^{(2)},\mathbf{v}^{(3)},\mathbf{v}^{(4)},\mathbf{v}^{(5)})$, is

$$I(\mathbf{v}^{(1)},\mathbf{v}^{(2)},\mathbf{v}^{(3)},\mathbf{v}^{(4)},\mathbf{v}^{(5)}) =\det\begin{pmatrix} v_1^{(1)} & v_2^{(1)} & v_3^{(1)} & v_4^{(1)} & v_5^{(1)} \\ v_1^{(2)} & v_2^{(2)} & v_3^{(2)} & v_4^{(2)} & v_5^{(2)} \\ v_1^{(3)} & v_2^{(3)} & v_3^{(3)} & v_4^{(3)} & v_5^{(3)} \\ v_1^{(4)} & v_2^{(4)} & v_3^{(4)} & v_4^{(4)} & v_5^{(4)} \\ v_1^{(5)} & v_2^{(5)} & v_3^{(5)} & v_4^{(5)} & v_5^{(5)} \end{pmatrix} =\pm v'^{(1)}v'^{(2)}v'^{(3)}v'^{(4)}v'^{(5)}. \tag{28c}$$

III. APPLICATIONS

The principal purpose of this section is to demonstrate the efficacy of the present approach for determining an orthogonal representation of the branching space along seams of conical intersection using a model Hamiltonian. In the course of that study interesting connectivities of the conical intersection seam were found and are also reported herein.

A. The model Hamiltonian

The model Hamiltonian describes six states (three doublet states) and has six internal coordinates, $\mathbf{Q}=(x,y,z,w_1,w_2,w_3)$. As noted earlier, the Hamiltonian was constructed, in part, to test procedures described in Sec. II. In this regard the region of the transition from $\eta=3$ to $\eta=5$ is of interest as it is particularly challenging. The simplest molecule that exhibits this transition is a tetra-atomic molecule. A situation of considerable practical interest is that of a nonrelativistic $^2\Pi-^2\Sigma^+$ conical intersection seam that is altered by spin–orbit coupling.[12] In this case a state with appreciable spin–orbit coupling to the two states involved in the nonrelativistic conical intersection is required. With these factors in mind, a composite Hamiltonian, not designed to be representative of a single molecule, was constructed with parameters from systems we have studied.[12,25] The parameters for the x,y,z coordinates describe a portion of the nonrelativistic $1,2\,^2A$ conical intersection seam in BH_2 (Ref. 25) with the

TABLE II. Parameters in the model Hamiltonians.

g	g_z	$ar1$	$ar2$	$ecrv$	app	bpp
−0.080 51[a]	0.001 36	0.001 76	−0.002 72	0.01	0.01	0.01
h	h_z	exd	$exd1$	eyd	ezd	$ezd1$
0.009 25	−0.001 148	0.1	0.1	0.1	0.01	0.01
b_{3r}	$ezw1$	$ezw3$	$ew22$	$g41$		
0.002	0.1	0.1	0.1	0.05		
h_{12}^{so}	h_{13}^{so}	h_{23}^{so}	h_{12}^{tso}	h_{13}^{tso}	h_{23}^{tso}	
0.005 695	0.005 695	0.011 391	0.005 695	0.005 695	0.005 695	

[a]Atomic units used throughout.

z axis as the seam coordinate. Seam curvature, which causes the seam not to coincide with the z axis, is included using the parameter $ecrv$. In order to describe a three state tetra-atomic molecule, a third, adjustable, electronic state and three additional coordinates w_i, $i=1,2,3$ were introduced. Since we are interested in the manner in which the $\eta=3$ and $\eta=5$ cases coalesce the molecule is assumed to be planar when $w_2=0$. As a consequence when $w_2=0$ the spin–orbit coupling between the ψ_i and $\hat{T}\psi_j$ vanishes. The spin–orbit coupling was chosen to be bounded in the w_i but a linear function of x,y,z, a choice which facilitated determination of conical intersections for $w_2\neq 0$.

In an ordered time reversal adapted basis the Hamiltonian $\mathbf{H}(\mathbf{Q})$ is a 6×6, T-type matrix, where

$$\mathbf{a}=\begin{pmatrix} a_1 & a_2+ib_2 & a_4 \\ \cdot & a_3 & ib_5 \\ \cdot & \cdot & a_6 \end{pmatrix},$$

$$\mathbf{b}=\begin{pmatrix} 0 & a_8 & a_{10}+ib_{10} \\ \cdot & 0 & ib_{11} \\ \cdot & \cdot & 0 \end{pmatrix} \tag{29}$$

and

$$\begin{aligned} a_1&=-(g\cdot x+g_z\cdot xz+ar1\cdot x^2+ar2\cdot y^2),\\ a_3&=-a_1+ecrv\cdot(z^2+w_1^2+w_2^2+w_3^2),\\ a_6&=app\cdot x^2+bpp\cdot y^2+ezd\cdot z^2+ezd1\cdot z\\ &\quad+exd\cdot(x^2-w_1^2)+exd1\cdot(x+w_3+xw_1)\\ &\quad+eyd\cdot(y^2+w_2^2+w_3^2),\\ a_2&=(h\cdot y+h_z\cdot yz)+b_{3r}\cdot xy+ezw1\cdot zw_1+ezw3\cdot zw_3\\ &\quad+ew22\cdot w_2^2,\\ a_4&=g41\cdot(0.01+x^2+z)+h_{13}^{so}(2-\tanh z^2)/2,\\ b_2&=-h_{12}^{so}(1-e^{-z^2})/2,\\ b_5&=h_{23}^{so}(3/4-e^{-z^2})5/4,\\ a_8&=a_{12}^{tso}(z-x),\quad a_{10}=a_{13}^{tso},\quad b_{10}=a_{13}^{tso}(z-y),\\ b_{11}&=a_{23}^{tso}(x-y),\\ a_{ij}^{tso}&=h_{ij}^{tso}(1-e^{-w_2^2})e^{-w_1^2-w_3^2}. \end{aligned} \tag{30}$$

The parameters for this representation are given in Table II.

B. Seams of conical intersection

According to the noncrossing rule[10] $\mathbf{H}(\mathbf{Q})$ has a two-dimensional seam with $\eta=3$ for planar geometries $(w_2=0)$ which merges into a one-dimensional seam with $\eta=5$ as w_2 differs from 0. From Eq. (28c) $I(\mathbf{v}^{(1)},\mathbf{v}^{(2)},\mathbf{v}^{(3)},\mathbf{v}^{(4)},\mathbf{v}^{(5)})$ is expected to approach 0 as w_2 approaches 0. These conclusions apply to either the eigenstates $(\Psi_1,\hat{T}\Psi_1)$ and $(\Psi_2,\hat{T}\Psi_2)$ or $(\Psi_2,\hat{T}\Psi_2)$ and $(\Psi_3,\hat{T}\Psi_3)$. Here we focus on the former pair (the lower states).

1. Locating the seam

An algorithm for locating the seam has been presented previously.[20] In the following, we briefly summarize the implementation of that approach employed here. We seek $\mathbf{Q}^x$ such that $E_1(\mathbf{Q}^x)=E_2(\mathbf{Q}^x)$ subject to additional geometric constraints, $J_k(\mathbf{Q}^x)=0$, $k=1,\ldots,N^{con}$. Since the condition $E_1(\mathbf{Q})=E_2(\mathbf{Q})$ provides η equations, we require $N^{con}=N^i-\eta$, where N^i is the number of internal coordinates. Then $N^{con}=1$ when the molecule has no symmetry $(\eta=5)$ and $N^{con}=3$ when the molecule is planar since $\eta=3$. In the latter case it is convenient to incorporate the constraint of C_s symmetry, $w_2=0$, explicitly and use $N^{con}=2$.

$\mathbf{Q}^x$ is determined iteratively. In the iterative determination of $\mathbf{Q}^x$ we write $\mathbf{Q}^x=\mathbf{Q}^0+\delta\mathbf{Q}$ and assume that $\mathbf{Q}^0$ is sufficiently close to $\mathbf{Q}^x$ that Eq. (2a) is valid. Then $\mathbf{Q}^x$ will be a point of intersection provided, in the branching space:

$$\begin{pmatrix} \mathbf{v}^{(1)}\cdot\delta\mathbf{Q}\\ \mathbf{v}^{(2)}\cdot\delta\mathbf{Q}\\ \mathbf{v}^{(3)}\cdot\delta\mathbf{Q}\\ \mathbf{v}^{(4)}\cdot\delta\mathbf{Q}\\ \mathbf{v}^{(5)}\cdot\delta\mathbf{Q} \end{pmatrix}=\begin{pmatrix} 0\\ 0\\ -\Delta E_{12}\\ 0\\ 0 \end{pmatrix} \tag{31}$$

subject to the N^{con} constraint equations

$$J_k(\mathbf{Q}^0)+\mathbf{j}_k(\mathbf{Q}^0)\cdot\delta\mathbf{Q}=0,\quad k=1,\ldots,N^{con}. \tag{32}$$

In general these equations converge rapidly. However the size of $\mathbf{v}^{(3)}$ depends on $\mathbf{Q}^0$. When $\mathbf{Q}^0$ is such that $\mathbf{v}^{(3)}$ is small, second-order contributions may be appreciable and extrapolation techniques were found useful.

2. The seam and its properties

For the lowest two eigenenergies E_1 and E_2 of $\mathbf{H}(\mathbf{Q})$, two distinct seams were found. One seam, denoted S_h, is comparatively high in energy. It exists only for C_s symmetry, $w_2=0$, structures, and therefore is a two-dimensional surface. The points on this seam will be denoted $\mathbf{Q}_h^{x,3}$. The second, lower energy seam, denoted S_l, has a C_s portion, with points labeled $\mathbf{Q}_l^{x,3}$, again a two-dimensional surface, that merges into an $\eta=5$ no symmetry portion, a one-dimensional line, with points labeled $\mathbf{Q}_l^{x,5}$. The $\mathbf{Q}_l^{x,3}$ and $\mathbf{Q}_l^{x,5}$ portions of S_l intersect at two points, $\mathbf{Q}_l^x(A)=(0.5933,0.5806,0.5931,-1.1607,0,1.0626)$ and $\mathbf{Q}_l^x(B)=(0.5902,0.5782,0.5900,0.9861,0,-1.0846)$. Interestingly S_l is a closed, bounded, set, while S_h is infinite in extent.

Figure 1(a) reports the locus $\mathbf{Q}_l^{x,5}(w_2)\equiv(x(w_2),y(w_2),z(w_2),w_1(w_2),w_2,w_3(w_2))$, the $\eta=5$ portion of S_l together with a section $y=y_A$, of the two parameter $\eta=3$ portion of S_l $\mathbf{Q}_l^{x,3}(x,y=y_A)\equiv(x,y=y_A,z(x),w_1(x),w_2=0,w_3(x))$, with $y_A=0.5806$, from $\mathbf{Q}_l^x(A)$. Figure 1(b) illustrates the two-dimensional, bounded character of $\mathbf{Q}_l^{x,3}$ reporting $\mathbf{Q}_l^{x,3}(x,y=y_i)$ for $y_i=-5$, y_A and 5, $\mathbf{Q}_l^{x,3}(x=x_A,y)\equiv(x=x_A,y,z(y),w_1(y),w_2=0,w_3(y))$, with $x_A=0.5933$, from $\mathbf{Q}_l^x(A)$. $\mathbf{Q}_l^x(A)$ is shown in Figs. 1(a) and 1(b). Figure 1(c) reports a section $\mathbf{Q}_h^{x,3}(x=x_A,y)\equiv(x=x_A,y,z(y),w_1(y),w_2=0,w_3(y))$, of S_h which illustrates its nonbounded character. Figure 2(a) reports energies on S_l, $E_1(\mathbf{Q}_l^{x,m})=E_2(\mathbf{Q}_l^{x,m})\equiv E^{x,m}(\mathbf{Q}_l^{x,m})$, $m=3,5$. Figure 2(b) reports energies on the sections of S_l depicted in Fig. 1(b).

The tangent vector to the $\eta=5$ portion of S_l at a point $\mathbf{Q}_l^{x,5}$, a vector perpendicular to the branching space, can be obtained from the six-dimensional vector product:

$$s_{1D}(\mathbf{Q}_l^{x,5})=\det\begin{pmatrix} \mathbf{e}_1 & \mathbf{e}_2 & \mathbf{e}_3 & \mathbf{e}_4 & \mathbf{e}_5 & \mathbf{e}_6 \\ v_1^{(1)} & v_2^{(1)} & v_3^{(1)} & v_4^{(1)} & v_5^{(1)} & v_6^{(1)} \\ v_1^{(2)} & v_2^{(2)} & v_3^{(2)} & v_4^{(2)} & v_5^{(2)} & v_6^{(2)} \\ v_1^{(3)} & v_2^{(3)} & v_3^{(3)} & v_4^{(3)} & v_5^{(3)} & v_6^{(3)} \\ v_1^{(4)} & v_2^{(4)} & v_3^{(4)} & v_4^{(4)} & v_5^{(4)} & v_6^{(4)} \\ v_1^{(5)} & v_2^{(5)} & v_3^{(5)} & v_4^{(5)} & v_5^{(5)} & v_6^{(5)} \end{pmatrix}, \tag{33}$$

where $\mathbf{v}^{(k)}=\Sigma_{i=1}^6 v_i^{(k)}\mathbf{e}_i$, $k=1-5$, with $\mathbf{Q}=x\mathbf{e}_1+y\mathbf{e}_2+z\mathbf{e}_3+w_1\mathbf{e}_4+w_2\mathbf{e}_5+w_3\mathbf{e}_6$. From the properties of the determinant, $\mathbf{s}_{1D}$ is perpendicular to all the degeneracy lifting vectors. It was confirmed numerically that the direction of $\mathbf{s}_{1D}(\mathbf{Q}_l^{x,5})$ and of $(\mathbf{Q}_l^{x,5}+\delta\mathbf{Q}_l^{x,5})-(\mathbf{Q}_l^{x,5})$ agree all along the seam. The tangent space to the $\eta=3$ seam cannot be determined from Eq. (33). It consists of two vectors that must be chosen orthogonal to the $\{\mathbf{e}_1',\mathbf{e}_2',\mathbf{e}_3'\}$.

C. Branching space

We now turn to the key aspect of this numerical study, the description of the branching space in terms of orthogonalized vectors. We consider the $\mathbf{v}'^{(k)}(\mathbf{Q}_l^{x,m})$, $k=1-m$, and $m=3,5$. The nascent counterparts of these vectors, the $\mathbf{v}^{(k)}(\mathbf{Q}_l^{x,m})$, are essentially randomly oriented *within* the $\eta=m$ branching space. The orthogonalization procedure must produce $\mathbf{v}'^{(k)}(\mathbf{Q}_l^{x,m})$ that are continuous. This continuity should not depend on $v'^{(k)}(\mathbf{Q}_l^{x,m})$, the magnitude of these vectors, since results are required as planar configurations,

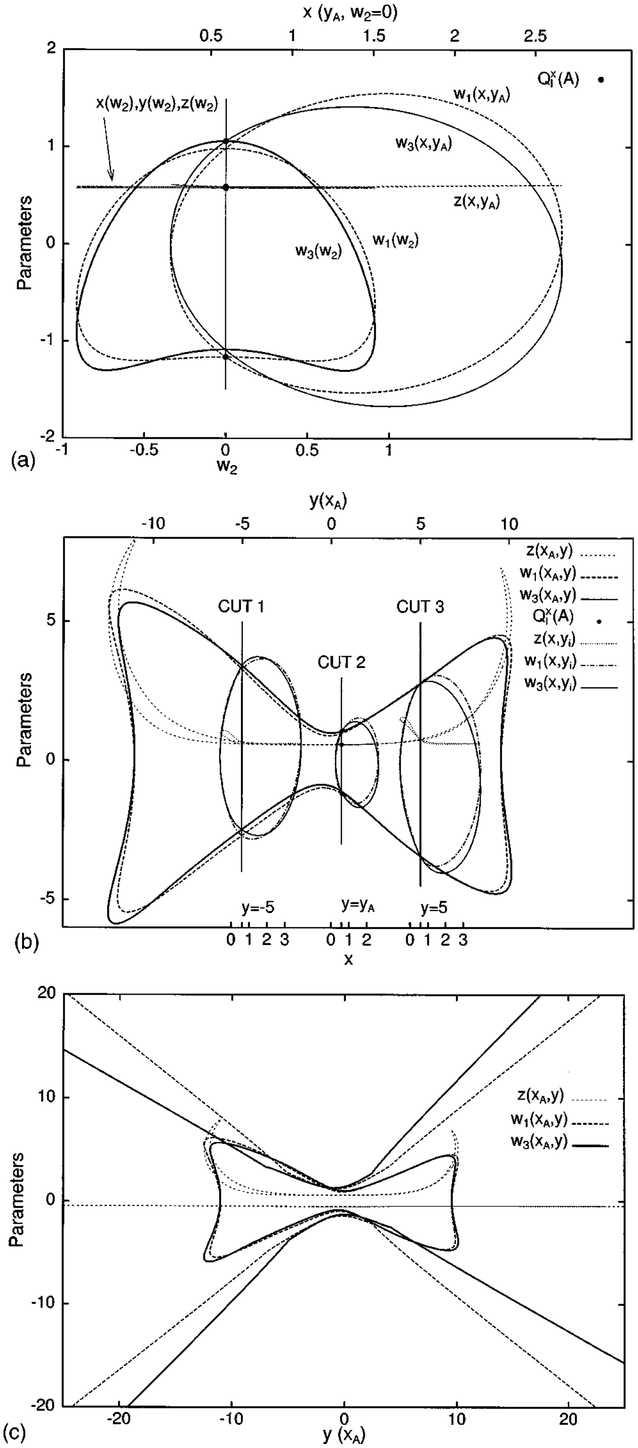

FIG. 1. (a) S_l closed conical intersection seam. $\mathbf{Q}_l^{x,5}(w_2)$, symmetric in w_2, together with $\mathbf{Q}_l^{x,3}(x,y_A)$, a one-dimensional section of $\eta=3$ seam as a parametric function of x with y fixed at $y_A=0.5806$. The intersection of these portions of the seam at $\mathbf{Q}_l^x(A)$ is shown. (b) For S_l, $\mathbf{Q}_l^{x,3}(x_A,y)$, a one-dimensional section of the seam as a parametric function of y with x fixed at $x_A=0.5933$. Also for $\mathbf{Q}_l^{x,3}(x,y_i)$, as a parametric function of x with y fixed at $y_i=-5$, 0.5806, and 5. (c) The section of S_h, $\mathbf{Q}_h^{x,3}(x_A,y)$ is shown and compared with the section of S_l, $\mathbf{Q}_l^{x,3}(x_A,y)$.

where $v'^{(k)}(\mathbf{Q}_l^{x,5})=0$, for $k=4,5$, are approached. Figure 3(a) reports $v'^{(k)}(\mathbf{Q}_l^{x,m})$, for $k=1-m$ while Fig. 3(b) reports the log $v'^{(k)}(\mathbf{Q}_l^{x,5})$, for $k=1-5$ to more clearly display the much smaller $v'^{(k)}(\mathbf{Q}_l^{x,5})$, $k=4,5$. These results are quite en-

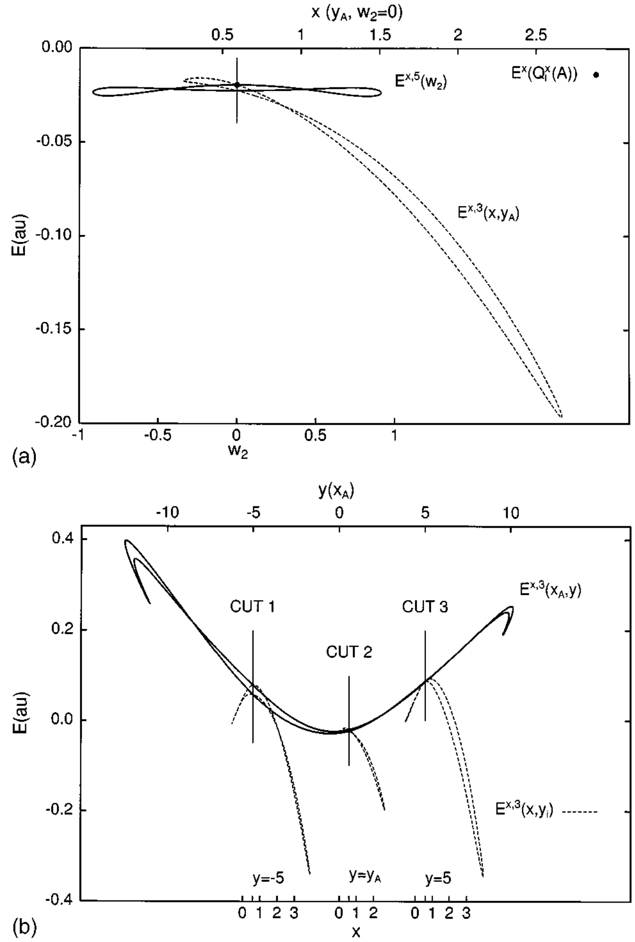

FIG. 2. (a) $E^{x,m}(\mathbf{Q}_l^{x,m})$ are shown along $\mathbf{Q}_l^{x,5}(w_2)$ [symmetric] and $\mathbf{Q}_l^{x,3}(x,y_A)$. (b) $E^{x,3}(\mathbf{Q}_l^{x,3})$ are shown along $\mathbf{Q}_l^{x,3}(x_A,y)$ and $\mathbf{Q}_l^{x,3}(x,y_i)$ for $y_i=-5$, 0.5806, 5.

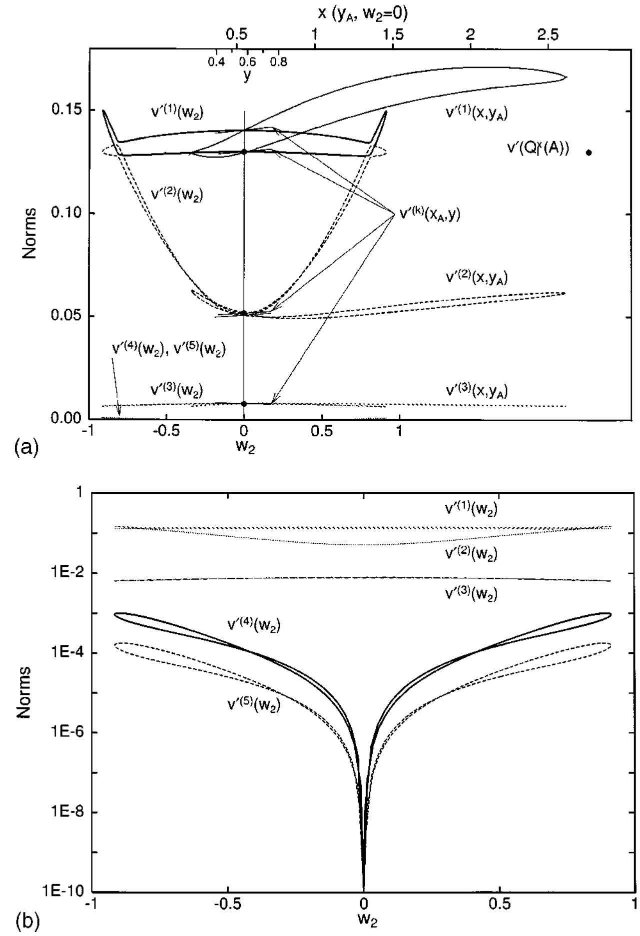

FIG. 3. (a) Norms of the degeneracy lifting vectors, $\mathbf{v}'^{(k)}(\mathbf{Q}_l^{x,m})$, $k=1-m$, along $\mathbf{Q}_l^{x,5}(w_2)$ and $\mathbf{Q}_l^{x,3}(x,y_A)$. The crossing point A is shown. Near A the norms of the three degeneracy lifting vectors along $\mathbf{Q}_l^{x,3}(x_A,y)$ are shown; (b) log $\mathbf{v}'^{(k)}(\mathbf{Q}_l^{x,5})$, $k=1-5$, is plotted.

couraging. All five norms are found to be continuous regardless of the size of $v'^{(k)}(\mathbf{Q}_l^{x,m})$. In addition as $\mathbf{Q}_l^{x,m} \to \mathbf{Q}_l^x(A)$, $v'^{(k)}(\mathbf{Q}_l^{x,5}) \to v'^{(k)}(\mathbf{Q}_l^{x,3})$, $k=1-3$. Similarly, continuity is obtained for the vectors themselves but the data are not presented here since they do not lend themselves to a compact representation.

Thus the orthogonalization procedure produces the requisite continuous representation of the branching space in a computationally efficient manner. Such a representation is essential if the pointwise results obtained from a numerical procedure are to be interpolated and extrapolated.

IV. SUMMARY AND CONCLUSIONS

Previously, procedures for obtaining an orthogonal representation of the branching space for two state conical intersections have been developed for the $\eta=2$ case (nonrelativistic Hamiltonian) and $\eta=3$ case (Hamiltonian that explicitly includes the spin–orbit interaction and has C_s spatial symmetry). Here a distinctly different approach is used to extend those results to the $\eta=5$ case (Hamiltonian that explicitly includes the spin–orbit interaction but has no spatial symmetry). A realization of the homomorphism connecting Sp(4), the subspace of SU(4), consistent with time reversal symmetry, to SO(5), $\mathbf{U}\to\mathbf{R}(\mathbf{U})$ with $\mathbf{U}\in \mathrm{Sp}(4)$, and $\mathbf{R}(\mathbf{U}) \in \mathrm{SO}(5)$, is developed. It is used to efficiently determine a transformation of the degenerate electronic states—which preserves the standard form of the electronic Hamiltonian near the conical intersection—and produces [via $\mathbf{R}(\mathbf{U})$] an orthogonal representation of the branching space. A quantity invariant under this transformation is also identified. The computational utility of this approach was demonstrated using a model Hamiltonian representing a tetra-atomic molecule with three coupled doublet electronic states. The seam of conical intersection is shown to have two distinct branches—one branch, which is bounded, includes both $\eta=3$ and $\eta=5$ portions while the second branch, which is unbounded, has only an $\eta=3$ component.

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APPENDIX: THE METHOD OBTAINING EQ. (27)

Here we describe how $\mathbf{R}^{(2n)}$ is obtained by a matrix multiplication of $\mathbf{R}^{(2n-2)}$ and $\mathbf{R}^{(P)}\mathbf{R}^{(2)}$. The initial elements in the recursion $\mathbf{R}^{(2)}(\phi_5,\theta_5)$ and $\mathbf{R}^{(P)}\mathbf{R}^{(2)}(\alpha,\beta)$ are obtained explicitly by matrix multiplication from data in Table I, and Eqs. (12) and (15a),

$$\mathbf{R}^{(2)}(\phi_5,\theta_5)=\left(\begin{array}{ccc|cc}\cos\theta_5\cos\phi_5 & \cos\theta_5\sin\phi_5 & -\boldsymbol{\sin\theta_5} & 0 & 0\\ -\sin\phi_5 & \cos\phi_5 & 0 & 0 & 0\\ \sin\theta_5\cos\phi_5 & \sin\theta_5\sin\phi_5 & \cos\theta_5 & 0 & 0\\ \hline 0 & 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 0 & 1\end{array}\right), \tag{A1}$$

$$\mathbf{R}^{(P)}\mathbf{R}^{(2)}(\alpha,\beta)=\left(\begin{array}{ccc|cc}0 & 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 0 & 1\\ \boldsymbol{\sin\beta\cos\alpha} & \boldsymbol{\sin\beta\sin\alpha} & \boldsymbol{\cos\beta} & 0 & 0\\ \hline -\cos\beta\cos\alpha & -\cos\beta\sin\alpha & \sin\beta & 0 & 0\\ \sin\alpha & -\cos\alpha & 0 & 0 & 0\end{array}\right). \tag{A2}$$

For the remaining matrices only the necessary elements are determined. The third row of $\mathbf{R}^{(2)}(\phi_5,\theta_5)$ [Eq. (A1)] gives immediately Eq. (27e): $(R_{31}^{(2)},R_{32}^{(2)},R_{33}^{(2)})=(\sin\theta_5\cos\phi_5, \sin\theta_5\sin\phi_5,\cos\theta_5)$.

$\mathbf{R}^{(4)}=\mathbf{R}^{(2)}\mathbf{P}^{(P)}\mathbf{R}^{(2)}(\phi_4,\theta_4)$ has the form

$$\mathbf{R}^{(4)}=\begin{pmatrix} R_{11}^{(4)} & R_{12}^{(4)} & R_{13}^{(4)} & \cdot & \cdot\\ 0 & 0 & 0 & -\sin\phi_5 & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \boldsymbol{\sin\theta_4} & 0 & 0\\ \sin\phi_4 & \cdot & 0 & 0 & 0\end{pmatrix}. \tag{A3}$$

Equation (27d) $(R_{11}^{(4)},R_{12}^{(4)},R_{13}^{(4)})=R_{13}^{(2)}(\sin\theta_4\cos\phi_4, \sin\theta_4\sin\phi_4,\cos\theta_4)$, where $R_{13}^{(2)}=-\sin\theta_5$, follows from the portion of the matrix product given by the boldfaced matrix elements in Eqs. (A1) and (A2). The remaining elements indicated in Eq. (A3) are similarly obtained.

$\mathbf{R}^{(6)}=\mathbf{R}^{(4)}\mathbf{R}^{(P)}\mathbf{R}^{(2)}(\phi_3,\theta_3)$ has the form

$$\mathbf{R}^{(6)}=\begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & -\boldsymbol{\sin\phi_5\sin\theta_3} & 0 & 0\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ R_{41}^{(6)} & R_{42}^{(6)} & R_{43}^{(6)} & \cdot & \cdot\\ 0 & 0 & 0 & \sin\phi_4 & \cdot\end{pmatrix}. \tag{A4}$$

Equation (27c) $(R_{41}^{(6)},R_{42}^{(6)},R_{43}^{(6)})=R_{43}^{(4)}(\sin\theta_3\cos\phi_3, \sin\theta_3\sin\phi_3,\cos\theta_3)$, where $R_{43}^{(4)}=\sin\theta_4$, follows from the portion of the matrix product given by the boldfaced matrix elements in Eqs. (A3) and (A2). The remaining elements indicated in Eq. (A4) are similarly obtained.

$\mathbf{R}^{(8)}=\mathbf{R}^{(6)}\mathbf{R}^{(P)}\mathbf{R}^{(2)}(\phi_2,\theta_2)$ has the form

$$\mathbf{R}^{(8)}=\begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot\\ R_{21}^{(8)} & R_{22}^{(8)} & R_{23}^{(8)} & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \boldsymbol{\sin\phi_4\sin\theta_2} & 0 & 0\end{pmatrix}. \tag{A5}$$

Equation (27b) $(R_{21}^{(8)},R_{22}^{(8)},R_{23}^{(8)})=R_{23}^{(6)}(\sin\theta_2\cos\phi_2, \sin\theta_2\sin\phi_2,\cos\phi_2)$, where $R_{23}^{(6)}=-\sin\phi_5\sin\theta_3$, follows from the portion of the matrix product given by the boldfaced matrix elements in Eqs. (A4) and (A2). The remaining elements indicated in Eq. (A5) are similarly obtained.

Finally, $\mathbf{R}^{(10)}=\mathbf{R}^{(8)}\mathbf{R}^{(P)}\mathbf{R}^{(2)}(\phi_1,\theta_1)$ has the form

$$\mathbf{R}^{(10)}=\begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ R_{51}^{(10)} & R_{52}^{(10)} & R_{53}^{(10)} & \cdot & \cdot\end{pmatrix}. \tag{A6}$$

Equation (27a) $(R_{51}^{(10)},R_{52}^{(10)},R_{53}^{(10)})=R_{53}^{(8)}(\sin\theta_1\cos\phi_1, \sin\theta_1\sin\theta_1,\cos\theta_1)$, where $R_{53}^{(8)}=\sin\phi_4\sin\theta_2$, follows from the portion of the matrix product given by the boldfaced matrix elements in Eqs. (A5) and (A2).

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