On the effects of spin-orbit coupling on conical intersection seams in molecules with an odd number of electrons. I. Locating the seam

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(Received 15 March 2001; accepted 20 April 2001)

In molecules with an odd number of electrons when the spin-orbit interaction is added to the nonrelativistic Coulomb Hamiltonian the dimension of the seam of conical intersection is reduced from $N^{\mathrm{int}}-2$ to $N^{\mathrm{int}}-3$ or $N^{\mathrm{int}}-5$. A generally applicable algorithm for locating points of conical intersection in such molecules is derived. The algorithm is based on a perturbative description of the vicinity of a point of conical intersection analogous to that used previously in the nonrelativistic case. It is tested using model Hamiltonians with quite promising results. An implementation of the algorithm based on *ab initio* wave functions is presented which treats the spin-orbit interaction within the Breit–Pauli approximation and incorporates it into the electronic Hamiltonian using the adiabatic states of the nonrelativistic Hamiltonian as a basis. An initial test of this implementation also yielded quite promising results.
[DOI: 10.1063/1.1378324]

I. INTRODUCTION

Conical intersections are known to play a key role in nonrelativistic, spin-conserving electronically nonadiabatic processes. In this case the Hamiltonian is real valued and the dimension of the seam of conical intersection is $N^{\mathrm{int}}-2$, where N^{int} is the number of internal coordinates. Including the spin-orbit interaction, a relativistic effect, can change the situation qualitatively. For molecules with an odd number of electrons, odd electron molecules, the spin-orbit interaction renders the Hamiltonian complex valued. The dimension of a seam of conical intersection for an otherwise nondegenerate complex Hermitian matrix is only $N^{\mathrm{int}}-3$.[1] However for odd electron systems, as a consequence of time reversal symmetry,[2] all eigenvalues are doubly degenerate, exhibiting Kramers' degeneracy.[3] When this degeneracy is taken into account[4] the dimension of the seam of conical intersection is reduced still further to $N^{C_s}-5$ in general or when C_s symmetry can be imposed to $N^{C_s}-3$, where N^{C_s} is the number of C_s preserving degrees of freedom.

The effects of this change in dimensionality can be profound. Spin-orbit coupling may, for example, decrease the probability of a nonadiabatic transition by reducing the size of the region of close approach of the potential energy surfaces in question. To study the ramifications of this change in the dimensionality of the seam of conical intersection the locus of the seam should be known. However, the lower dimensionality, $N^{\mathrm{int}}-5$ or $N^{C_s}-3$ when compared to the nonrelativistic case, $N^{\mathrm{int}}-2$, makes determining this locus quite challenging. In this work we address this problem reporting an algorithm for locating conical intersections in the presence of the spin-orbit interaction. To our knowledge there are no previous reports of algorithms for locating this class of conical intersection.

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The algorithm is applicable to any of the multistate, parametrized, analytic model Hamiltonians frequently used to include spin-orbit effects into surface crossing problems. Particularly relevant in this regard is the recent study[5] of the geometric phase effect in spin-orbit coupled systems which employed a three state pseudo Jahn–Teller model.[6] The algorithm, however, is expected to find its principal application in the context of *ab initio* Hamiltonians in which the spin-orbit interaction is treated using large component only wave functions[7] constructed at the multireference configuration interaction level. To this end we report and test an implementation of this algorithm in which the spin-orbit interaction is treated at the Breit–Pauli level[7–10] and included in the Hamiltonian using quasidegenerate perturbation theory.[11,12] This approach is commonly used in nuclear dynamics and is adequate for molecules containing only atoms with atomic numbers no larger than that of Kr. The implementation takes full advantage of analytic gradient techniques, a key point in the formulation. In this context spin-orbit coupling affects the electronic structure problem in either of two ways. It couples states of different spin multiplicity whose intersections otherwise would not be conical and as noted above it alters the dimension of a seam of conical intersection of the nonrelativistic Hamiltonian. This work is primarily concerned with the later, arguably the more significant, issue. It should be emphasized that this change in the dimension of the seam is not observed in molecules with an even number of electrons since in that case the wave functions can be chosen so that the Hamiltonian is real valued.

Section II presents the mathematical basis for the algorithm, which exploits a degenerate perturbation theory previously used to describe conical intersections in nonrelativistic systems[13,14] and Mead's seminal discussion of the noncrossing rule in molecules with an odd number of electrons.[15] In the Appendix an implementation for extended multireference configuration interaction wave functions that exploits analytic gradient techniques is described. Section III demonstrates the rapid convergence of our approach using both model and *ab initio* Hamiltonians and uses several model Hamiltonians to examine the range of solutions and potential pitfalls of the algorithm. Section IV summarizes and discusses directions for future work.

II. THEORY

The total electronic Hamiltonian $H^e(\mathbf{r};\mathbf{R})$ is given by $H^e(\mathbf{r};\mathbf{R})=H^0(\mathbf{r};\mathbf{R})+H^{\mathrm{so}}(\mathbf{r};\mathbf{R})$, where $H^0(\mathbf{r};\mathbf{R})$ is the nonrelativistic Coulomb Hamiltonian and $H^{\mathrm{so}}(\mathbf{r};\mathbf{R})$ is the spin-orbit Hamiltonian.[7] The nonrelativistic eigenstates, Ψ_I^0 eigenfunctions of $H^0(\mathbf{r};\mathbf{R})$ are conventionally expanded in a basis of antisymmetrized N^{el}-electron functions, the configuration state functions (CSFs),[16] which are eigenfunctions of S^2 and M_s and carry an irreducible representation A of the spatial point group. However for the relativistic eigenstates $\Psi_i^e(\mathbf{r};\mathbf{R})$ (approximate) eigenfunctions of $H^e(\mathbf{r};\mathbf{R})$ with energies $E_i^e(\mathbf{R})$, it is desirable to use a basis that also takes into account the effects of time-reversal symmetry,[2] a time-reversal adapted basis.[17]

Section II A reviews the role of time reversal symmetry in the determination of the conditions for a conical intersection of states i and j at $\mathbf{R}^{e,x}$ and Sec. II B summarizes those conditions. In Sec. II C perturbation theory is used to determine $H_{kl}^e(\mathbf{R}^{e,x})+\nabla\mathbf{H}_{kl}^e(\mathbf{R}^{e,x})\cdot\delta\mathbf{R}$, $k,l\in i,j$, $H_{kl}^e(\mathbf{R}^{e,x}+\delta\mathbf{R})$ up to linear terms in $\delta\mathbf{R}$. This expansion gives the conditions defining a conical intersection near $\mathbf{R}^{e,x}$ in terms of $\nabla\mathbf{H}_{kl}^e(\mathbf{R}^{e,x})$ which is readily determined using analytic gradient techniques. In Sec. II D this analysis is used to construct an algorithm for locating $\mathbf{R}^{e,x}$ which essentially steps "backward" from $\mathbf{R}^{e,x}+\delta\mathbf{R}$ to $\mathbf{R}^{e,x}$, subject to additional constraints as may be required to yield a unique solution in tetra-atomic and larger molecules.

A. Time reversal adapted bases and Kramers' degeneracy

T, the time reversal operator, is given by[2,18]

$$T=\prod_{j=1}^{N^{\mathrm{el}}}(-i\sigma_y K)(j), \quad \text{and} \quad \sigma_y=\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}, \tag{1}$$

σ_y is a Pauli spin matrix and K denotes complex conjugation. From Eq. (1) T is seen to be antiunitary, $\langle T\phi|T\psi\rangle=\langle\psi|\phi\rangle$, and for molecules with an odd number of electrons, odd electron molecules, $T^2=-1$. As a consequence, in odd electron molecules ψ and $T\psi$ are orthogonal and since H^e has time reversal symmetry, that is T commutes with H^e, if Ψ is an eigenstate of H^e, $T\Psi$ is linearly independent and degenerate. This Kramers' degeneracy[3] makes all eigenvalues of an odd electron Hamiltonian (at least) doubly degenerate. Thus when describing such a molecule it is convenient to work in a time reversal adapted basis, a basis where $\psi(\mathbf{r};\mathbf{R})$ and $T\psi(\mathbf{r};\mathbf{R})$ are always included in pairs. The construction of such a basis, denoted χ_α, $T\chi_\alpha$, from a standard CSF[16] basis is described in the Appendix. When it is not necessary to distinguish between χ_α and $T\chi_\alpha$ (Ψ_1^0 and $T\Psi_1^0$) the CSFs (nonrelativistic eigenstates) will be denoted $\boldsymbol{\psi}$, ($\boldsymbol{\Psi}^0$).

B. Conditions for a conical intersection

For odd electron molecules the conditions for a conical intersection have been given by Mead.[17] Here we summarize the requisite portion of that seminal work. For an odd electron molecule, Kramers' degeneracy renders a point of conical intersection of states i and j, $\mathbf{R}^{e,x}$, a point of fourfold degeneracy. However it also constrains the $N\times N$ matrix representation of H^e so that it does not have the usual number, N^2 (see Refs. 1 and 19) of free parameters. In particular, for functions ψ_i, $T\psi_i$, ψ_j, $T\psi_j$, since T is antiunitary

$$\begin{aligned}&H_{ii}^e(\mathbf{R})=H_{T_iT_i}^e(\mathbf{R}) \qquad H_{iT_i}^e(\mathbf{R})=0\\ &H_{iT_j}^e(\mathbf{R})=-H_{T_ij}^e(\mathbf{R})^*.\end{aligned} \tag{2}$$

Thus the most general 4×4 Hamiltonian matrix, constructed in the ψ_1, ψ_2, $T\psi_1$, $T\psi_2$ basis, has the form

$$\begin{pmatrix}H_{11} & H_{12} & 0 & H_{1T_2}\\ & H_{22} & -H_{1T_2} & 0\\ & & H_{11} & H_{12}^*\\ & & & H_{22}\end{pmatrix}. \tag{3}$$

A conical intersection constitutes a fourfold degeneracy of this Hamiltonian which requires that five conditions be fulfilled:

$$H_{11}-H_{22}=0 \quad (\text{only a real part}), \tag{4a}$$

$$H_{12}=H_{12}^r+iH_{12}^i=0, \tag{4b}$$

$$H_{1T_2}=H_{1T_2}^r+iH_{1T_2}^i=0, \tag{4c}$$

where $a=a^r+ia^i$. For molecules with C_s symmetry Eq. (4c) is satisfied by symmetry provided the ψ_i and $T\psi_j$ are chosen to carry distinct irreducible representations of the C_s double group.[15,20] This choice is not available in the absence of C_s symmetry. Using degenerate perturbation theory[13,14] and the conditions in Eqs. (4a)–(4c) the working equations for locating a point of conical intersection will be derived.

C. H^e near a conical intersection and the $g-h$ space: gradient formulation

We consider two approaches currently used to incorporate spin-orbit effects into the nonrelativistic Coulomb Hamiltonian, within a large component only[7] description. In the relativistic configuration interaction (CI) approach,[21] the Ψ_i^e are the eigenstates of $\mathbf{H}^{e,\mathrm{CSF}}$, H^e in the CSF basis, where

$$H_{\alpha\beta}^{e,\mathrm{CSF}}(\mathbf{R})=\langle\psi_\alpha(\mathbf{r};\mathbf{R})|H^e(\mathbf{r};\mathbf{R})|\psi_\beta(\mathbf{r};\mathbf{R})\rangle_{\mathbf{r}}. \tag{5a}$$

In the quasidegenerate perturbation theory approach,[12] the Ψ_I^0 eigenstates of H^0, are used to define a subspace of the full CSF space, the q space, and its orthogonal complement the p space. The relativistic eigenstates are the eigenfunctions of $\mathbf{H}^{e,\mathrm{CI},q}$, H^e in the q space, where

$$\begin{aligned}&H_{IJ}^{e,\mathrm{CI},q}(\mathbf{R})=\langle\Psi_I^0(\mathbf{r};\mathbf{R})|H^e(\mathbf{r};\mathbf{R})|\Psi_J^0(\mathbf{r};\mathbf{R})\rangle_{\mathbf{r}}\\ &\qquad\qquad \Psi_I^0,\Psi_J^0\in q.\end{aligned} \tag{5b}$$

The representation of the spin-orbit operator varies with the implementation. The differences are inconsequential here.

1. Relativistic CI

The eigenstates of H^e are expanded in terms of (time reversal adapted) $\boldsymbol{\psi}$ so that

$$\Psi_i^e(\mathbf{r};\mathbf{R})=\sum_{\alpha=1}^{N^{\mathrm{CSF}}} d_\alpha^{\mathrm{CSF},i}\psi_\alpha(\mathbf{r};\mathbf{R}), \tag{6a}$$

$$(\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R})-E_i^e(\mathbf{R}))\mathbf{d}^{\mathrm{CSF},i}(\mathbf{R})=\mathbf{0}. \tag{6b}$$

Define the crude adiabatic basis as $\Psi_k^e(\mathbf{r};\mathbf{R}^{e,x})$, $k=1-N^{\mathrm{CSF}}$, where $\mathbf{R}^{e,x}$ is a point of conical intersection of states i and j. The $\mathbf{d}^{\mathrm{CSF},i}$ (and other vectors encountered in this work) when collected columnwise in a matrix, will be denoted $\mathbf{d}^{\mathrm{CSF}}$. Partition this space into a four dimensional Q space $k=i,j,T_i$, T_j and its orthogonal complement, the P space. In the crude adiabatic basis Eq. (6b) becomes

$$\begin{pmatrix} \mathbf{H}^{e,ca,QQ}(\mathbf{R})-E_i^e(\mathbf{R}) & \mathbf{H}^{e,ca,QP}(\mathbf{R}) \\ \mathbf{H}^{e,ca,PQ}(\mathbf{R}) & \mathbf{H}^{e,ca,PP}(\mathbf{R})-E_i^e(\mathbf{R}) \end{pmatrix}\begin{pmatrix}\mathbf{d}^{ca,i}(\mathbf{R})\\ \mathbf{D}^{ca,i}(\mathbf{R})\end{pmatrix}=\begin{pmatrix}\mathbf{0}\\ \mathbf{0}\end{pmatrix}, \tag{7a}$$

$$(\mathbf{H}^{e,ca,QQ}(\mathbf{R})+\mathbf{H}^{e,ca,QP}(\mathbf{R})(E_i^e(\mathbf{R})-\mathbf{H}^{e,ca,PP}(\mathbf{R}))^{-1}\mathbf{H}^{e,ca,PQ}(\mathbf{R})-E_i^e(\mathbf{R}))\mathbf{d}^{ca,i}(\mathbf{R})=0, \tag{7b}$$

where

$$H_{kl}^{e,ca,RS}(\mathbf{R})=\mathbf{d}^{\mathrm{CSF},k}(\mathbf{R}^{e,x})^\dagger\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R})\mathbf{d}^{\mathrm{CSF},l}(\mathbf{R}^{e,x}),\quad k\in R,\quad l\in S. \tag{7c}$$

Next expand $\mathbf{d}^{ca,i}(\mathbf{R})$, $\mathbf{D}^{ca,i}(\mathbf{R})$, $E_i^e(\mathbf{R})$ and $\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R})$ around $\mathbf{R}^{e,x}$ as follows:

$$\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R})=\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R}^{e,x})+\nabla\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R}^{e,x})\cdot\delta\mathbf{R}, \tag{8}$$

$$\mathbf{d}^{ca,i}(\mathbf{R})=\mathbf{d}^{ca,i(0)}(\mathbf{R}^{e,x})+\nabla\mathbf{d}^{ca,i}(\mathbf{R}^{e,x})\cdot\delta\mathbf{R}, \tag{9a}$$

$$\mathbf{D}^{ca,i}(\mathbf{R})=\mathbf{0}+\nabla\mathbf{D}^{ca,i}(\mathbf{R}^{e,x})\cdot\delta\mathbf{R}, \tag{9b}$$

$$E_i^e(\mathbf{R})=E_i^{e(0)}(\mathbf{R}^{e,x})+E_i^{e(1)}(\mathbf{R}). \tag{9c}$$

The gradient in Eq. (8) takes full account of the changes in both the Hamiltonian operator *and* the CSF basis functions. See Appendix B and Ref. 22. From Eqs. (7c) and (8)

$$\mathbf{H}_{kl}^{e,ca,QQ}(\mathbf{R})=E_i^e(\mathbf{R}^{e,x})\mathbf{I}+\mathbf{d}^{\mathrm{CSF},k}(\mathbf{R}^{e,x})^\dagger\nabla\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R}^{e,x})\mathbf{d}^{\mathrm{CSF},l}(\mathbf{R}^{e,x})\cdot\delta\mathbf{R}, \tag{10a}$$

$$\mathbf{H}_{km}^{e,ca,QP}(\mathbf{R})=\mathbf{0}+\mathbf{d}^{\mathrm{CSF},k}(\mathbf{R}^{e,x})^\dagger\nabla\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R}^{e,x})\mathbf{d}^{\mathrm{CSF},m}(\mathbf{R}^{e,x})\cdot\delta\mathbf{R},\quad \text{for}\quad k,l\in Q,\ m\in P. \tag{10b}$$

Since $\mathbf{H}_{km}^{e,ca,QP}(\mathbf{R})$ begins at first order, the second term in Eq. (7b) begins at second order. Thus to first order in displacements from $\mathbf{R}^{e,x}$ Eq. (7b) becomes:

$$(\mathbf{d}^{\mathrm{CSF}}(\mathbf{R}^{e,x})^\dagger\nabla\mathbf{H}^{\mathrm{CSF}}(\mathbf{R}^{e,x})\mathbf{d}^{\mathrm{CSF}}(\mathbf{R}^{e,x})\cdot\delta\mathbf{R}-E_i^{e(1)}(\mathbf{R}))\mathbf{d}^{ca,i,(0)}=\mathbf{0}. \tag{11}$$

Since the CSF basis is time-reversal adapted (see Appendix A) the crude adiabatic representation also is and the Hamiltonian in Eq. (11) has the form of that in Eq. (3). Thus for the relativistic CI formulation $\mathbf{H}^e(\mathbf{R}^{e,x}+\delta\mathbf{R})$ is to first (linear) order in $\delta\mathbf{R}$:

$$\mathbf{H}^e=(E_i^e(\mathbf{R}^{e,x})+\mathbf{s}^{ij}\cdot\delta\mathbf{R})\mathbf{I}+\begin{pmatrix} -\mathbf{g}^{ji}\cdot\delta\mathbf{R} & \mathbf{h}^{ji}\cdot\delta\mathbf{R} & 0 & \mathbf{h}^{jTi}\cdot\delta\mathbf{R} \\ \mathbf{h}^{ji*}\cdot\delta\mathbf{R} & \mathbf{g}^{ji}\cdot\delta\mathbf{R} & -\mathbf{h}^{jTi}\cdot\delta\mathbf{R} & 0 \\ & & -\mathbf{g}^{ji}\cdot\delta\mathbf{R} & \mathbf{h}^{ji*}\cdot\delta\mathbf{R} \\ & & \mathbf{h}^{ji}\cdot\delta\mathbf{R} & \mathbf{g}^{ji}\cdot\delta\mathbf{R} \end{pmatrix}, \tag{12a}$$

where $2\mathbf{s}^{ij}(\mathbf{R})=\mathbf{g}^i(\mathbf{R})+\mathbf{g}^i(\mathbf{R})$,

$$\mathbf{g}^i(\mathbf{R})=\mathbf{d}^{\mathrm{CSF},i}(\mathbf{R}^{e,x})^\dagger\nabla\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R})\mathbf{d}^{\mathrm{CSF},i}(\mathbf{R}^{e,x}), \tag{13a}$$

$$2\mathbf{g}^{ij}(\mathbf{R})=\mathbf{g}^i(\mathbf{R})-\mathbf{g}^j(\mathbf{R})\equiv v^{(1)}(\mathbf{R}), \tag{13b}$$

$$\begin{aligned}\mathbf{h}^{ij}(\mathbf{R})&\equiv\mathbf{h}^{r,ij}(\mathbf{R})+i\mathbf{h}^{i,ij}(\mathbf{R})\\&=\mathbf{d}^{\mathrm{CSF},i}(\mathbf{R}^{e,x})^\dagger\nabla\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R})d^{\mathrm{CSF},j}(\mathbf{R}^{e,x})\\&\equiv v^{(2)}(\mathbf{R})+iv^{(3)}(\mathbf{R}),\end{aligned} \tag{13c}$$

$$\begin{aligned}\mathbf{h}^{iTj}(\mathbf{R})&\equiv\mathbf{h}^{r,iTj}(\mathbf{R})+i\mathbf{h}^{i,iTj}(\mathbf{R})\\&=\mathbf{d}^{\mathrm{CSF},i}(\mathbf{R}^{e,x})^\dagger\nabla\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R})\mathbf{d}^{\mathrm{CSF},Tj}(\mathbf{R}^{e,x})\\&\equiv v^{(4)}(\mathbf{R})+iv^{(5)}(\mathbf{R}),\end{aligned} \tag{13d}$$

Here we have observed that at $\mathbf{R}^{e,x}$ only,

$$\mathbf{d}^{\mathrm{CSF},i}(\mathbf{R}^{e,x})^\dagger\nabla\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R}^{e,x})\mathbf{d}^{\mathrm{CSF},j}(\mathbf{R}^{e,x})=\mathbf{d}^{ca,i}(\mathbf{R}^{e,x})^\dagger\nabla\mathbf{H}^{e,ca,QQ}(\mathbf{R}^{e,x})\mathbf{d}^{ca,j}(\mathbf{R}^{e,x}).$$

From Eq. (12a) the five vectors $\mathbf{g}^{ij}(\mathbf{R})$, $\mathbf{h}^{r,ij}(\mathbf{R})$, $\mathbf{h}^{i,ij}(\mathbf{R})$, $\mathbf{h}^{r,iTj}(\mathbf{R})$, $\mathbf{h}^{i,iTj}(\mathbf{R})$ (or $v^{(i)}i=1-5$) define the **g-h** or branching space, the space in which the degeneracy at $\mathbf{R}^{e,x}$ is lifted linearly in displacements. As in the theory of conical intersections for real-valued Hamiltonians the **g-h** or branching space plays a privileged role.[23]

When C_s symmetry can be imposed Ψ_j^e and $T\Psi_j^e$ carry distinct irreducible representations, of the C_s double group, so that $\mathbf{h}^{r,iTj}(\mathbf{R})=\mathbf{h}^{i,iTj}(\mathbf{R})=0$ by symmetry, the branching space has dimension 3, and $\mathbf{H}^e$ consists of two uncoupled 2×2 matrices with the form

$$\mathbf{H}^e=(E_i^e(\mathbf{R}^{e,x})+\mathbf{s}^{ij}\cdot\delta\mathbf{R})\mathbf{I}+\begin{pmatrix}-\mathbf{g}^{ji}\cdot\delta\mathbf{R} & \mathbf{h}^{ji}\cdot\delta\mathbf{R}\\ \mathbf{h}^{ji*}\cdot\delta\mathbf{R} & \mathbf{g}^{ji}\cdot\delta\mathbf{R}\end{pmatrix}. \tag{12b}$$

In the nonrelativistic case $\mathbf{h}^{i,ij}(\mathbf{R})=\mathbf{h}^{r,iTj}(\mathbf{R})=\mathbf{h}^{i,iTj}(\mathbf{R})=0$, $d^j\to\mathbf{c}^J$ (Appendix A) so that the branching space has dimension 2 and

$$\mathbf{H}^0=(E_I^0(\mathbf{R}^x)+\mathbf{s}^{IJ}\cdot\delta\mathbf{R})\mathbf{I}+\begin{pmatrix}-\mathbf{g}^{JI}\cdot\delta\mathbf{R} & \mathbf{h}^{JI}\cdot\delta\mathbf{R}\\ \mathbf{h}^{JI}\cdot\delta\mathbf{R} & \mathbf{g}^{JI}\cdot\delta\mathbf{R}\end{pmatrix}. \tag{12c}$$

2. A nonrelativistic eigenstate state partitioning approach

The size of the relativistic CI expansion can be quite large since S^2 is no longer a good quantum number. The size of the problem to be treated can be reduced by observing that for molecules comprised of atoms with atomic number less than that of say Kr, the eigenstates of H^0 can often be grouped such that the separation from the lowest group is large compared to the spin-orbit interaction coupling the groups. To take advantage of this separation the electronic space is partitioned into a q space comprised of the lowest N^a eigenstates of H^0, and its orthogonal complement the p space. As the q space consists only of the states relevant for nuclear dynamics, it is significantly truncated. When treating radiative processes this approach must be modified to include the effects of higher energy electronic states.[12]

The electronic eigenstates, $\Psi_i^e(\mathbf{r};\mathbf{R})$ and $T\Psi_i^e(\mathbf{r};\mathbf{R})$, are expanded in a basis of the eigenstates of H^0, Ψ_I^0

$$\Psi_I^0(\mathbf{r};\mathbf{R}) = \sum_{\alpha=1}^{N^{\mathrm{CSF}}} c_\alpha^I(\mathbf{R})\psi_\alpha(\mathbf{r};\mathbf{R}), \tag{14}$$

see Eq. (A5) so that

$$\Psi_i^{e,\mathrm{CI}}(\mathbf{r};\mathbf{R}) = \sum_{I=1}^{N^a} d_I^{\mathrm{CI},q,i}\Psi_I^0(\mathbf{r};\mathbf{R}), \tag{15a}$$

$$(\mathbf{H}^{e,\mathrm{CI},q}(\mathbf{R}) - E_i(\mathbf{R}))\mathbf{d}^{\mathrm{CI},q,i}(\mathbf{R}) = \mathbf{0}, \tag{15b}$$

where using Eqs. (5a) and (5b)

$$H_{IJ}^{e,\mathrm{CI},q}(\mathbf{R}) = \mathbf{c}^{I^\dagger}(\mathbf{R})\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R})\mathbf{c}^J(\mathbf{R}) \quad I,J\in q. \tag{15c}$$

Solutions in the q space, $\mathbf{d}^{\mathrm{CI},q,i}$, are to a good approximation solutions to the relativistic CI problem provided the spin-orbit induced coupling between the q and p spaces can be neglected.

To determine the form of $\mathbf{H}^e$ near a conical intersection we again define the Q space of a crude adiabatic basis as $\Psi_k^{e,\mathrm{CI}}(\mathbf{r};\mathbf{R}^{e,x})$ $k=i,j,Ti,\ Tj$ and its orthogonal complement, P space. In this case $Q+P=q$, rather than the entire electronic space. In terms of the original CSF basis the $\Psi_k^{e,\mathrm{CI}}(\mathbf{r};\mathbf{R}^{e,x})$ are given by

$$\Psi_i^{e,\mathrm{CI},q}(\mathbf{r};\mathbf{R}^{e,x}) = \sum_{\substack{\alpha=1-N^{\mathrm{CSF}}\\ I=1-N^a}} d_I^{\mathrm{CI},q,i}(\mathbf{R}^{e,x})c_\alpha^I(\mathbf{R}^{e,x})\psi_a(\mathbf{r};\mathbf{R}^{e,x}). \tag{16}$$

In the crude adiabatic basis Eq. (15b) becomes

$$\begin{pmatrix} \mathbf{H}^{e,\mathrm{CI}q,ca,QQ} - E_i & \mathbf{H}^{e,\mathrm{CI}q,ca,QP} \\ \mathbf{H}^{e,\mathrm{CI}q,ca,PQ} & \mathbf{H}^{e,\mathrm{CI}q,ca,PP} - E_i \end{pmatrix}\begin{pmatrix} \mathbf{d}^{\mathrm{CI},ca,q,i} \\ \mathbf{D}^{\mathrm{CI},ca,q,i}\end{pmatrix} = \begin{pmatrix}\mathbf{0}\\ \mathbf{0}\end{pmatrix}, \tag{17a}$$

where

$$H_{kl}^{e,\mathrm{CI}q,ca,RS}(\mathbf{R}) = \mathbf{d}^{\mathrm{CI},q,k}(\mathbf{R}^{e,x})^\dagger\mathbf{H}^{e,\mathrm{CI},q}(\mathbf{R})\mathbf{d}^{\mathrm{CI},q,l}(\mathbf{R}^{e,x}),$$
$$k\in R, \quad l\in S. \tag{17b}$$

With Eq. (16) in mind it is tempting to proceed as above, transform Eq. (8) to this crude adiabatic basis and expand Eq. (17a) to first order to obtain the working equations. In fact we will find this to be a useful (approximate) approach. It is an approximation, albeit a potentially good one, since it neglects the fact that the CSF space spanned by the $\Psi_I^0(\mathbf{r};\mathbf{R})$, $I\in q$ may, in principle, change with $\mathbf{R}$. Thus Eq. (8) should be replaced with

$$\mathbf{H}^{e,\mathrm{CI}}(\mathbf{R}) = \mathbf{H}^{e,\mathrm{CI}}(\mathbf{R}^{e,x}) + \nabla\mathbf{H}^{e,\mathrm{CI}}(\mathbf{R}^{e,x})\cdot\delta\mathbf{R}, \tag{18a}$$

where

$$\nabla\mathbf{H}^{e,\mathrm{CI}} = \delta\mathbf{H}^{e,\mathrm{CI}} + \delta_{\mathrm{CI}}\mathbf{H}^{e,\mathrm{CI}}, \tag{18b}$$

$$\delta_{\mathrm{CI}}\mathbf{H}_{IJ}^{e,\mathrm{CI}} = (\nabla\mathbf{c}^{I^\dagger})\mathbf{H}^{e,\mathrm{CSF}}\mathbf{c}^J + \mathbf{c}^{I^\dagger}\mathbf{H}^{e,\mathrm{CSF}}\nabla\mathbf{c}^J$$
$$= \sum_{K=1}^{N^a}(\mathbf{f}^{KI}H_{KJ}^{e,\mathrm{CI}} + H_{IK}^{e,\mathrm{CI}}\mathbf{f}^{KJ}), \tag{18c}$$

$$\delta H^{e,\mathrm{CI}}(\mathbf{R})_{IJ} \equiv \mathbf{c}^{I^\dagger}\nabla\mathbf{H}^{e,\mathrm{CSF}}\mathbf{c}^J = \delta H^{e,\mathrm{CI}q}(\mathbf{R})_{IJ} \quad \text{if } I,J\in q, \tag{18d}$$

and the derivative couplings are given by

$$\mathbf{f}^{KL}(\mathbf{R}) = \mathbf{c}^K(\mathbf{R})^\dagger\nabla\mathbf{c}^L(\mathbf{R}) = \delta\mathbf{H}_{KL}^{0,\mathrm{CI}}(E_L^0(\mathbf{R}) - E_K^0(\mathbf{R}))^{-1}. \tag{18e}$$

As above Eq. (17a) becomes, through first order

$$(\nabla\mathbf{H}^{e,\mathrm{CI}q,ca,QQ}(\mathbf{R}^{e,x})\cdot\delta\mathbf{R} - E_i^{e,(1)}(\mathbf{R}))\mathbf{d}^{\mathrm{CI},ca,q,(0),i}(\mathbf{R}) = 0, \tag{19a}$$

where

$$\nabla\mathbf{H}_{kl}^{e,\mathrm{CI}q,ca,QQ}(\mathbf{R}) = \sum_{\substack{\alpha,\beta=1-N^{\mathrm{CSF}}\\ K,L=1-N^a}} d_K^{\mathrm{CI},q,k}(\mathbf{R}^{e,x})$$
$$\times\nabla[c_\alpha^K(\mathbf{R})H_{\alpha\beta}^{e,\mathrm{CSF}}(\mathbf{R})c_\beta^L(\mathbf{R})]d_L^{\mathrm{CI},q,l}(\mathbf{R}^{e,x})$$
$$k,l\in Q. \tag{19b}$$

The discussion preceding Eq. (18a) suggests two computational useful approximations, which we term the diabatic and adiabatic limits.

Diabatic limit. In the diabatic limit the CSF space implicitly defined by the N^a adiabatic states does not change with $\mathbf{R}$ (near $\mathbf{R}^{e,x}$). In this case the approximation $\mathbf{c}^1(\mathbf{R}) \to \mathbf{c}^1(\mathbf{R}^{e,x})$ is valid and Eq. (19a) becomes

$$(\mathbf{d}^{\mathrm{CI},q}(\mathbf{R}^{e,x})^\dagger\delta\mathbf{H}^{e,\mathrm{CI}q}(\mathbf{R}^{e,x})\mathbf{d}^{\mathrm{CI},q}(\mathbf{R}^{e,x})\cdot\delta\mathbf{R}$$
$$- E_i^{e,(1)}(\mathbf{R}))\mathbf{d}^{\mathrm{CI},ca,q,i,(0)}(\mathbf{R}) = 0. \tag{20}$$

Thus in the q space diabatic limit, $\mathbf{H}^e(\mathbf{R}^{e,x}+\delta\mathbf{R})$ is given by Eqs. (12a) or (12b) provided Eqs. (13a), (13c), and (13d) are replaced with

$$\mathbf{g}^i(\mathbf{R}) = \sum_{\substack{\alpha,\beta=1,N^{\mathrm{CSF}}\\ I,J=1,N^a}} d_I^{\mathrm{CI},q,i}(\mathbf{R}^{e,x})c_\alpha^I(\mathbf{R}^{e,x})$$
$$\times\nabla H_{\alpha\beta}^{e,\mathrm{CSF}}(\mathbf{R})d_J^{\mathrm{CI},q,i}(\mathbf{R}^{e,x})c_\beta^J(\mathbf{R}^{e,x}), \tag{13a$'$}$$

$$\mathbf{h}^{ij}(\mathbf{R}) = \sum_{\substack{\alpha,\beta=1,N^{\mathrm{CSF}}\\ I,J=1,N^a}} d_I^{\mathrm{CI},q,i}(\mathbf{R}^{e,x})c_\alpha^I(\mathbf{R}^{e,x})$$
$$\times\nabla H_{\alpha\beta}^{e,\mathrm{CSF}}(\mathbf{R})d_J^{\mathrm{CI},q,j}(\mathbf{R}^{e,x})c_\beta^J(\mathbf{R}^{e,x}), \tag{13c$'$}$$

$$\mathbf{h}^{iTj}(\mathbf{R}) = \sum_{\substack{\alpha,\beta=1,N^{\mathrm{CSF}}\\ I,J=1,N^a}} d_I^{\mathrm{CI},q,i}(\mathbf{R}^{e,x}) c_\alpha^I(\mathbf{R}^{e,x}) \times \nabla H_{\alpha\beta}^{e,\mathrm{CSF}}(\mathbf{R}) d_J^{\mathrm{CI},q,Tj}(\mathbf{R}^{e,x}) c_\beta^J(\mathbf{R}^{e,x}), \quad (13\mathrm{d}')$$

where we have noted that at $\mathbf{R}^{e,x}$ *only* $d_J^{\mathrm{CI},q,i}(\mathbf{R}^{e,x}) = d_f^{\mathrm{CI},ca,q,i}(\mathbf{R}^{e,x})$.

Nondegenerate adiabatic state approach. When contributions from $\delta_{\mathrm{CI}}\mathbf{H}^{e,\mathrm{CI},q}$ cannot be ignored both terms in Eq. (18b) must be included. Then provided $E_I^0(\mathbf{R})$ is nondegenerate near $\mathbf{R}^{e,x}$, there is some cancellation in the contributions to Eq. (18b) since

$$\nabla H_{KL}^0(\mathbf{R}) = \nabla[\mathbf{c}^K(\mathbf{R})^\dagger \mathbf{H}^{0,\mathrm{CSF}}(\mathbf{R}) \mathbf{c}^L(\mathbf{R})] = 0 \quad \text{for } K \neq L, \quad (21)$$

so that

$$\nabla \mathbf{H}_{KL}^{e,\mathrm{CI}q} = \left[\sum_{M=1}^{N^a} (\mathbf{f}^{MK}\mathbf{H}^{e,\mathrm{CI}}(\mathbf{R})_{ML} + \mathbf{H}^{e,\mathrm{CI}}(\mathbf{R})_{KM}\mathbf{f}^{ML}(\mathbf{R})) \right] + \delta\mathbf{H}^{e,\mathrm{CI}}(\mathbf{R})_{KL}$$
$$= [\delta_{\mathrm{CI}} H_{KL}^{\mathrm{so,CI}}] + \delta\mathbf{H}_{KL}^{\mathrm{so,CI}} + \delta\mathbf{H}_{KK}^{0,\mathrm{CI}}\delta_{KL}$$
$$\equiv \nabla \mathbf{H}_{KL}^{\mathrm{so,CI}} + \delta\mathbf{H}_{KK}^{0,\mathrm{CI}}\delta_{KL}. \quad (22)$$

In this case Eq. (19a) becomes

$$(\mathbf{d}^{\mathrm{CI},q}(\mathbf{R}^{e,x})^\dagger \nabla \mathbf{H}^{e,\mathrm{CI}q}(\mathbf{R}^{e,x}) \mathbf{d}^{\mathrm{CI},q}(\mathbf{R}^{e,x}) \cdot \delta\mathbf{R} - E_i^{e,(1)}(\mathbf{R})) \mathbf{d}^{\mathrm{CI},ca,q,i,(0)}(\mathbf{R}) = 0, \quad (23)$$

giving the nondegenerate adiabatic state approach. The nondegenerate adiabatic state approach is exact provided $\mathbf{R}^{e,x} \neq \mathbf{R}^x$, a point of conical intersection of H^0. When $\mathbf{R}^{e,x} = \mathbf{R}^x$, for states I and J, then $\nabla H_{IJ}^0(\mathbf{R}) = \delta H_{IJ}^0(\mathbf{R})$, rather than Eq. (21) should be used.

In the nondegenerate adiabatic state approach $\mathbf{H}^e(\mathbf{R}^{e,x} + \delta\mathbf{R})$ is given to first order by Eqs. (12a) or (12b) provided Eqs. (13a), (13c), and (13d) are replaced with

$$\mathbf{g}^i(\mathbf{R}) = \sum_{I,J=1,N^a} d_I^{\mathrm{CI},q,i}(\mathbf{R}^{e,x}) \nabla H_{IJ}^{e,\mathrm{CI}q}(\mathbf{R}) d_J^{\mathrm{CI},q,i}(\mathbf{R}^{e,x}), \quad (13\mathrm{a}'')$$

$$\mathbf{h}^{ij}(\mathbf{R}) = \sum_{I,J=1,N^a} d_I^{\mathrm{CI},q,i}(\mathbf{R}^{e,x}) \nabla H_{IJ}^{e,\mathrm{CI}q}(\mathbf{R}^{e,x}) d_J^{\mathrm{CI},q,j}(\mathbf{R}^{e,x}), \quad (13\mathrm{c}'')$$

$$\mathbf{h}^{iTj}(\mathbf{R}) = \sum_{I,J=1,N^a} d_I^{\mathrm{CI},q,i}(\mathbf{R}^{e,x}) \nabla H_{IJ}^{e,\mathrm{CI}q}(\mathbf{R}^{e,x}) d_J^{\mathrm{CI},q,Tj}(\mathbf{R}^{e,x}), \quad (13\mathrm{d}'')$$

where $\nabla H_{IJ}^{e,\mathrm{CI}q}$ is given by Eq. (22).

3. The g-h space in terms of orthogonal vectors

As in the nonrelativistic case continuity of $\mathbf{g}^{ij}(\mathbf{R})$, $\mathbf{h}^{r,ij}(\mathbf{R})$, $\mathbf{h}^{i,ij}(\mathbf{R})$, $\mathbf{h}^{r,iTj}(\mathbf{R})$, $\mathbf{h}^{i,iTj}(\mathbf{R})$, along the seam is key to their use in a perturbative description of the vicinity of that seam. In the nonrelativistic case orthogonality of $\mathbf{g}^{IJ}$ and $\mathbf{h}^{IJ}$ provided the requisite continuity and revealed any local or global symmetries that may exist.[24] While somewhat tangential to this work, below we outline how the orthogonality requirement can be extended to the case at hand.

At a point of conical intersection the four degenerate wave functions are defined up to a proper rotation $\mathbf{U}$, consistent with the time reversal adapted basis, that is

$$\tilde{\mathbf{d}}_i^e = \sum_{i=1}^{4} \mathbf{d}_k^e U_{ki}. \quad (24\mathrm{a})$$

Transforming the wavefunctions transforms the $\mathbf{v}^{(i)}$ as follows:

$$\tilde{\mathbf{v}}^{(1)} = \tilde{\mathbf{d}}_i^{e\dagger}(\nabla\mathbf{H}^e)\tilde{\mathbf{d}}_i^e - \tilde{\mathbf{d}}_j^{e\dagger}(\nabla\mathbf{H}^e)\tilde{\mathbf{d}}_j^e = \sum_{k,k'=1}^{4} \mathbf{d}_k^{e\dagger}(\nabla\mathbf{H}^e)\mathbf{d}_{k'}^e(U_{ki}U_{k'i} - U_{kj}U_{k'j}), \quad (24\mathrm{b})$$

$$\tilde{\mathbf{v}}^{(2)} + i\tilde{\mathbf{v}}^{(3)} = \tilde{\mathbf{d}}_i^{e\dagger}(\nabla\mathbf{H}^e)\tilde{\mathbf{d}}_j^e = \sum_{k,k'=1}^{4} \mathbf{d}_k^{e\dagger}(\nabla\mathbf{H}^e)^e\mathbf{d}_{k'}^e U_{ki}U_{k'j}, \quad (24\mathrm{c})$$

$$\tilde{\mathbf{v}}^{(4)} + i\tilde{\mathbf{v}}^{(5)} = \tilde{\mathbf{d}}_i^{e\dagger}(\nabla\mathbf{H}^e)\tilde{\mathbf{d}}_{Tj}^e = \sum_{k,k'=1}^{4} \mathbf{d}_k^{e\dagger}(\nabla\mathbf{H}^e)\mathbf{d}_{k'}^e U_{ki}U_{k'Tj}, \quad (24\mathrm{d})$$

where $\nabla\mathbf{H}^e$ is obtained from Eqs. (11), (20), or (23). Then the requirements $\tilde{\mathbf{v}}^{(k)} \cdot \tilde{\mathbf{v}}^{(l)} = 0 \; k \neq 1$ determine, from a set of transcendental equations, ten arbitrary parameters of the restricted four dimensional proper rotation.

To illustrate we consider the case of C_s symmetry. From Eq. (3) $\mathbf{U}$ can be written as

$$\mathbf{U} = \begin{pmatrix} \mathbf{u} & \mathbf{0} \\ \mathbf{0} & \mathbf{u}^* \end{pmatrix}, \quad (25\mathrm{a})$$

where

$$\mathbf{u} = \begin{pmatrix} e^{i(\alpha+\gamma)/2}\cos\beta/2 & -e^{i(-\alpha+\gamma)/2}\sin\beta/2 \\ e^{-i(-\alpha+\gamma)/2}\sin\beta/2 & e^{-i(\alpha+\gamma)/2}\cos\beta/2 \end{pmatrix}. \quad (25\mathrm{b})$$

Thus $\mathbf{U}$ has only three unique parameters which can be determined in either the Ψ_i^e or $T\,\Psi_i^e$ subspace. In the Ψ_i^e subspace

$$\begin{pmatrix} \tilde{\mathbf{d}}^i \\ \tilde{\mathbf{d}}^j \end{pmatrix}^\dagger = (\mathbf{d}^i \; \mathbf{d}^j) \begin{pmatrix} e^{i(\alpha+\gamma)/2}\cos\beta/2 & -e^{i(-\alpha+\gamma)/2}\sin\beta/2 \\ e^{-i(-\alpha+\gamma)/2}\sin\beta/2 & e^{-i(\alpha+\gamma)/2}\cos\beta/2 \end{pmatrix}. \quad (25\mathrm{c})$$

Using Eq. (25c), Eqs. (24a)–(24c) become

$$\tilde{g}^{ji} = (-g^{ji}\cos\beta + h^{r,ji}\sin\beta\cos\gamma - h^{i,ji}\sin\beta\sin\gamma), \quad (26\mathrm{a})$$

$$\tilde{h}^{ji} = \tilde{h}^{r,ji} + i\tilde{h}^{i,ji}$$
$$= [g^{ji}\sin\beta\cos\alpha - h^{r,ji}(-\cos\beta\cos\gamma\cos\alpha + \sin\gamma\sin\alpha) + h^{i,ji}(\cos\beta\sin\gamma\cos\alpha + \sin\alpha\cos\gamma)]$$
$$+ i[-g^{ji}\sin\beta\sin\alpha + h^{r,ji}(\cos\beta\sin\alpha\cos\gamma - \sin\gamma\cos\alpha) + h^{i,ji}(\cos\beta\sin\alpha\cos\gamma - \cos\gamma\cos\alpha)]. \quad (26\mathrm{b})$$

Then the requirements $\tilde{\mathbf{g}}^{ji}\cdot\tilde{\mathbf{h}}^{r,ji}=\tilde{\mathbf{g}}^{ji}\cdot\tilde{\mathbf{h}}^{i,ji}=\tilde{\mathbf{h}}^{r,ji}\cdot\tilde{\mathbf{h}}^{i,ji}=0$ yield, in a straightforward albeit tedious manner, a set of three nonlinear equations which must be solved numerically. The resulting orthogonal vectors will be discussed in a future work.

It is significant to note that using $\tilde{\mathbf{d}}^{i}$ the form of $\mathbf{H}^{e}$ in Eq. (12b) (denoted $\tilde{\mathbf{H}}^{e}$) simplifies considerably since: $\mathbf{g}^{IJ}\cdot\delta\mathbf{R}\rightarrow g\,dx$, $\mathbf{h}^{IJ}\cdot\delta\mathbf{R}\rightarrow h_{y}^{r}dy+h_{z}^{i}dz$, where $\delta\mathbf{R}=(dx,dy,dz)$. $\tilde{\mathbf{H}}^{e}$ is the Hamiltonian used by Berry in his classic analysis of the geometric phase effect.[25] This demonstrates the equivalence of seemingly more general $\mathbf{H}^{e}$ and $\tilde{\mathbf{H}}^{e}$.

D. Locating conical intersections

Equations (12a) together with Eqs. (13a), (13c), and (13d) or (13a′), (13c′), and (13d′), or (13a″), (13c″), and (13d″) form the basis for an algorithm for locating conical intersections. We seek $\delta\mathbf{R}$ such that $\mathbf{R}^{0}+\delta\mathbf{R}=\mathbf{R}^{e,x}$ and assume that $\mathbf{R}^{0}$ is sufficiently near a point of conical intersection $\mathbf{R}^{e,x}$ that the linear expansion of $\mathbf{H}^{e}$ in Eqs. (12a) or (12b) is valid. In this case Eqs. (4a)–(4c) become

$$\Delta E_{ij}(\mathbf{R}^{0})+\mathbf{g}^{ij}(\mathbf{R}^{0})^{\dagger}\cdot\delta\mathbf{R}=0, \tag{27a}$$

$$\mathrm{Re}[\mathbf{h}^{ij}(\mathbf{R}^{0})^{\dagger}\cdot\delta\mathbf{R}]=0, \tag{27b}$$

$$\mathrm{Im}[\mathbf{h}^{ij}(\mathbf{R}^{0})^{\dagger}\cdot\delta\mathbf{R}]=0, \tag{27c}$$

$$\mathrm{Re}[\mathbf{h}^{iTj}(\mathbf{R}^{0})^{\dagger}\cdot\delta\mathbf{R}]=0, \tag{27d}$$

$$\mathrm{Im}[\mathbf{h}^{iTj}(\mathbf{R}^{0})^{\dagger}\cdot\delta\mathbf{R}]=0, \tag{27e}$$

or more succinctly as

$$V^{(i)}(\mathbf{R}^{0})+\mathbf{v}^{(i)}(\mathbf{R}^{0})^{\dagger}\cdot\delta\mathbf{R}=0,\quad i=1-5, \tag{27f}$$

where $\Delta E_{ij}^{e}=(E_{i}^{e}-E_{j}^{e})$, $V^{k}(\mathbf{R}^{0})=\delta_{1k}\Delta E_{ij}^{e}(\mathbf{R}^{0})$ and $\nabla V^{(i)}\equiv\mathbf{v}^{(i)}$. In Eqs. (27a)–(27e) the $\mathbf{g}^{ij}$, $\mathbf{h}^{ij}$, and $\mathbf{h}^{iTj}$ are taken from Eqs. (13a), (13c), and (13d), (13a′), (13c′), (13d′), or (13a″), (13c″) and (13d″). In the Appendix the efficient evaluation of these quantities using analytic gradient techniques is described.

It may seem contradictory that motion along a single coordinate reduces ΔE_{ij}^{e} [Eq. (27a)], whereas in Eqs. (12a) [(12b)] five (three) directions change the energy linearly. This is in fact the correct result since at the conical intersection the "linear" directions can be interconverted by a transformation $\mathbf{U}$ of the form in Eq. (25a), whereas this is not possible away from the degeneracy where the $\mathbf{g}^{ij}$ is uniquely determined.

Equations (27a)–(27e) determine five (or three in C_s symmetry) internal nuclear coordinates. Any remaining internal degrees of freedom require additional constraints. Here we employ the approach used in our algorithm for determining seams of conical intersection for a nonrelativistic Hamiltonian,[26] where geometrical constraints $\mathbf{K}^{i}(\mathbf{R})=0$, and/or minimization of the energy of the crossing, provide the additional conditions. As discussed in Sec. III, geometrical constraints can also be used to map out the seam of conical intersection in its full dimensionality. This constrained minimization can be accomplished by minimizing the following Lagrangian:[26]

$$L^{ij}(\mathbf{R},\boldsymbol{\xi},\boldsymbol{\lambda})=E_{i}^{e}(\mathbf{R})+\sum_{i=1}^{5}V^{i}(\mathbf{R})\xi_{i}+\sum_{i=1}^{N^{\mathrm{con}}}K^{i}(\mathbf{R})\lambda_{i}, \tag{28}$$

where $\boldsymbol{\xi}$ and $\boldsymbol{\lambda}$ are Lagrange multipliers. Expanding L^{ij} through second order yields the Newton–Raphson equations[26]

TABLE I. Model Hamiltonians.

			H^{0}				
			$1,2\,^{2}A'$				
g	h	$h^{(z2)}$	$a_1^{(z)}$	$b_2^{(z)}$	$a_1^{(\rho)}$	$a_2^{(\rho)}$	$b_3^{(\rho)}$
-0.08051	0.00952	0.01	0.00136	-0.001148	0.00176	-0.00272	0.002
				$1\,^{2}A''$			
E_0	$e_1^{(\rho)}$	$e_2^{(\rho)}$	$e^{(z1)}$	$e^{(z2)}$			
0	0.01	0.01	0	0.01			
			H^{so}				
	$H_{iA'1A''}^{\mathrm{so},x}$			$H_{iA1A''}^{\mathrm{so},z}$			$H_{1A'2A'}^{\mathrm{so},y}$
$m1$	$C_i^{\mathrm{so}}(2-z)/2$			$d_i^{\mathrm{so}}(1+z^2)/2$			$-b^{\mathrm{so}}\lvert x\rvert(1+z^2)$
$m2$	$C_i^{\mathrm{so}}(2-\tanh(z^2))/2$			$d_i^{\mathrm{so}}(1+e^{-z^2})/2$			$-b^{\mathrm{so}}(1+e^{-z^2})/2$
$m3$	$C_i^{\mathrm{so}}(2-\tanh(z^2))/2$			$d_i^{\mathrm{so}}(1-e^{-z^2})/2$			$-b^{\mathrm{so}}(1-e^{-z^2})/2$
$m4$	$C_i^{\mathrm{so}}(2-\tanh(z^2))/2$			$d_i^{\mathrm{so}}(1-e^{-z^2})/2$			$-b^{\mathrm{so}}\left(\frac{15}{16}-\frac{5}{4}e^{-z^2}\right)$
	C_1^{so}	b^{so}	d_2^{so}				
so100	50	50	100				
so500	250	250	500				
so1000	500	500	1000				
so2500	1250	1250	2500				

[a]Atomic units used except for the spin-orbit parameters which are given in cm^{-1}.

$$\begin{bmatrix} \mathbf{Q}^{ij}(\mathbf{R},\xi,\boldsymbol{\lambda}) & \mathbf{v}(\mathbf{R}) & \mathbf{k}(\mathbf{R}) \\ \mathbf{v}(\mathbf{R})^{\dagger} & \mathbf{0} & \mathbf{0} \\ \mathbf{k}(\mathbf{R})^{\dagger} & \mathbf{0} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \delta\mathbf{R} \\ \delta\boldsymbol{\xi} \\ \delta\boldsymbol{\lambda} \end{bmatrix} = -\begin{bmatrix} \mathbf{g}^{i}(\mathbf{R}) + \mathbf{v}^{\dagger}\boldsymbol{\xi} + \mathbf{k}^{\dagger}\boldsymbol{\lambda} \\ \mathbf{V}(\mathbf{R}) \\ \mathbf{K}(\mathbf{R}) \end{bmatrix}, \tag{29}$$

which are to be solved iteratively until the right hand side vanishes. The gradients $\mathbf{v}$ are more costly to evaluate than their nonrelativistic counterparts. For this reason it is useful to search along the direction corresponding to $\delta\mathbf{R}$, while ΔE_{ij}^{e} decreases, or its increase is less than a preset value provided E_{i}^{e} decreases. This simple extension of an idea from conjugate gradient theory can significantly reduce the computational effort needed to solve Eq. (29).

III. NUMERICAL RESULTS

In this section the numerical solution of Eq. (29) is considered in the frequently occurring situation in which a conical intersection seam for the nonrelativistic Hamiltonian is modified by the inclusion of spin-orbit coupling. In this initial work, we focus on model Hamiltonians in order to explore a range of situations. The convergence of the nondegenerate adiabatic, and diabatic, approaches is compared. However as the primary application of this algorithm is the direct determination of conical intersections in the context of *ab initio* multiconfigurational configuration interaction (MRCI) wave functions a numerical example based on an MRCI treatment of the $\mathrm{OH}(X\,^2\Pi, A\,^2\Sigma^+) + \mathrm{H}_2$ seam of conical intersection[27] is also provided.

A. $1,2\,^2A'$ and $1\,^2A''$ model Hamiltonians

The models consist of the three electronic states, the $1,2\,^2A'$ and $1\,^2A''$ states and three internal degrees of freedom (x,y,z). A seam of conical intersections exists for the $1,2\,^2A'$ nonrelativistic states. Since the system has C_s symmetry, the ψ and $T\psi$ subspaces are uncoupled [Eq. (4c) is satisfied by symmetry]. The six state problem factors into two three state problems given by $\mathbf{H}^{e,\mathrm{CI}}(\mathbf{R})$ and $\mathbf{H}^{e,\mathrm{CI}}(\mathbf{R})^*$, where

$$\mathbf{H}^{e,\mathrm{CI}} = \begin{pmatrix} E^{0}_{1^2A'} & -iH^{\mathrm{so},y}_{1A'2A'} & -H^{\mathrm{so},x}_{1A'1A''} - iH^{\mathrm{so},z}_{1A'1A''} \\ iH^{\mathrm{so},y}_{1A'2A'} & E^{0}_{2^2A'} & -H^{\mathrm{so},x}_{2A'1A''} - iH^{\mathrm{so},z}_{2A'1A''} \\ -H^{\mathrm{so},x}_{1A'1A''} + iH^{\mathrm{so},z}_{1A'1A''} & -H^{\mathrm{so},x}_{2A'1A''} + iH^{\mathrm{so},z}_{2A'1A''} & E^{0}_{1^2A''} \end{pmatrix} \tag{30}$$

and all $H^{\mathrm{so},w}_{ij}$ are real valued. $H^{0,\mathrm{CSF}}$ is given by

$$\begin{pmatrix} H_{11} & H_{12} & 0 \\ H_{12} & H_{22} & 0 \\ 0 & 0 & E^{0}_{1^2A''} \end{pmatrix} \tag{31a}$$

and is parametrized (using atomic units) as follows:

$$H_{11} = -(gx + D(x,y,z;\mathbf{a}))$$
$$H_{22} = (gx + D(x,y,z;\mathbf{a})) + a^{(z2)}z^2, \tag{32a}$$

$$H_{12} = hy + D(x,y,z;\mathbf{b}), \tag{32b}$$

$$D(x,y,z;\mathbf{a}) = (a_1^{(\rho)}x^2 + a_2^{(\rho)}y^2 + a_3^{(\rho)}xy) + \sum_i z_i(a_1^{(z_i)}x + a_2^{(z_i)}y), \tag{32c}$$

$$E^{0}_{1^2A''} = E_0 + e^{(z2)}z^2 + e^{(z1)}z + D(x,y,z;\mathbf{e}). \tag{32d}$$

The form of $H_{ij}\ i,j=1,2$ is consistent with a recent perturbative analysis of the vicinity of a conical intersection, which provides a piecewise linear description of the seam.[24] The $a^{(z2)}$ term is included to account for seam curvature. The parameters for this representation are taken from Ref. 24 and are given in Table I. The nonzero spin-orbit interactions and their parametrization (in cm^{-1}) are also given in that table. The included contributions are those that are nonvanishing for C_{2v} and $C_{\infty v}$ nuclear configurations.

By varying mk, $k=1-4$ and so$j$, $j=100$, 500, 1000, 2500 a range of model Hamiltonians, denoted $\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R};mk,\mathrm{so}j)$, were considered. Note that for $\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R};m1,\mathrm{so}j)$, the spin orbit coupling can become quite large accentuating its effect. In $\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R};m2-m4,\mathrm{so}j)$ the spin-orbit parameters are bounded. The key difference between $m3$ and $m4$ is that in the former $H^{\mathrm{so},z}_{iA1A''}$ and $H^{\mathrm{so},y}_{1A'2A'}$ can vanish simultaneously. In $m2$ neither of these matrix elements can vanish. Finally in order to study the adiabatic state truncation an additional interaction $g31(0.01+x^2+z)$ was added to the otherwise 0 matrix element H^{0}_{31}. When this is done the Hamiltonian is denoted $\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R};mk,\mathrm{so}j,g31)$.

1. Convergence

Figure 1(a) compares the performance of the adiabatic and diabatic methods for locating intersections of states 1 and 2 of $\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R};m1,\mathrm{so}1000)$. The diabatic and adiabatic searches are started from two distinct points, $\mathbf{R}^f = (0.1,0.1\,3.0)$ far from the seam for $\mathbf{H}^{0,\mathrm{CSF}}(\mathbf{R};m1)$ (discussed below) and $\mathbf{R}^n = (0.1,0.1,0.4)$ much closer to that seam. In general convergence is seen to be quite rapid, reducing ΔE_{21} to $<10^{-6}$ in less than eight iterations despite the large changes in $\mathbf{R}$. Starting from $\mathbf{R}^n$ the adiabatic state approach is less satisfactory initially, owing to the large derivative couplings attributable to the proximity of the seam for $\mathbf{H}^{0,\mathrm{CSF}}(\mathbf{R};m1)$. Starting from $\mathbf{R}^f$ the two approaches per-

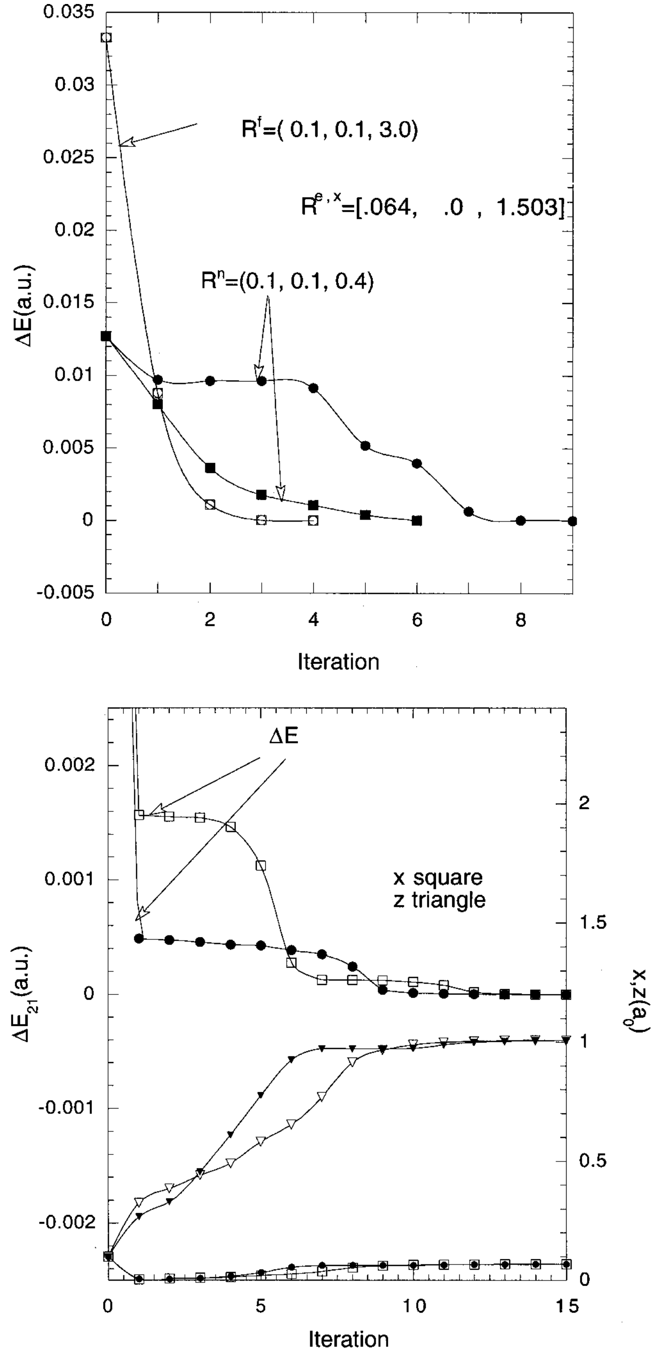

FIG. 1. (a) Convergence of diabatic (squares) and adiabatic (circles) methods to point of conical intersection ($\mathbf{R}^{e,x}$) for $H^e(\mathbf{R};m1,\mathrm{so}1000)$, with $N^a=3$ starting near to (filled markers $\mathbf{R}^n$) or far from (open markers $\mathbf{R}^f$) the nonrelativistic seam. (b) Convergence of diabatic (open symbols) and adiabatic (filled symbols) methods to point of conical intersection for $H^e(\mathbf{R};m3,\mathrm{so}1000,g31)$, with $N^a=2$.

form equally well. This conclusion was unaltered when the quadratic terms $a_i^{(\rho)}$ and $b_i^{(\rho)}$ were increased by a factor of 10.

Figure 1(b) compares the performance of the adiabatic and diabatic approaches in a truncated space, $N^a=2$, $N^{\mathrm{CSF}}=3$, for states $i=1$ and $j=2$ using $\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R};m1,\mathrm{so}1000,g31)$. While again both approaches are highly efficient the diabatic approach is modestly superior.

2. Implications for conical intersection seams

Figures 2(a) and 2(b) consider the effect that spin orbit coupling has on $\mathbf{R}^x(z)=(x(z),y(z),z)$, the seam of conical intersection in $\mathbf{H}^{0,\mathrm{CSF}}$. In these figures the seam for $\mathbf{H}^{0,\mathrm{CSF}}(\mathbf{R};m2)$, $E_1^0(\mathbf{R}^x(z))=E_2^0(\mathbf{R}^x(z))\equiv E_x^0(z)$ is reported. Note that $E_x^0(z)$ is the same for $m1-m4$. Also reported in Fig. 2(a) is $\Delta E_{21}^e(z;mk,\mathrm{so}1000)=E_2^e(\mathbf{R}^x(z))-E_1^e(\mathbf{R}^x(z))$ the energy separation along the seam for $mk=m2$, $m3$, $m4$. For each mk, with $k=2-4$, $\Delta E_{21}^e(z;mk,\mathrm{so}1000)$ is appreciable for significant portions of the nonrelativistic seam,

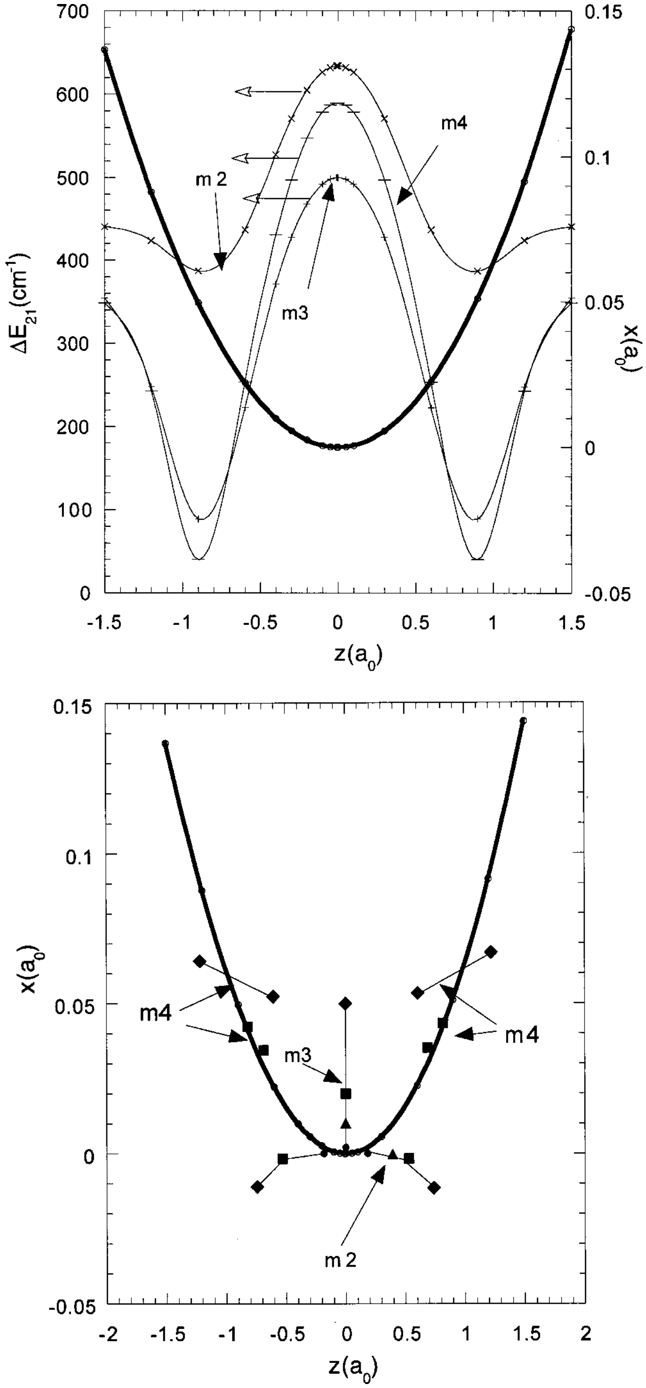

FIG. 2. (a) Seam of conical intersection $(x(z),0,z)$ of nonrelativistic Hamiltonian $H^0(\mathbf{R};m2)$ (circles—thick solid line); separation of relativistic energies, ΔE_{21}^e along the nonrelativistic seam for $H^0(\mathbf{R};mi,\mathrm{so}1000)$, $i=2$, 3, 4. (b) Seam of conical intersection $(x(z),0,z)$ of nonrelativistic Hamiltonian $H^0(\mathbf{R};m2)$ (circles—thick solid line) together with x, z $(y=0)$ coordinates of $\mathbf{R}^{e,x}(mi,\mathrm{so}k)$ $k=100$, 250, 1000, and 2500 denoted by circle, triangle, square, and diamond, respectively, $i=2$, 3, 4.

suggesting a diminution of the impact of the nonrelativistic seam of conical intersection. Figure 2(b) reports $\mathbf{R}^{e,x}(mi,\mathrm{so}k)$, the points of conical intersection for $\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R};mi,\mathrm{so}k)$, with $i=2$, 3, 4. For $m3$ the conical intersections are found for $z=0$, where $H^{\mathrm{so},z}_{1A1A''}$ and $H^{\mathrm{so},y}_{1A2A'}$ simultaneously vanish. When this feature is removed in $m4$ the location of the conical intersections changes dramatically. Note too that for $\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R};m4,\mathrm{so}j)$, $j=1000$, and 2500, four distinct but (necessarily) *isolated* points of conical intersections were found. Perhaps most significant is the fact that for $\mathbf{H}^{e,\mathrm{CSF}}(\mathbf{R};m4,\mathrm{so}j)$, $j=100$ and 500 no point of conical intersection was found.

This final observation illustrates a potential pitfall when a more time consuming search based on *ab initio* wave functions is used. It may therefore be useful to precede an *ab initio* wave function based search with a search based on a simple model Hamiltonian (similar perhaps to those presented above) developed from *ab initio* energies, spin-orbit interactions, and their gradients.

B. $1,2\,^2A'$ and $1\,^2A''$ states of H_2+OH

The results of the previous section demonstrate the convergence of our algorithm over a wide range of conditions. In these examples the requisite matrix elements and their derivatives are known to machine precision. It remains to be seen whether for an *ab initio* Hamiltonian these quantities can be calculated with sufficient precision to obtain a comparable level of performance. The following example shows that for the implementation presented in the Appendix this is in fact the case.

The nonrelativistic $1,2\,^2A'$ conical intersection seam in the H_2+OH supermolecule has been studied previously[27–29] because of its role in the nonadiabatic quenching reaction

$$H_2+OH(A\,^2\Sigma^+)\rightarrow H_2+OH(X\,^2\Pi) \quad \text{or} \quad H_2O+H(^2S).$$

The $C_{\infty v}$ portion of this seam, a $^2\Sigma^+-^2\Pi$ symmetry-allowed conical intersection, will be modified by spin-orbit coupling with the $^2A''$ component of the $^2\Pi$ state. Here we use this seam of conical intersection to demonstrate the viability of our algorithm in the context of *ab initio* MRCI wave functions. As seen below, this system provides a stringent test of the algorithm since the spin-orbit interaction is relatively modest and the energy splitting changes rapidly in the region of interest.

As in the above cited studies the molecule is restricted to C_s symmetry. In a time reversal adapted nonrelativistic eigenstate basis, constructed as described in Appendix A, conical intersections are the degenerate roots of the Hamiltonian in Eq. (30). However in this case there are five internal degrees of freedom (the out of plane mode is excluded to preserve C_s symmetry) so that two additional constraints are needed. These are provided by the energy minimization requirement. The nonrelativistic states are described at the first order configuration interaction level using a six orbital, eight electron, active space with the oxygen 1*s* orbital kept doubly occupied. The molecular orbitals were constructed from a state averaged multiconfigurational self consistent field procedure[22] using an extended atomic orbital basis on oxygen and hydrogen. The details of this description can be found in Ref. 27.

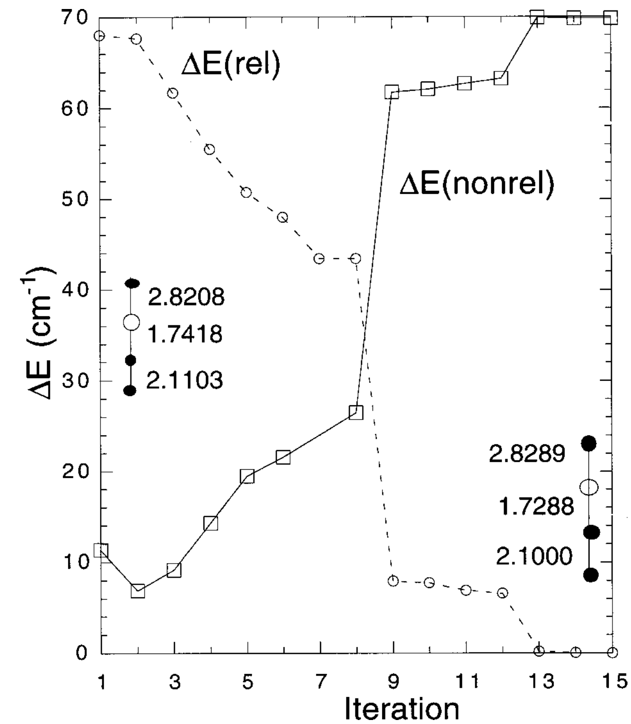

FIG. 3. ΔE^e_{32} and $\Delta E_{2^2A',1^2A'}$ at each iteration of the solution of Eq. (29) for OH+H_2 using multireference configuration interaction wave functions.

Figure 3 considers convergence of Eq. (29) to a point of conical intersection, reporting the relativistic energy separation ΔE^e_{32} and the nonrelativistic energy separation $\Delta E_{2^2A',1^2A'}$. Since the solution is expected to be near the nonrelativistic seam the diabatic states method was used. The search was initiated at the structure indicated on the left hand side of Fig. 3, a point slightly displaced by the nonrelativistic seam. At this point $\Delta E_{2^2A',1^2A'}\approx 11\,\mathrm{cm}^{-1}$ and $\Delta E^e_{32}\approx 70\,\mathrm{cm}^{-1}$. At the converged structure achieved after 15 iterations, pictured on the right hand side, $\Delta E^e_{32}<0.2\,\mathrm{cm}^{-1}$ while $\Delta E_{2^2A',1^2A'}\approx 70\,\mathrm{cm}^{-1}$. The convergence behavior is qualitatively similar to that seen in Figs. 2(a) and 2(b) although the distances involved here are much smaller. The large changes in ΔE^e_{32} between iterations 8 and 9, and 12 and 13 reflect, in part, the use of the "conjugate gradient" extrapolation noted in Sec. II D. These results strongly support the utility of the present approach. It is worth noting that once an initial point on a seam is found locating additional points is facilitated by the fact that given an $\mathbf{R}^{e,x}$ corresponding to given $\mathbf{K}$, Eq. (29) can be used to predict a good starting value for a neighboring $\mathbf{R}'^{e,x}$ corresponding to $\mathbf{K}'$.[30]

In the full six dimensional space, a 1 $(=N^{\mathrm{int}}-5)$ dimensional seam of conical intersection with no spatial symmetry may exist. Points on this portion of the seam can be located as a function of a dihedral angle using Eq. (29) with a geometrical constraint. This portion of the seam should merge with the C_s symmetry portion, a surface of dimension 2 $(=N^{C_s}-3)$. Thus the vicinity of the C_s seam of conical intersection will provide a useful starting point for that search. A detailed treatment of this issue will be the subject of a future publication.

IV. SUMMARY AND CONCLUSIONS

A generally applicable algorithm for locating points of conical intersection in molecules with an odd number of electrons in which the spin-orbit interaction is added to the nonrelativistic Coulomb Hamiltonian is presented. The algorithm is based on a perturbative description of the vicinity of a point of conical intersection used previously to treat the nonrelativistic case. Two formulations of algorithm, the diabatic limit and the nondegenerate adiabatic approach (in principle exact), were tested using model Hamiltonians. The results are found to be quite promising.

An implementation of the algorithm is presented which makes use of analytic gradient techniques, treats the spin-orbit interaction within the Breit–Pauli approximation, and incorporates it into the electronic Hamiltonian using the adiabatic states of the nonrelativistic Hamiltonian as a basis. An initial test of this implementation yielded quite promising results.

Here we considered the effect of the spin-orbit interaction on a nonrelativistic seam of conical intersection. Model Hamiltonian studies showed that the spin-orbit interaction could entirely eliminate the conical intersection seam. The model Hamiltonian studies suggest that for molecules containing atoms with atomic number near or greater than that of chlorine, even when conical intersections persist with the spin-orbit interaction included, diminution of the impact of the seam of conical intersection is likely. For this reason we are currently using the above noted implementation to consider the effect of spin-orbit interactions on the role of conical intersections in the reaction of H_2 with $Cl(^2P)$ a topic of recent interest.[31,32] We will also consider systems with smaller spin-orbit interactions but for which the nonrelativistic cone is less steep. The van der Waals complex of Al with H_2 (Refs. 33 and 34) is a candidate in this regard.

ACKNOWLEDGMENT

This work was supported by NSF grant No. CHE 9700771.

APPENDIX

Here the implementation of Eq. (29) is considered using as Ψ_1^0 a multireference CI wave function[16] expanded in a CSF basis constructed with molecular orbitals $\boldsymbol{\phi}(\mathbf{r}_j;\mathbf{R})$ determined from a state-averaged multiconfigurational self-consistent field (MCSCF) optimization. As this represents an extension of the techniques used to locate conical intersections for H^0, only the issues unique to the relativistic case are addressed.

The ϕ_i are a linear combination of the atomic orbitals (AOs) $\boldsymbol{\kappa}(\mathbf{r}_j;\mathbf{R})$

$$\phi_i(\mathbf{r}_j;\mathbf{R})=\sum_\alpha \kappa_\alpha(\mathbf{r}_j;\mathbf{R})t_{\alpha i}(\mathbf{R}), \tag{A1}$$

where $\mathbf{r}=(\mathbf{r}_1,\mathbf{r}_2,\cdots\mathbf{r}_{N^{el}})$. The derivative of ϕ_j with respect to changes in the nuclear coordinates is given by

$$\frac{\partial}{\partial R_\beta}\phi_j(\mathbf{r}_k,\mathbf{R})=\sum_i \phi_i(\mathbf{r}_k,\mathbf{R})U_{ij}^\beta(\mathbf{R})+\sum_\alpha t_{\alpha j}(\mathbf{R})\frac{\partial}{\partial R_\beta}\kappa_\alpha(\mathbf{r}_k,\mathbf{R}). \tag{A2}$$

The $\mathbf{U}^\beta$ are determined from the usual coupled perturbed state-averaged MCSCF equations.[22]

1. Time reversal adapted bases

The N^e-electron CSFs $\boldsymbol{\chi}^{A,S,M_s}$ are antisymmetrized eigenfunctions of S^2 and M_s and carry an irreducible representation A of the spatial point group. For odd electron molecules, the construction of a time reversal adapted basis is facilitated by these symmetry properties. The time reversal adapted CSF basis functions are given in terms of the $\boldsymbol{\chi}^{A,S,M_s}$ by

$$\chi^{A,S,|M_s|,+}=(\chi^{A,S,M_s}+i\chi^{A,S,-M_s})/\sqrt{2}, \tag{A3a}$$

$$\chi^{A,S,|M_s|,-}=-i(-1)^{S+M_s}(\chi^{A,S,M_s}-i\chi^{A,S,-M_s})/\sqrt{2}. \tag{A3b}$$

To see this note that from the properties of Clebsch–Gordon coefficients[35] used to construct the χ^{A,S,M_s} in a geneological[36] manner, one shows that

$$T\chi^{A,S,M_s}=(-1)^{S+M_s}\chi^{A,S,-M_s} \tag{A4a}$$

Then using Eq. (A4a) in definitions (A3a) and (A3b) gives

$$T\chi^{A,S,|M_s|,+}=\chi^{A,S,|M_s|,-};\quad T\chi^{A,S,|M_s|,-}=-\chi^{A,S,|M_s|,+}. \tag{A4b}$$

As Eqs. (A4b) are the defining properties of a time reversal adapted basis, the space of pairs $(\boldsymbol{\chi}^{A,S,|M_s|,+},\boldsymbol{\chi}^{A,S,|M_s|,-})$ are a time reversal adapted CSF basis.

The time reversal adapted nonrelativistic eigenstates $(\Psi_I^0,T\Psi_I^0)$ are also required. The Ψ_I^{0,A,S,M_s}, the nonrelativistic eigenstates in the original CSF basis, are given by

$$\Psi_I^{0,A,S,M_s}(\mathbf{r};\mathbf{R})=\sum_\alpha c_\alpha^{I,A,S}(\mathbf{R})\chi_\alpha^{A,S,M_s}(\mathbf{r};\mathbf{R}). \tag{A5a}$$

The $\mathbf{c}^{I,A,S}$, which are independent of M_s, satisfy

$$(\mathbf{H}^{0,\mathrm{CSF},A,S}(\mathbf{R})-E_{I,A,S}^0(\mathbf{R}))\mathbf{c}^{I,A,S}(\mathbf{R})=\mathbf{0}, \tag{A5b}$$

with $H_{\alpha\beta}^{0,\mathrm{CSF},A,S}=\langle\chi_\alpha^{A,S}(\mathbf{r};\mathbf{R})|H^0(\mathbf{r};\mathbf{R})|\chi_\beta^{A,S}(\mathbf{r};\mathbf{R})\rangle_r$. Then using the $\mathbf{c}^{I,A,S}$ and the CSFs $\chi^{A,S,|M_s|,\pm}$ define

$$\Psi_I^{0,A,S,|M_s|,+}=\sum_\alpha c_\alpha^{I,A,S}\chi_\alpha^{A,S,|M_s|,+}=(\Psi_I^{0,A,S,M_s}+i\Psi_I^{0,A,S,-M_s})/\sqrt{2}, \tag{A6a}$$

$$\Psi_I^{0,A,S,|M_s|,-}=\sum_\alpha c_\alpha^{I,A,S}\chi_\alpha^{A,S,|M_s|,-}=-i(-1)^{S+M_s}(\Psi_I^{0,A,S,M_s}-i\Psi_I^{0,A,S,-M_s})/\sqrt{2}. \tag{A6b}$$

Then $(\Psi_I^0, T\Psi_I^0)$ are given by

$$(\Psi_I^{0,A,S,|M_s|,+}(\mathbf{r};\mathbf{R}),\Psi_I^{0,A,S,|M_s|,-}(\mathbf{r};\mathbf{R}))$$
$$\equiv(\overline{\Psi}_I^{0,A,S,|M_s|,+},-i(-1)^{S+M_s}\overline{\Psi}_I^{0,A,S,|M_s|,-}).$$

To simplify the notation superscripts *A*, *S*, and M_s will be suppressed when no confusion will result. When point group symmetry is not an issue *A* will be suppressed.

2. Matrix elements of H^{so}

The spin-orbit operator in the Breit–Pauli approximation has the form[16]

$$H^{so}=\sum_{i=1}^{N^{el}}\left[\mathbf{h}^{(so1)}(\mathbf{r}_i)+\sum_{j=1}^{N^{el}}\mathbf{h}^{(so2)}(\mathbf{r}_i,\mathbf{r}_j)\right]\cdot\mathbf{s}^i$$
$$\equiv\sum_{i=1}^{N^{el}}[\mathbf{h}^{(so,1-2)}(\mathbf{r}_i,\mathbf{r})]\cdot\mathbf{s}^i. \tag{A7}$$

Here $\mathbf{h}^{(so,1-2)}$ can be expressed in either Cartesian components, $h^{(so,1-2),w}$ $w=x,y,z$, or rank-1 spherical components, $h^{(so,1-2),m}$ $m=-1$, 0, 1, with

$$h^{(so,1-2),\pm}=\mp(h^{(so,1-2),x}\pm ih^{(so,1-2),y})/\sqrt{2}, \tag{A8a}$$

$$h^{(so,1-2),0}=h^{(so,1-2),z}, \tag{A8b}$$

and the corresponding components for $\mathbf{s}^i$ labeled s_w^i and s_m^i.

The matrix elements in the time-reversal adapted nonrelativistic eigenstate basis are

$$\langle\Psi_I^{0,S,|M_s|,+}|H^{so}|\overline{\Psi}_J^{0,S',|M_s'|,\pm}\rangle=1/2\{H_{IJ}^{so}(S,M_s,S',M_{s'})$$
$$\pm H_{IJ}^{so}(S,-M_s,S',-M_{s'})+i[-H_{IJ}^{so}(S,-M_s,S',M_{s'})$$
$$\pm H_{IJ}^{so}(S,M_s,S',-M_{s'})]\}, \tag{A9}$$

where using McWeeny's tensor formalism[37]

$$H_{IJ}^{so}(S,M_s,S',M_s')=\begin{pmatrix}S' & 1 & S\\ S' & S-S' & S\end{pmatrix}^{-1}$$
$$\times\sum_{m=-1,0,1}H_{IJ}^{so,m}(S,S,S',S')$$
$$\times\begin{pmatrix}S' & 1 & S\\ M_s' & m & M_s\end{pmatrix} \tag{A10}$$

$\begin{pmatrix}* & * & *\\ * & * & *\end{pmatrix}$ is a Clebsch–Gordon coefficient[35] and

$$H_{IJ}^{so,\nu}(S,S,S',S')$$
$$=\left\langle\Psi_I^{0,S,S}\left|\sum_{i=1}^{N^{el}}[h^{(so,1-2),\nu}(\mathbf{r}_i,\mathbf{r})]s_{S-S'}^i\right|\Psi_J^{0,S',S'}\right\rangle$$
$$=\mathbf{c}^{I,S\dagger}\mathbf{H}^{so,CSF,S,S',\nu}\mathbf{c}^{J,S'}, \tag{A11a}$$

where ν can be any of -1, 0, 1 or x,y,z and

$$H_{\alpha\beta}^{so,CSF,S,S',\nu}=\left\langle\chi_\alpha^{S,S}\left|\sum_{i=1}^{N^{el}}[h^{(so,1-2),\nu}(\mathbf{r}_i,\mathbf{r})]s_{S-S'}^i\right|\chi_\beta^{S',S'}\right\rangle. \tag{A11b}$$

From Eqs. (A8)–(A11)

$$\langle\Psi_I^{0,S,|M_s|,+}|H^{so}|\overline{\Psi}_J^{0,S',|M_s'|,\pm}\rangle$$
$$=\sum_{w=x,y,z}H_{IJ}^{so,w}(S,S,S',S')$$
$$\times\sum_{\substack{m=-1,0,1\\ M_s,M_s'}}\zeta^{S,S',\pm}(m,w,M_s',M_s), \tag{A12}$$

where the ζ are linear combinations of Clebsch–Gordon coefficients, readily determined from Eqs. (A8)–(A10).

$H_{IJ}^{so,w}(S,S,S',S')$ is most conveniently (see Sec. A3) evaluated by expressing it in terms of $\boldsymbol{\gamma}^{IJ}$ a one particle density matrix, and $\boldsymbol{\Gamma}^{JI}$ a two particle density matrix (in the MO representation)

$$H_{IJ}^{so,w}(S,S,S',S')=\sum_{ab}\gamma_{ab}^{JI}h_{ab}^{(so1),w}+\sum_{abcd}\Gamma_{ab,cd}^{JI}h_{ab,cd}^{(so2),w}, \tag{A13a}$$

where γ^{JI} and Γ^{JI} contain the $\mathbf{c}^K$, $K=I,J$ dependence,

$$h_{ab}^{(so1),w}=\langle\phi_a(\mathbf{r}_1;\mathbf{R})|h^{(so1),w}(\mathbf{r}_1;\mathbf{R})|\phi_b(\mathbf{r}_1;\mathbf{R})\rangle_{\mathbf{r}_1}, \tag{A13b}$$

and

$$h_{abcd}^{(so2),w}=\langle\phi_a(\mathbf{r}_1;\mathbf{R})\phi_b(\mathbf{r}_1;\mathbf{R})|h^{(so2),w}(\mathbf{r}_1,\mathbf{r}_2)|\phi_c(\mathbf{r}_2;\mathbf{R})$$
$$\times\phi_d(\mathbf{r}_2;\mathbf{R})\rangle_{\mathbf{r}_1,\mathbf{r}_2}. \tag{A13c}$$

3. Evaluation of $\nabla H_{JI}^{so,CI}$

The principal new computational task is the evaluation of $\nabla\mathbf{H}_{JI}^{so,CI}$ where Ψ_I^0 and Ψ_J^0 are expanded in a time-reversal adapted CSF basis. In the notation of this Appendix $\nabla\mathbf{H}_{IJ}^{so,CI}\rightarrow\nabla\langle\Psi_I^{0,S,|M_s|,+}|H^{so}|\overline{\Psi}_J^{0,S',|M_s'|,\pm}\rangle$. From Eq. (18b) the requisite derivative quantities are

$$\delta H_{IJ}^{so,CI}\rightarrow\sum_{w=x,y,z}\mathbf{c}^{I,S,\dagger}\nabla\mathbf{H}^{so,CSF,S,S',w}\mathbf{c}^{J,S'}$$
$$\times\sum_{\substack{m=-1,0,1\\ M_s,M_s'}}\zeta^{S,S',\pm}(m,w,M_s',M_s). \tag{A14}$$

and the derivative couplings for time reversal adapted eigenstates of H^0.

(i) Derivative couplings

The derivative couplings in the time reversal adapted basis are simply related to those in the conventional CSF basis [see also Eq. (18b)]

$$\mathbf{f}^{IJ}\equiv\langle\Psi_I^{0,S,M_s}(\mathbf{r};\mathbf{R})|\nabla\Psi_J^{0,S,M_s}(\mathbf{r};\mathbf{R})\rangle_{\mathbf{r}} \tag{A15}$$

as follows:

$$\langle \overline{\Psi}_I^{0,S,|M_s|,+}(\mathbf{r};\mathbf{R})|\nabla \overline{\Psi}_J^{0,S,|M_s|,\pm}(\mathbf{r};\mathbf{R})\rangle = 1/2[\langle \Psi_I^{0,S,M_s}(\mathbf{r};\mathbf{R})|\nabla \Psi_J^{0,S,M_s}(\mathbf{r};\mathbf{R})\rangle \pm \langle \Psi_I^{0,S,-M_s}(\mathbf{r};\mathbf{R})|\nabla \Psi_J^{0,S,-M_s}(\mathbf{r};\mathbf{R})\rangle] = \delta_{+-}\mathbf{f}^{IJ}, \tag{A16}$$

(ii) $\delta \mathbf{H}_{JI}^{\mathrm{so,CI}}$

The evaluation of the captioned matrix element is the most computational demanding step in the solution of Eq. (29). Its efficient evaluation follows from Eqs. (A13) and (A14), and exploits techniques used to evaluate nonrelativistic energy gradients. Using definitions (A2) and (A11) and Eq. (A13), it follows from standard nonrelativistic gradient theory[22] that

$$\mathbf{c}^{JS}(\mathbf{R})^\dagger \frac{\partial \mathbf{H}^{\mathrm{so,CSF},S,S',w}}{\partial R_\alpha} \mathbf{c}^{IS}(\mathbf{R}) \equiv H_{JI}^{\mathrm{so},U^\alpha,w} + H_{JI}^{\mathrm{so},\alpha,w}, \tag{A17}$$

where

$$H_{JI}^{\mathrm{so},\alpha,w} = \sum_{\substack{ab\\rs}} \gamma_{ab}^{JI}\left(t_{ra}\left(\frac{\partial}{\partial R_\alpha} h_{rs}^{(\mathrm{so1}),w}\right) t_{sb}\right) + \sum_{\substack{abcd\\rspq}} \Gamma_{ab,cd}^{JI}\left(t_{ra}t_{sb}\left(\frac{\partial}{\partial R_\alpha} h_{rs,pq}^{(\mathrm{so2}),w}\right) t_{pc}t_{qd}\right), \tag{A18a}$$

a,b,c,d $[p,q,r,s]$ label molecular [atomic] orbitals

$$h_{rs}^{(\mathrm{so1}),w} = \langle \kappa_r(\mathbf{r}_1;\mathbf{R})|h^{(\mathrm{so1}),w}(\mathbf{r}_1;\mathbf{R}_1)|\kappa_s(\mathbf{r}_1;\mathbf{R}_1)\rangle_{\mathbf{r}_1}, \tag{A18b}$$

$$h_{pqrs}^{(\mathrm{so2}),w} = \langle \kappa_p(\mathbf{r}_1;\mathbf{R})\kappa_q(\mathbf{r}_1;\mathbf{R})|h^{(\mathrm{so2}),w}(\mathbf{r}_1,\mathbf{r}_2)|\kappa_r(\mathbf{r}_2;\mathbf{R}) \times \kappa_s(\mathbf{r}_2;\mathbf{R})\rangle_{\mathbf{r}_1,\mathbf{r}_2} \tag{18c}$$

and

$$H_{JI}^{\mathrm{so},U^\beta,w} = \sum_{aba'} (-\gamma_{ab}^{JI} h_{ba'}^{(\mathrm{so1}),w} U_{a'a}^\beta + \gamma_{ba}^{JI\dagger} h_{aa'}^{(\mathrm{so1}),w} U_{a'b}^\beta) + \sum_{abcda'} (-\Gamma_{ab,cd}^{JI} h_{ba',cd}^{(\mathrm{so2}),w} U_{a'a}^\beta + \Gamma_{ba,cd}^{JI\,\dagger(1)} h_{aa',cd}^{(\mathrm{so2}),w} U_{a'b}^\beta) + \Gamma_{ab,cd}^{JI} h_{ab,da'}^{(\mathrm{so2}),w} U_{a'c}^\beta + \Gamma_{ab,cd}^{JI} h_{ab,ca'}^{(\mathrm{so2}),w} U_{a'd}^\beta). \tag{A19}$$

Performing the sums over rs and $rspq$ gives in Eq. (A18a)

$$H_{JI}^{\alpha,\mathrm{so},w} = \sum_{rs} \gamma_{rs}^{ao,JI}\left(\frac{\partial}{\partial R_\alpha} h_{rs}^{(\mathrm{so1}),w}\right) + \sum_{rspq} \Gamma_{rs,pq}^{ao,JI}\left(\frac{\partial}{\partial R_\alpha} h_{rs,pq}^{(\mathrm{so2}),w}\right), \tag{A20}$$

where $\gamma^{ao,JI}$ and $\Gamma^{ao,IJ}$ are the one, and two, particle density matrices transformed to the AO basis. $H_{JI}^{\mathrm{so},U^\beta,w}$ is efficiently evaluated by performing, in Eq. (A19), the partial sums over the indices not involved in $\mathbf{U}^\beta$, defining the Lagrangian $\mathbf{L}^{JI,w}$ where

$$L_{aa'}^{JI,w} = \sum_l (-\gamma_{al}^{J,I} h_{la'}^{(\mathrm{so1}),w} + \gamma_{al}^{JI\dagger} h_{la'}^{(\mathrm{so1}),w}) + \sum_{mnl} (-\Gamma_{al,mn}^{JI} h_{la',mn}^{(\mathrm{so2}),w} + \Gamma_{al,mn}^{JI\ \dagger(1)} h_{la',mn}^{(\mathrm{so2}),w}) + \Gamma_{mn,al}^{JI} h_{mn,la'}^{(\mathrm{so2}),w} + \Gamma_{mn,la}^{JI} h_{mn,la'}^{(\mathrm{so2}),w}) \tag{A21}$$

and $\dagger(n)$ indicates that the transposition is performed on the nth pair of indices. With this definition

$$H_{JI}^{U^\beta,\mathrm{so},w} \equiv \sum_{a'a} L_{a'a}^{JI,w} U_{a'a}^\beta = \mathrm{tr}\, L^{JI,w\dagger} U^\beta. \tag{A22}$$

To evaluate the right hand side of Eq. (A17) only one pair $(\boldsymbol{\gamma}^{JI},\boldsymbol{\Gamma}^{JI})$ is required while three Lagrangians $L^{JI,w}$, $w=x,y,z$ must in general be constructed. However the construction of $L^{JI,w}$ from $(\boldsymbol{\gamma}^{JI},\boldsymbol{\Gamma}^{JI})$ is a fairly inexpensive task. The computational effort can be reduced even further by utilizing standard techniques, such as the Z-vector method,[38] from nonrelativistic analytic gradient theory.[39]

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