

# Determination of diabatic states through enforcement of configurational uniformity

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**Abstract.** An electronic structure-based construction of diabatic states from adiabatic states is formulated that is applicable when individual diabatic states contain several dominant configurations. It is accomplished by maximizing the *electronic uniformity* of the diabatic states with respect to their dominant configurations throughout the entire nuclear coordinate region. The configurations are generated from unambiguously defined *diabatization-adapted molecular orbitals*. The orthogonal transformation from adiabatic to diabatic states is deduced by an intrinsic analysis of the adiabatic CI coefficients, without calculating matrix elements of additional, derivative or non-derivative operators. The practicality of the method is demonstrated by applying it to the conical intersection region of the  $1^1A_1$  and  $2^1A_1$  states of ozone.

**Key words:** Diabatic states – Potential energy surfaces – Avoided crossings – Conical intersections – Diabatization adapted orbitals – Configuration interaction

## 1 Introduction

Regions in coordinate space where two or more potential energy surfaces closely approach each other and exhibit avoided crossings, or even conical intersections, are of great chemical interest in as much as they are likely places for the occurrence of radiationless transitions, phenomena of importance in many physicochemical contexts. Unfortunately, the wavefunctions as well as energies of the interacting states typically undergo rapid changes in these regions, and this circumstance gives rise to nontrivial difficulties in quantitative theoretical treatments, quantum chemical as well as dynamical, of the relevant processes. An effective approach to overcoming these problems is the resolution of such states, called *adiabatic* in this context,

in terms of *diabatic* states, since the latter typically exhibit considerably simpler behavior and, in particular, less rapid changes. The interpolation and parametric modeling, too, of adiabatic energy surfaces in such regions can be simplified by decomposition in terms of diabatic states, since the energy matrix elements between the latter are more easily fitted by such approximate representations.

However, while (aside from degeneracies) adiabatic wavefunctions are unique by virtue of their unambiguous definition as eigenfunctions of the hamiltonian, such is not the case for diabatic states and their optimal definition depends upon the specific use to which they are put. There exist two basically different *conceptual* approaches to this problem, namely one from the dynamic perspective and the other from the electronic structure perspective. In the dynamic context, one has to deal with a set of coupled differential equations between the adiabatic states *with large coupling terms* (nuclear-derivative matrix elements between electronic states) and the construction of diabatic states is guided by the goal of *minimizing the coupling terms in the dynamic equations* so that they can be accounted for perturbatively [1]. In the electronic structure context, on the other hand, one starts with the observation that, in certain regions of coordinate space, *drastic changes occur in the electronic structures* of the adiabatic states and the construction of diabatic states is guided by the goal of finding wavefunctions whose *electronic structures maintain their essential characteristics over the entirety of such regions*. Such diabatic resolutions can be useful in various quantum chemical analyses, e.g., in the study of intersections. The expectation is furthermore justified that dynamic coupling elements between quantum chemically determined diabatic states, too, are very much smaller than those between adiabatic states and, while perhaps not perfectly minimal, certainly amenable to a perturbative treatment.

The construction of diabatic states on the basis of electronic structure criteria has been considered in the past. Already in 1952 Mulliken had suggested the use of dipole moments to sort out diabatic states [2] and this method was further pursued by Hush et al. [3]. Recently,

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Cave and Newton have developed this approach even further [4]. Hendekovic et al. suggested two methods, one based on the maximization of the sum of squares of natural spin orbital occupation numbers and another based on the interpolation of one-electron densities [5]. Spiegelman and Malrieu have advanced methods based on effective hamiltonians [6] and so have Gadea, Pelissier et al. [7]. Werner et al. used a weighted sum of squares of adiabatic configuration coefficients for special types of wavefunctions [8]. Hirsch et al. as well as Peric et al. [9] have explored methods based on the optimization of suitable expectation values, such as dipole moments, quadrupole moments, transition moments and angular moment components. Pacher et al. introduced a “minimal block diagonalization” for forming diabatic states and this approach has been further developed by Domcke et al. [10]. A review has recently been given by Pacher et al. [11].

Another method based on the configurational expansion of electronic wavefunctions has recently been developed by the present authors [12]. Its particular emphasis is on the treatment of situations where the diabatic states contain *several* essential dominant electronic configurations rather than only one. The diabatic states are obtained as orthogonal superpositions of the adiabatic wavefunctions by *maximizing the configurational uniformity* of the former. In the present note, this approach is further pursued, simplified and generalized, and some issues that were not previously addressed are resolved. In particular, an algorithm is given for determining those molecular orbitals (MOs) that are most effective for the decomposition of adiabatic states into diabatic states.

## 2 Fundamental aspects of the electronic structure approach

### 2.1 Configurational expansions of adiabatic and diabatic states

Let

$$\psi_n = \sum_a^L \chi_a c_{an} \quad n = 1, 2, \dots, N \ll L \quad (1)$$

denote the CI expansions of  $N$  given adiabatic states  $\psi_n$  in terms of a large number,  $L$ , of configurations  $\chi_a$ . The goal is to express these adiabatic states as superpositions of an equal number of diabatic states  $\phi_k$  by an orthogonal transformation, i.e.,

$$\psi_n = \sum_k T_{nk} \phi_k, \quad k, n = 1, 2, \dots, N, \quad \mathbf{T}\mathbf{T}^\dagger = \mathbf{I}, \quad (2)$$

where the  $\phi_k$  satisfy certain criteria of electronic structure uniformity over some region in nuclear coordinate space. This objective will be accomplished by deducing the diabatic states from the known adiabatic states through the inverse transformation

$$\phi_k = \sum_n \psi_n T_{nk} \quad k, n = 1, 2 \dots N, \quad (3)$$

whence

$$\phi_k = \sum_\alpha^L \chi_\alpha d_{\alpha k}, \quad k = 1, 2, \dots, N, \quad (4)$$

with

$$d_{\alpha k} = \sum_n c_{\alpha n} T_{nk}, \quad \text{for all } \alpha. \quad (5)$$

The matrix  $\mathbf{T}$  will be determined by enforcing the electronic structure uniformity requirement. Diagonalization of the  $N \times N$  hamiltonian matrix  $H_{jk} = \langle \phi_j | H | \phi_k \rangle$  will manifestly recover the original adiabatic states as superpositions of the diabatic states and yield the adiabatic state energies.

### 2.2 Uniformity of electronic structure

What is meant by “uniformity of electronic structure”? The implementation of such an assessment requires the ability (i) *to quantitatively assess the character of the structure of a wavefunction in electronic coordinate space* and (ii) *to monitor changes in these characteristics as functions of the nuclear positions over regions in nuclear coordinate space*. When these characteristics change only little for a wavefunction in such a region, then we consider the electronic structure of that wavefunction uniform in that region. The present approach to this problem is based on the following premises regarding adiabatic states which are satisfied for many electronic wavefunctions.

1. The  $N$  adiabatic states can *all* be expressed in terms of the *same*  $L$  orthonormal configurations  $\chi_a$  which, in turn, are constructed from the *same* set of orthonormal molecular orbitals. For the purpose of the following derivations, it will soon be seen expedient to assume that the configurations span a full configuration space, such as is the case when the  $N$  states are obtained from an  $N$ -state-averaged multiconfigurational self-consistent field MCSCF calculation in a full configuration space. However, we shall see in Sect. 7 that the method to be developed is equally applicable for wavefunctions not given by full-space expansions. Because of the orbital freedom in a full configuration space, an additional appropriate condition must be imposed to define the MOs *unambiguously*. This problem will be addressed in Sect. 3. Under these premises, *the electronic structure of each wavefunction  $\psi_n$  of Eq.(1) can be characterized by its CI expansion coefficients  $c_a$* .

2. More specifically we presume that, in each expansion given by Eq.(1), there are a relatively small number of dominant configurations and *we consider the electronic structure of  $\psi_n$  to be characterized by this dominant part of its CI expansion*. The definition of “dominance” is of course somewhat fuzzy but, as a rule of thumb, configurations with CI coefficients larger than about 0.2 in at least some part of the nuclear coordinate region under scrutiny are reasonable candidates. Typically, the various  $\psi_n$  embody different dominant configurations and we denote by  $\chi_\delta$  with  $\delta = 1, 2, \dots, M (N \leq M \ll L)$

the collection of all  $M$  configurations that are dominant in at least one of the  $N$  states.

3. In order to compare the electronic structure of a state at different points in a nuclear coordinate region, we must compare the dominant part of the configurational expansions of its wavefunctions at these points.

To this end, it is necessary to be able to follow the deformations of the individual MOs in *electronic* coordinate space as the molecule deforms corresponding to following a continuous path in *nuclear* coordinate space. From an operational point of view, this means that one must be able to *establish a one-to-one correspondence between the unambiguously determined MOs of a state at different points in nuclear coordinate space when these points lie close to each other*. This problem will be addressed in Sect. 4.

Having thus determined, for a given set of adiabatic states, a specific set of consistent MOs that deform continuously as the nuclear coordinates follow any continuous path in the nuclear coordinate region of interest, one can then form the configurations  $\chi_\alpha$  from this orbital set by a specified space and spin coupling scheme. It is obvious that the  $\chi_\alpha$  too, will deform continuously and can be unambiguously followed along any path in nuclear coordinate space.

4. It is now presumed that strong changes in the electronic structures of molecular wavefunctions along such paths typically result from strong changes in their configurational expansion coefficients rather than from sudden drastic changes in orbital shapes. This premise is based on the general experience that orbitals change only gradually with molecular deformations.

5. The changes in the electronic structure of a wavefunction, as it deforms along such paths, can then be identified by *monitoring the changes of its expansion coefficients in terms of the problem-adapted deforming configurations discussed under item 3*, in particular for the short dominant part of the expansion that determines the electronic structure characteristics. A wavefunction is considered *to essentially maintain its electronic structure along a nuclear coordinate path if the (deforming) configurations in its dominant part remain the same*. If this holds true for all points in a nuclear coordinate region, then we consider the state to have a uniform electronic structure in this region. In this sense, we equate electronic structure uniformity with *configurational uniformity*.

### 2.3 Using configurational uniformity as a criterion for the construction of diabatic states

Assume then that in the expansions of  $\psi_1, \psi_2, \dots, \psi_N$  given by Eq.(1), a relatively small number of dominant configurations  $\chi_\delta [\delta = 1, 2, \dots, M, (N \leq M \ll L)]$  can be identified as determining the electronic structures of the  $N$  adiabatic states. *In the vicinity of real or avoided crossings, those configurations that dominate in a given adiabatic state will then be different in different local regions of the nuclear coordinate space*, i.e. the adiabatic states will not exhibit configurational uniformity over the entire region.

*It is now furthermore assumed that the  $M$  dominant configurations can be divided into  $N$  groups, say*

Group  $G_1$ : Configurations corresponding to the indices  $\delta = 1, 2, \dots, a_1$ ,

Group  $G_2$ : Configurations corresponding to the indices  $\delta = (a_1 + 1), \dots, a_2$ ,

...

Group  $G_k$ : Configurations corresponding to the indices  $\delta = (a_{k-1} + 1), \dots, a_k$ ,

...

Group  $G_N$ : Configurations corresponding to the indices  $\delta = (a_{N-1} + 1), \dots, a_N = M$ ,

such that, *in any given adiabatic wavefunction, all members of any one group  $G_k$  are always simultaneously dominant or not*. The example discussed in Sect. 6 illustrates these general statements.

If the described conditions prevail, then it is reasonable to surmise that the  $N$  adiabatic states  $\psi_n$  can be expressed as superpositions of  $N$  diabatic states  $\phi_k$ , each of which is dominated, *everywhere in nuclear coordinate space*, by the configurations of one and the same configuration group  $G_k$ . We therefore postulate the existence of  $N$  diabatic states  $\phi_k$  with configurational expansions as given by Eq. (4) such that *the expansion of  $\phi_k$  is dominated by the configurations belonging to one group  $G_k$  everywhere in the considered nuclear coordinate region*. It will be shown in Sect. 5 how this criterion can be used to determine the matrix  $\mathbf{T}$ .

## 3 Adaptation of MOs to diabaticization

### 3.1 Criterion

The possibility of associating configuration groups  $G_k$  with diabatic states is contingent upon an appropriate choice of MOs. Consider, for instance, two adiabatic states  $\psi_1, \psi_2$  constructed from two MOs  $u_1, u_2$  as follows

$$\psi_1 = 0.9950\chi_1 + 0.0999\chi_2, \quad \psi_2 = -0.0999\chi_1 + 0.9950\chi_2,$$

where

$$\chi_1 = \mathcal{A}\{u_1 u_1 \alpha \beta\}, \quad \chi_2 = \mathcal{A}\{u_2 u_2 \alpha \beta\}.$$

In this case, the two determinants  $\chi_1$  and  $\chi_2$  manifestly dominate in  $\psi_1$  and  $\psi_2$  respectively and, hence, can be chosen as diabatic states  $\phi_1, \phi_2$ . If we use, however, the orbitals  $v_1, v_2$ , defined by

$$u_1 = (v_1 + v_2)/\sqrt{2}, \quad u_2 = (v_1 - v_2)/\sqrt{2},$$

to express the same adiabatic states, then we have

$$\psi_1 = 0.5475(\chi'_1 + \chi'_2) + 0.4476(\chi'_3 + \chi'_4),$$

$$\psi_2 = 0.4476(\chi'_1 + \chi'_2) - 0.5475(\chi'_3 + \chi'_4),$$

where

$$\chi'_1 = \mathcal{A}\{v_1 v_1 \alpha \beta\}, \quad \chi'_2 = \mathcal{A}\{v_2 v_2 \alpha \beta\}, \quad \chi'_3 = \mathcal{A}\{v_1 v_2 \alpha \beta\}, \\ \chi'_4 = \mathcal{A}\{v_2 v_1 \alpha \beta\}.$$

In this expansion, none of the configurations  $\chi'_k$  are dominant and they are of no help in recognizing diabatic component states.

This observation exhibits the conceptual advantage of the full configuration space concept for the problem at hand in as much as, in such a space, the orbitals can be transformed so as to become optimally suited for the generation of dominant configurations that form distinct groups  $G_k$ , as presumed above for the diabaticization procedure. In many instances, the natural orbitals of the state-averaged density matrix have been found satisfactory for this purpose and we shall see an example in Sect. 6. But this is not always so, as is in fact also illustrated by the paradigm just examined. In that case, the state-averaged density matrix happens to have degenerate eigenvalues and, hence, no unique natural orbitals.

A general diabaticization adaptation of MOs in a full space can be inferred from the discussed paradigm by examining its orbital occupation numbers  $p(u_\tau), p(v_\nu)$  listed in Table 1. It is apparent that the following postulate is promising:

*The MOs  $u_\tau$  most likely to generate configurations effective for the resolution of adiabatic states in terms of diabatic states are those that maximize the sum  $\Sigma_n \Sigma_\tau [p(u_\tau, \psi_n)]^2$ , where  $p(u_\tau, \psi_n)$  denotes the occupation number of the orbital  $u_\tau$  in the adiabatic state  $\psi_n$ .*

### 3.2 Determination of diabaticization-adapted orbitals

Let  $v_\nu (\nu = 1, 2, 3, \dots)$  be the original orbitals and  $u_\tau (\tau = 1, 2, 3, \dots)$  the diabaticization-adapted orbitals to be found:

$$u_\tau = \Sigma_\nu v_\nu U_{\nu\tau}, \quad UU^\dagger = I.$$

The first-order density matrix elements  $p_{\mu\nu}^n$  of the adiabatic wavefunctions  $\psi_n$  in the basis  $v_\nu$ , defined by

$$\rho^n(1, 2) = \Sigma_{\mu\nu} p_{\mu\nu}^n v_\mu(1) v_\nu(2),$$

are known. The density matrix elements in the basis  $u_\tau$  are then given by

$$\rho^n(1, 2) = \Sigma_{\sigma\tau} (\mathbf{U}^\dagger \mathbf{p}^n \mathbf{U})_{\sigma\tau} u_\sigma(1) u_\tau(2).$$

Since the occupation numbers are the diagonal elements, the criterion stated above requires thus maximization of the sum

$$D(\mathbf{U}) = \Sigma_n \Sigma_\tau [(\mathbf{U}^\dagger \mathbf{p}^n \mathbf{U})_{\tau\tau}]^2 \quad (6a)$$

$$= \Sigma_{\kappa\lambda} \Sigma_{\mu\nu} \mathbf{P}_{\kappa\lambda, \mu\nu} \Sigma_\tau \mathbf{U}_{\kappa\tau} \mathbf{U}_{\lambda\tau} \mathbf{U}_{\mu\tau} \mathbf{U}_{\nu\tau},$$

where

$$P_{\kappa\lambda, \mu\nu} = \Sigma_n p_{\kappa\lambda}^n p_{\mu\nu}^n. \quad (6b)$$

This expression is, however, identical in structure with the ‘‘localization sum’’ encountered in the context of orbital localization and Edmiston and Ruedenberg [13] have shown how to maximize such an expression with respect to the orthogonal transformation  $\mathbf{U}$ . Adaptation of their method to the present form of the four-index quantities  $P_{\kappa\lambda, \mu\nu}$  yields the following procedure.

The maximization of  $D$  is achieved iteratively by a sequence of orthogonal  $2 \times 2$  Jacobi rotations  $\mathbf{J}^{12}, \mathbf{J}^{13}, \mathbf{J}^{23}, \mathbf{J}^{14}, \mathbf{J}^{24}, \mathbf{J}^{34}, \mathbf{J}^{15}, \mathbf{J}^{25}, \dots$  where each  $\mathbf{J}^{ij}$  has the form

$$(\mathbf{J}^{ij})_{ii} = (\mathbf{J}^{ij})_{jj} = \cos \gamma_{ij}, \quad (\mathbf{J}^{ij})_{ij} = -(\mathbf{J}^{ij})_{ji} = \sin \gamma_{ij},$$

$$(\mathbf{J}^{ij})_{\mu\nu} = \delta_{\mu\nu}, \quad \text{for } \mu\nu \neq ii, jj, ij, ji. \quad (7a)$$

After a Jacobi rotation  $\mathbf{J}^{ij}$  has been determined, the density matrix  $\mathbf{p}$  of the previous iteration is updated to the new density matrix  $(\mathbf{J}^{ij})^\dagger \mathbf{p}^n \mathbf{J}^{ij}$ . The value of  $\gamma_{ij}$  used for  $\mathbf{J}^{ij}$  is determined so that the partial sum

$$\Sigma_n \{ ((\mathbf{J}^{ij})^\dagger \mathbf{p}^n \mathbf{J}^{ij})_{11}^2 + ((\mathbf{J}^{ij})^\dagger \mathbf{p}^n \mathbf{J}^{ij})_{22}^2 \}$$

(formed from the updated matrices) is maximized. According to Ref. [13], this is accomplished by choosing for  $\gamma_{ij}$  the value satisfying the equations

$$\cos 4\gamma_{ij} = A_{ij}/[A_{ij}^2 + B_{ij}^2]^{1/2},$$

$$\sin 4\gamma_{ij} = B_{ij}/[A_{ij}^2 + B_{ij}^2]^{1/2}, \quad -\pi \leq 4\gamma_{ij} \leq \pi, \quad (7b)$$

with

$$A_{ij} = P_{ij,ij} - (P_{ii,ii} + P_{jj,jj} - 2P_{ii,jj})/4, \quad B_{ij} = P_{ii,ij} - P_{jj,ji}.$$

In the present case, the expressions become

$$A_{ij} = \Sigma_n A_{ij}^n, \quad A_{ij}^n = (p_{ij}^n)^2 - (p_{ii}^n - p_{jj}^n)^2/4, \quad (7c)$$

$$B_{ij} = \Sigma_n B_{ij}^n, \quad B_{ij}^n = (p_{ii}^n - p_{jj}^n) p_{ij}^n. \quad (7d)$$

Thereby, the sum  $D$  of Eq.(6a) is found to increase by the amount

$$\Delta D(\mathbf{J}^{ij}) = \Sigma_n \{ ((\mathbf{J}^{ij})^\dagger \mathbf{p}^n \mathbf{J}^{ij})_{11}^2 + ((\mathbf{J}^{ij})^\dagger \mathbf{p}^n \mathbf{J}^{ij})_{22}^2 \}$$

$$- \Sigma_n \{ (\mathbf{p}_{11}^n)^2 + (\mathbf{p}_{22}^n)^2 \} \quad (8)$$

$$= A_{ij} + [(A_{ij})^2 + (B_{ij})^2]^{1/2}.$$

The sequence of the rotations  $\mathbf{J}^{ij}$  is determined by going through all possible off-diagonal  $ij$ -combinations in a systematic order. Several passes through all  $ij$ -index pairs are usually required to achieve a desired convergence. Before executing any one transformation  $\mathbf{J}^{ij}$ , the gain is calculated according to Eq. (8) and, if it lies below the convergence threshold, this transformation is skipped. Upon approach to overall convergence, this happens for a larger and larger fraction of the possible

**Table 1.** Occupation numbers  $p(u_\tau), p(v_\nu)$  of the orbitals  $u_\tau, v_\nu$  discussed in Sect. 3

	$p(u_1)$	$p(u_2)$	$[p(u_1)]^2 + [p(u_2)]^2$	$p(v_1)$	$p(v_2)$	$[p(v_1)]^2 + [p(v_2)]^2$
In $\psi_1$	1.98	0.02	3.92	1.00	1.00	2.00
In $\psi_2$	0.02	1.98	3.92	1.00	1.00	2.00
Sum	2	2	7.84	2	2	4.00

Jacobi rotations. Further details are given in the papers of Ref. [13].

After the aggregate optimizing orbital transformation  $\mathbf{U}$  has been determined, the adiabatic  $\psi_n$  must be expanded in terms of the configurations generated by the diabaticization-adapted orbitals  $u_k$ . There exist two methods for accomplishing this without repeating the CI calculation, one by Malmqvist [14] and another by Atchity and Ruedenberg [15]. We call the resulting configurations and expansion coefficients, too, *diabatization-adapted*.

#### 4 Following MO deformations

As discussed under item 3 of Sect. 2.2, the assessment of configurational uniformity over a region in coordinate space depends upon the ability to follow MO deformations in electronic coordinate space as the molecule deforms along a continuous path in nuclear coordinate space. This tracking requires the establishment of a one-to-one correspondence between MOs, defined by an unambiguous intrinsic procedure such as given in Sect. 3, for different but close-lying points in nuclear coordinate space.

In order to obtain a rough idea as to which MO for one such nuclear coordinate point ought to be considered as a deformed version of a given MO of the same system for a neighboring point, one can examine the occupation numbers and their orderings for the two wavefunctions. However, such orderings do change with geometrical deformations and it is therefore necessary to compare the MOs themselves.

A basis for such a comparison is manifestly provided by the overlap integrals between the MOs in question. If the molecular deformation is only slight, however, a simpler procedure is adequate and, perhaps, more appropriate. Both wavefunctions are presumably expressed in terms of the same type of atomic orbital basis sets, the only difference being that the nuclear coordinates at which these sets are centered correspond to two *slightly* different points in nuclear coordinate space, say  $P'$  and  $P''$ . Let the bases for these two points be denoted by  $AO'_i$  and  $AO''_i$ , respectively, and let

$$MO' = \sum_i a_i AO'_i, \quad \text{and} \quad MO'' = \sum_i b_i AO''_i$$

be the expansions of the molecular orbitals  $MO'$  and  $MO''$  for these two neighboring points in nuclear coordinate space. Since, by virtue of the standard construction conventions, a manifest one-to-one correspondence exists between the orbital bases  $AO'_i$  and  $AO''_i$  at these two points, the similarity between the molecular orbitals  $MO'$  and  $MO''$  can be simply assessed by examining the inner-product-like quantity

$$\langle ab \rangle = \sum_i \hat{a}_i \hat{b}_i, \quad \hat{a}_i = a_i / \sqrt{\sum_j a_j^2}, \quad \hat{b}_i = b_i / \sqrt{\sum_j b_j^2},$$

which satisfies the Schwarz inequality  $-1 \leq \langle ab \rangle \leq 1$ . The correspondence between the various MOs at point  $P'$  and those at point  $P''$  can thus be established by comparing the quantities  $\langle ab \rangle$  for all orbital pairs

between the two points. Two corresponding MOs should have a value of  $|\langle ab \rangle|$  close to unity. If  $\langle ab \rangle$  should turn out to be close to  $-1$ , then the sign of one of the two MOs must be reversed.

If the molecule has the same symmetry for the points  $P'$  and  $P''$ , then the orbitals  $MO'$  and  $MO''$  must of course belong to the same irreducible representation.

### 5 The diabatic transformation

Assume, then, that by means of the tools outlined in Sect. 3 and 4, a set of diabaticization-adapted configurations has been determined that deform unambiguously throughout the nuclear coordinate region and among which a set of dominant configurations can be identified that fall into groups  $G_1, G_2, \dots$  as described in the final subsection of Sect. 2. *The transformation matrix  $T$  will now be determined from the projections of the adiabatic states on the space of the dominant configurations.* According to Eqs. (3) and (5), it will then be applied to the *full* expansions of the adiabatic states to generate diabatic states exhibiting configurational uniformity.

#### 5.1 Calculation of $T$

We first state the formulas for calculating the transformation matrix  $\mathbf{T}$ . The derivation will be given in the next subsection.

The transformation from adiabatic to diabatic states is achieved by the orthogonal matrix

$$\mathbf{T} = \tilde{\mathbf{T}}(\tilde{\mathbf{T}}^\dagger \tilde{\mathbf{T}})^{-1/2} \quad (9)$$

where  $\tilde{\mathbf{T}}$  is the nonorthogonal matrix whose  $k$ -th column,  $\tilde{T}_{nk}$  ( $n = 1, 2, \dots, N$ ) is obtained as the *eigenvector with the largest eigenvalue* of the positive definite  $N \times N$  symmetric matrix

$$\mathbf{R}^{(k)} = \mathbf{S}^{-1/2} \mathbf{S}^{(k)} \mathbf{S}^{-1/2} \quad (10)$$

whose factors are defined as follows. The elements of the matrix  $\mathbf{S}$  are given by

$$S_{nm} = \sum_{\alpha}^* c_{\alpha n} c_{\alpha m}, \quad \text{where} \quad \sum_{\alpha}^* \text{ implies } \alpha = 1, 2, \dots, M, \quad (11)$$

and the elements of the matrix  $S^{(k)}$  are obtained as the sums

$$S_{nm}^{(k)} = \sum_{\alpha}^k c_{\alpha n} c_{\alpha m}, \quad (12)$$

where  $\sum_{\alpha}^k$  implies  $\alpha = a_{k-1} + 1, \dots, a_k$ .

Thus, the sum in Eq. (11) goes over *all* dominant configurations whereas the summation in Eq. (12) goes only over the dominant configurations in the group  $G_k$  and, hence, is different for every  $k$ . It is readily verified that the elements of the matrix  $\mathbf{R}^{(k)}$  can also be expressed in the form

$$R_{mn}^k = \sum_{\alpha}^k c'_{\alpha m} c'_{\alpha n} \quad (13)$$

with

$$c'_{\alpha m} = \sum_m c_{\alpha m} (\mathbf{S}^{-1/2})_{m\alpha}. \quad (14)$$

As in Sect. 2, the indices  $k, m, n$  always run from 1 to  $N$ .

### 5.2 Derivation

According to the discussion in Sect. 2, the desired transformation is to be deduced from the information contained in the dominant parts of the adiabatic states which are given by the truncated expansions

$$\psi'_n = \sum_a^* \lambda_a c_{an} \quad (15)$$

[the definition of the summation symbol was given in Eq. (11)]. By virtue of the orthonormality of the configurational basis, these truncated states are seen to have the overlap matrix

$$\langle \psi'_n | \psi'_m \rangle = S_{nm} \neq \delta_{nm}, \quad (16)$$

where  $\mathbf{S}$  is the matrix defined in Eq. (11). Hence, the  $\psi'_n$  are in general nonorthogonal. Since our objective is the deduction of an orthogonal transformation, the first step is to orthogonalize the  $\psi'_n$  while changing them as little as possible. This is accomplished by a symmetric orthogonalization which yields the *orthogonalized truncated adiabatic states*

$$\psi'_n = \sum_{\alpha}^* \lambda_{\alpha} c'_{\alpha n}, \quad (17)$$

where the  $c'_{\alpha n}$  are the coefficients defined in Eq. (14). As before, all summations over  $n$  and  $m$  run from 1 to  $N$ .

We now determine the particular normalized linear combination of these  $\psi'_n$  which has the largest projection on the configuration space of a specific group  $G_k$ , i.e. which is dominated by the configurations of this group. If such a linear combination is denoted by

$$f = \sum_m \psi'_m t_m = \sum_{\alpha}^* \lambda_{\alpha} d_{\alpha}, \quad d_{\alpha} = \sum_m c'_{\alpha m} t_m, \quad \sum_m t_m^2 = 1, \quad (18)$$

then the square of its projection onto the space of the group  $G_k$  is

$$P_k^2 = \sum_{\alpha}^k d_{\alpha}^2 = \sum_{\alpha}^k \left( \sum_m c'_{\alpha m} t_m \right)^2 = \sum_m \sum_n R_{mn}^k t_m t_n, \quad (19)$$

where the summation over  $\alpha$  is now the one given in Eq. (12) and the matrix  $\mathbf{R}^{(k)}$  is the one defined in Eq. (13). Since the square of the projection is always positive, it assumes its maximal value when the column vector  $\{t_1, t_2, \dots, t_N\}^{\dagger}$  is equal to the eigenvector with the largest eigenvalue of  $\mathbf{R}^{(k)}$ , say  $\{\tilde{T}_{1k}, \tilde{T}_{2k}, \dots, \tilde{T}_{Nk}\}^{\dagger}$ . The linear combination of the orthogonalized truncated diabatic states with the largest projection in the configuration space of group  $G_k$  is thus given by

$$f_k = \sum_m \psi'_m \tilde{T}_{mk}. \quad (20)$$

Such a linear combination can be found for every group  $G_k$ , so that Eq. (20) becomes an  $N \times N$  transformation. However, since the various column vectors in this matrix  $\mathbf{T}$  come from different eigenvalue problems, they are not, in general, mutually orthogonal. Since the  $\psi'_n$ , on the other hand, are orthogonal, the overlap matrix of the functions  $f_k$  is found to be

$$\langle f_j | f_k \rangle = (\tilde{\mathbf{T}}^{\dagger} \tilde{\mathbf{T}})_{jk}. \quad (21)$$

The final step is then to construct orthogonal truncated states  $\phi'_k$  which differ as little as possible from the nonorthogonal functions  $f_k$ . This is achieved by symmetrically orthogonalizing them which leads to

$$\phi'_k = \sum_n \psi'_n T_{nk}, \quad (22)$$

where  $\mathbf{T}$  is just the orthogonal matrix defined in Eq. (9).

These  $N$  orthogonal linear combinations of the orthonormalized truncated adiabatic states are such that each  $\phi'_k$  is dominated by the configurations in one corresponding group  $G_k$ . They thus furnish appropriate diabatic wavefunctions for the truncated adiabatic wavefunctions. Since the latter embody the essential electronic structure characteristics of the actual adiabatic states, it stands to reason that the orthogonal transformation matrix  $\mathbf{T}$  will, similarly, generate diabatic states  $\phi_k$  when used in conjunction with the actual adiabatic states  $\psi_n$ , as expressed by Eqs. (4) and (5).

### 5.3 Sign adjustments

A particular numerical aspect of the diabaticization procedure requires special attention, namely the *continuity of the variation of the diabatic states* and, consequently, of any matrix elements calculated between them over the nuclear coordinate range of interest. Two possible ambiguities in the adiabatic states can lead to apparent discontinuities in the diabatic states. One arises from the fact that the adiabatic wavefunctions are originally obtained by independent CI calculations at different points, a circumstance which can easily cause arbitrary sign changes in going from one point to a neighboring one. The other arises from the geometric phase theorem [16] according to which the adiabatic wavefunctions must change sign after the path followed has completed a full loop around an intersection point, even if their continuity is carefully monitored from point to point.

Since diabatic states do not suffer from the latter complication, numerical confusion is most simply sidestepped by monitoring the resulting *diabatic* states, adjusting their signs, and possibly interchanging their labels, such that *their* configurational coefficients vary continuously over the *entire* region. *Consistent adiabatic* states can then be obtained, a posteriori, by changing, if necessary, the sign of one or several rows of the orthogonal matrix  $\mathbf{T}$  of Eq. (9) at any one point so that the elements of  $\mathbf{T}$  vary continuously relative to neighboring

points. Of course, if a continuous path is followed to completion on a loop around an intersection, then each adiabatic state will have changed its sign after returning to the same point [16].

## 6 Quantitative application

### 6.1 The $1^1A_1$ and $2^1A_1$ states of ozone

We illustrate the described procedure by applying it to the two lowest  $1^1A_1$  states of the  $O_3$  molecule in a region of strong interaction between them, namely in the vicinity of a conical intersection.

We have shown previously [17] that these two adiabatic states have the  $C_{2v}$  restricted PES shown in Fig. 1. The internal coordinates are explained by Fig. 2. They are the Cartesian coordinates of the end atom inside the box with the central atom fixed. The  $1^1A_1$  ground state surface, shown on the left-hand panel, has two minima, viz. the experimentally observed open structure, with an angle of  $116^\circ$ , and the, as yet, experimentally unobserved equilateral triangle ring structure. The latter lies about 30 kcal/mol above the open minimum and slightly above the dissociated species  $O_2 + O$ . A ridge separates the

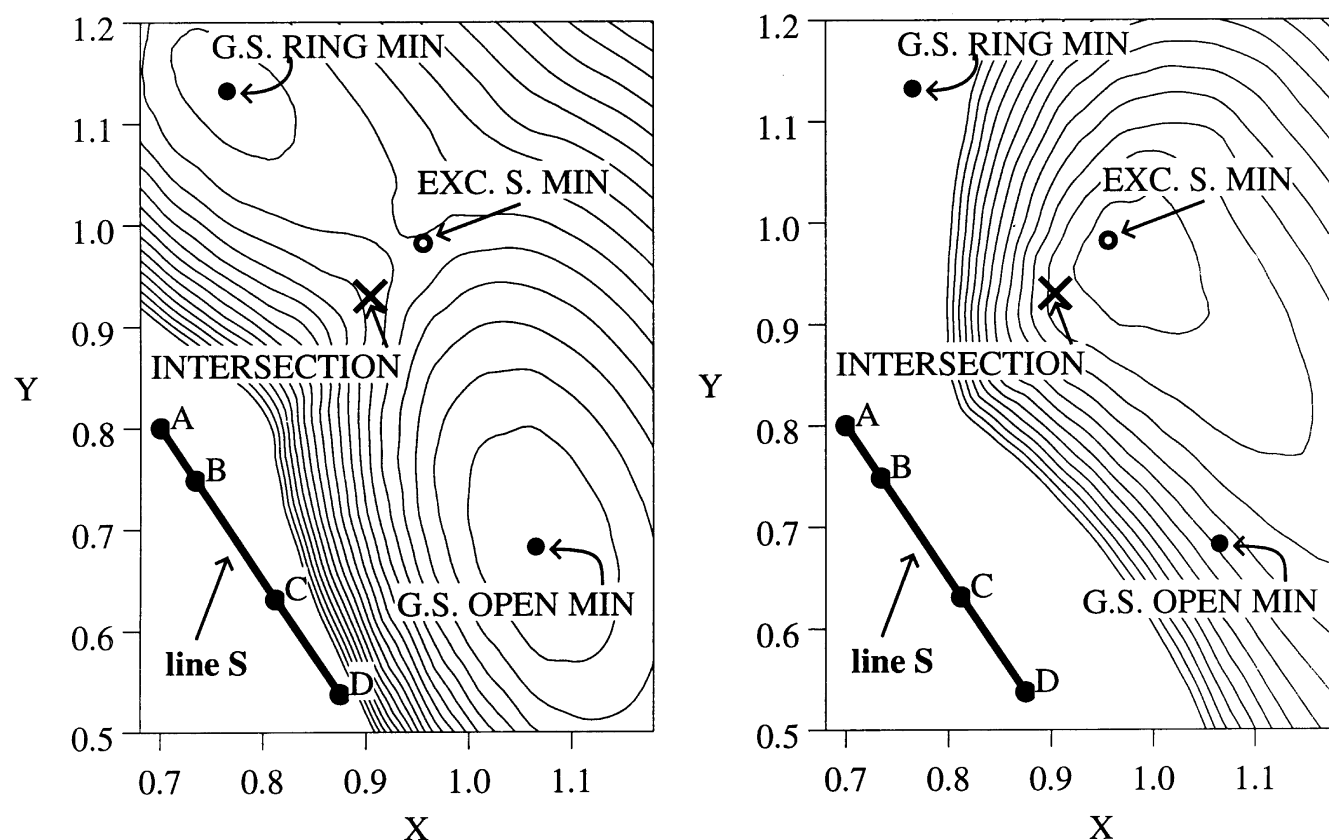
ring-structure basin from the open-structure basin and the minimum on this ridge is the transition state between the aforementioned minima. The excited  $2^1A_1$  state PES, on the other hand, has a minimum which, as shown on the right-hand panel of Fig. 1, lies within  $0.04 \text{ \AA}$  of the transition state of the  $1^1A_1$  PES. In the very same region these two PES of like symmetry touch at the indicated conical intersection.

The previous full-optimized-reaction-space (FORS) calculation [17] utilized a full-valence-space consisting of 4067 configuration state functions (CSFs). Since it showed that the 2s-type MOs are always nearly doubly occupied, we included the latter in the inactive space for the present calculations. This left nine active MOs, generating a full space of 666 spin-adapted CSFs (1788 determinants).

### 6.2 Determination of diabaticization adapted orbitals and configurations

To illustrate our method, we first consider points on the line S in Fig. 1. The determination of the diabaticization adapted orbitals is illustrated for two points,  $B_-$  and  $B_+$ , located within  $0.017 \text{ \AA}$  on either side of the point B

## Adiabatic PES of Ozone



**Fig. 1.** Adiabatic PES of the two lowest  $1^1A_1$  states of ozone. *Left panel:*  $1^1A_1$  ground state, denoted by *G.S.* *Right panel:*  $2^1A_1$  excited state, denoted by *EXC.S.*

which lies on the ridge separating the ring-minimum basin and the open-minimum basin of the ground state. Table 2 shows the distribution of the 12 active electrons over the 9 active orbitals for three orbital types, all of which span the state-averaged-MCSCF optimized full active space, namely the diabaticization-adapted orbitals, the state-averaged natural orbitals and the atom-localized orbitals [18]. It is apparent that, in this case, the diabaticization adaptation method yields orbitals very

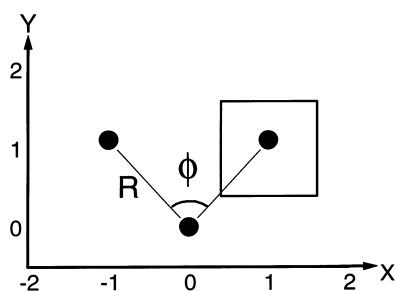


Fig. 2.  $C_{2v}$  restricted internal Cartesian coordinate system for ozone

Table 2. Orbital populations in the adiabatic states  $\psi_1$  and  $\psi_2$  at the points  $B_-$  and  $B_+$  for various molecular orbital choices in the full valence space

MO <sup>a</sup>	Diab-Adpt <sup>b</sup>		Avge-NO <sup>c</sup>		Atom-Loc <sup>d</sup>	
	In $\psi_1$	In $\psi_2$	In $\psi_1$	In $\psi_2$	In $\psi_1$	In $\psi_2$
<i>At point B<sub>+</sub></i>						
1a <sub>1</sub>	1.983	1.986	1.984	1.986	1.108	1.018
2a <sub>1</sub>	1.993	1.864	1.993	1.864	1.502	1.467
3a <sub>1</sub>	0.019	0.016	0.019	0.016	1.385	1.382
1b <sub>2</sub>	1.977	1.981	1.977	1.981	1.034	1.170
2b <sub>2</sub>	1.906	0.235	1.906	0.235	1.899	0.233
3b <sub>2</sub>	0.026	0.020	0.026	0.019	0.975	0.832
1b <sub>1</sub>	1.983	1.999	1.983	1.998	0.867	1.950
2b <sub>1</sub>	0.283	1.922	0.283	1.922	1.399	1.970
1a <sub>2</sub>	1.829	1.977	1.829	1.977	1.829	1.977
SOSQ <sup>e</sup>	45.8094		45.8092		35.8964	
<i>At point B<sub>-</sub></i>						
1a <sub>1</sub>	1.985	1.983	1.985	1.983	1.015	1.110
2a <sub>1</sub>	1.881	1.993	1.881	1.993	1.493	1.521
3a <sub>1</sub>	0.017	0.019	0.017	0.019	1.375	1.365
1b <sub>2</sub>	1.981	1.976	1.981	1.976	1.165	1.021
2b <sub>2</sub>	0.170	1.955	0.170	1.955	0.175	1.952
3b <sub>2</sub>	0.020	0.027	0.020	0.027	0.831	0.984
1b <sub>1</sub>	1.999	1.983	1.999	1.983	1.965	0.863
2b <sub>1</sub>	1.949	0.274	1.949	0.274	1.983	1.393
1a <sub>2</sub>	1.999	1.790	1.999	1.791	1.999	1.791
SOSQ <sup>e</sup>	46.0682		46.0681		36.1375	

<sup>a</sup> The labels a<sub>1</sub>, b<sub>2</sub> denote  $\sigma$  orbitals, symmetric with respect to the molecular plane; the labels b<sub>1</sub>, a<sub>2</sub> denote  $\pi$  orbitals, anit-symmetric with respect to that plane. The molecular orbitals (MOs) of the first two columns are almost identical with those of the third and fourth columns, but different from those in the last two columns

<sup>b</sup> Diabatization-adapted MOs

<sup>c</sup> State-averaged natural orbitals

<sup>d</sup> Atom-localized FORS MOs

<sup>e</sup> Sum of squares of all MO populations in  $\Psi_1$  and  $\Psi_2$

similar to the state-averaged natural orbitals. It is furthermore seen that, for these orbitals,

- (i) the electron population is concentrated into fewer essential orbitals than is the case for the atom-localized orbitals;
- (ii) the two states  $\psi_1, \psi_2$  differ essentially in the occupations of only two orbitals, viz. orbitals Nos. 5 and 8;
- (iii) the occupations of these two orbitals switch their magnitudes upon crossing the ridge from  $B_-$  to  $B_+$ .

The coefficients of the dominant configurations in  $\psi_1$  and  $\psi_2$ , generated from the diabaticization-adapted orbitals, are given in Table 3 for four points shown on the line  $S$  of Fig. 1. It is seen that the expansion in terms of diabaticization-adapted configurations accomplishes

- (i) a separation of dominant configurations from configurations with small coefficients in  $\psi_1$  as well as in  $\psi_2$  since, in both states, four configurations account for over 96% of the normalization;
- (ii) a separation of the dominant configurations in  $\psi_1$  from those in  $\psi_2$ , the configurations  $\chi_1, \chi_2$  forming group  $G_1$  and the configurations  $\chi_3, \chi_4$  forming group  $G_2$ ;
- (iii) that the configurations in each group stay together through the transition region (point B) where both groups contribute to both states.

The renormalized coefficients of the four dominant CSFs  $\chi_1, \chi_2, \chi_3, \chi_4$  for both adiabatic states are displayed in Fig. 3, where the points A, B, C, D of the line  $S$  are also marked. Between A and B, the CSFs  $\chi_3, \chi_4$  dominate in  $1^1A_1$  whereas  $\chi_1, \chi_2$  dominate in  $2^1A_1$ . Both states undergo a switch in character near point B, where the pair of coefficients labeled  $c_1$  and  $c_2$  exchange dominance with the two coefficients  $c_3$  and  $c_4$ . Between C and D, the CSFs  $\chi_1, \chi_2$  dominate in  $1^1A_1$  whereas  $\chi_3, \chi_4$  dominate in  $2^1A_1$ .

### 6.3 Determination of diabaticization transformation

We thus have the situation presumed in Sect. 2, and it is reasonable to expect that two diabatic states can be constructed, each of them dominated throughout by one and the same pair of CSFs.

Application of Eq. (9) at 36 points along the line  $S$  in Fig. 1 yields a continuously varying orthogonal  $2 \times 2$  transformation

$$\mathbf{T} = \begin{pmatrix} \cos \gamma & \sin \gamma \\ -\sin \gamma & \cos \gamma \end{pmatrix}.$$

The variation of the angle  $\gamma$  along the line  $S$  is shown in Fig. 4. The continuity of this curve was achieved by appropriate sign adjustments as discussed in Sect. 5.3. Following  $\gamma$  on a closed loop will of course result in a change of  $\gamma$  by  $\pi$ , yielding the geometric phase change of the adiabatic states [16].

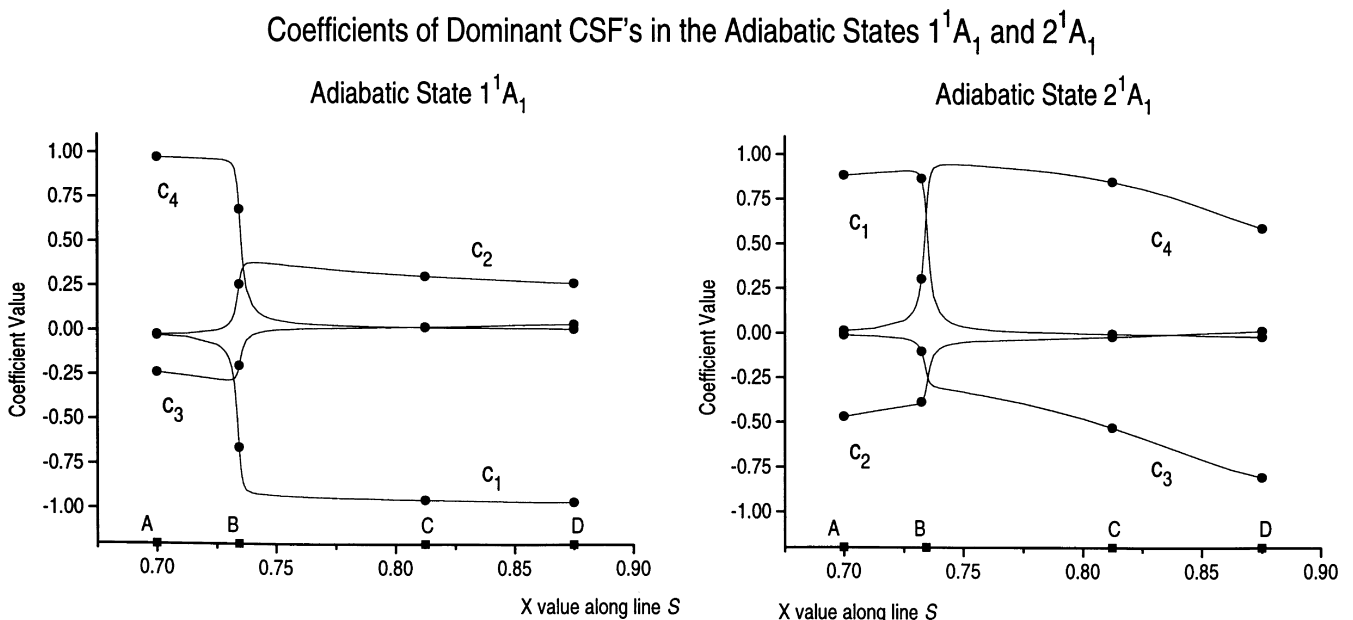
Transformation of the adiabatic states by the matrix  $\mathbf{T}$  yields the coefficients of the diabatic states. The normalized dominant coefficients  $d_{\alpha k}$  of the latter along  $S$



**Table 3.** Coefficients of dominant diabatization-adapted configurations in  $\psi_1$  and  $\psi_2$  at four points on the line  $S$

Configuration <sup>a</sup>	Point A	Point B <sub>-</sub>	Point C	Point D
<i>State <math>\psi_1</math></i>				
$\chi_1 = \dots(2a_1)^2 (2b_2)^2 (2b_1)^2 (1a_2)^0$	-0.0261	0.0099	0.2279	0.2012
$\chi_2 = \dots(2a_1)^2 (2b_2)^2 (2b_1)^0 (1a_2)^2$	-0.0423	-0.1557	-0.9561	-0.9624
$\chi_3 = \dots(2a_1)^2 (2b_2)^0 (2b_1)^2 (1a_2)^2$	0.9634	0.9467	0.0137	0.0068
$\chi_4 = \dots(2a_1)^0 (2b_2)^2 (2b_1)^2 (1a_2)^2$	-0.2090	-0.2335	0.0158	0.0294
$\Sigma c_i^2$	0.9743	0.9751	0.9665	0.9676
<i>State <math>\psi_2</math></i>				
$\chi_1 = \dots(2a_1)^2 (2b_2)^2 (2b_1)^2 (1a_2)^0$	-0.3488	-0.3154	-0.0292	0.0188
$\chi_2 = \dots(2a_1)^2 (2b_2)^2 (2b_1)^0 (1a_2)^2$	0.9158	0.9166	-0.0021	-0.0164
$\chi_3 = \dots(2a_1)^2 (2b_2)^0 (2b_1)^2 (1a_2)^2$	0.0279	0.1446	0.8641	0.5759
$\chi_4 = \dots(2a_1)^0 (2b_2)^2 (2b_1)^2 (1a_2)^2$	-0.0167	-0.0483	-0.4843	-0.8080
$\Sigma c_i^2$	0.9614	0.9629	0.9821	0.9851

<sup>a</sup> Twelve electrons doubly occupy the same six orbitals in all four dominant configurations. Listed are only those orbital occupations in which these configurations differ



**Fig. 3.** Dominant coefficients of the two adiabatic states along the line  $S$  of Fig. 1. The labels  $c_1 - c_4$  refer to the four CSFs in Table 3

are shown in Fig. 5. Each diabatic state is seen to be dominated by only two configurations whose coefficients, moreover, vary only slowly along  $S$ . It should be noted that the two nondominant configurations do *not* have zero coefficients. In both diabatic states, they have an order of magnitude of about  $10^{-2}$ . Comparison of Figs. 3 and 5 reveals the configurational simplification obtained by the transformation to diabatic states.

#### 6.4 The diabatic states

The results obtained along the line  $S$  are in fact found to hold across the entire region encompassing the three minima and the intersection. Indeed, we have shown previously [17, 19, 20] that the adiabatic wavefunctions of the two states are dominated by only four configuration state functions out of a total of 4067 CSFs in the FORS space based on state-averaged natural orbitals. In

the ring basin (the upper left-hand part of each panel in Fig. 1), two of these CSFs are dominant in  $1^1A_1$  and the other two are dominant in  $2^1A_1$ . In the open basin (the lower right-hand part of each panel), the roles of the dominant CSFs in the adiabatic states are reversed.

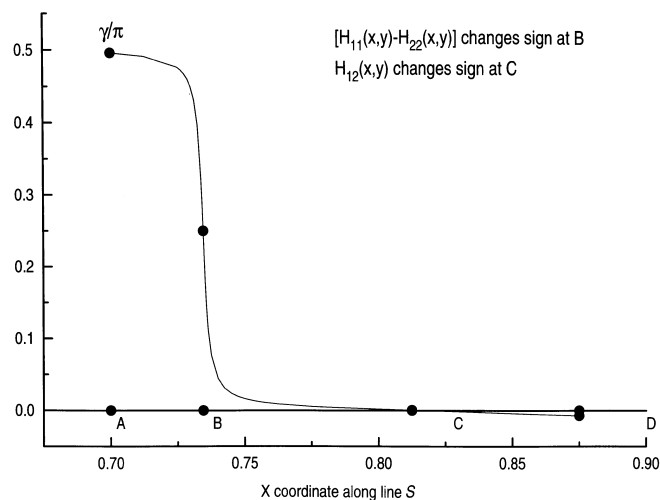
Application of the described procedure over the entire region yields the transformation matrix  $\mathbf{T}$  everywhere. From it, the diabatic states  $\phi_1, \phi_2$  as well as their matrix elements  $H_{jk} = \langle \phi_j | H | \phi_k \rangle$  are found. The diabatic PES  $H_{ii}$  are exhibited in Fig. 6.

Also shown in this figure are the curves  $(H_{11} - H_{22}) = 0$  and  $H_{12} = 0$ . We have discussed elsewhere [21] that the dominance of the diabatic states in the adiabatic states switches upon crossing the curve  $(H_{11} - H_{12}) = 0$  and that the coefficients of the nondominant diabatic admixtures in the adiabatic states change their signs upon crossing the curve  $H_{12} = 0$ . This is indeed confirmed by the plot of Fig. 4 displaying the mixing angle  $\gamma$  along the line  $S$ . It crosses the former curve at point  $B$  where

$\gamma = \pi/2$ , and it crosses the latter curve at point *C* where  $\gamma$  changes its sign. As is well known [22], the conical intersection occurs where the curves  $(H_{11} - H_{22}) = 0$  and  $H_{12} = 0$  cross on Fig. 6.

### 6.5 Comparison to previous algorithm

In Table 4, the diabaticization transformation obtained by the present procedure is compared with the transformation obtained by the algorithm we have given previously [12]. It is apparent that, in this case, the diabatic states obtained by the two methods are identical. For the case of two adiabatic/diabatic states, the previous construc-



**Fig. 4.** Transformation angle  $\gamma$ , expressed in units of  $\pi$ , along the line *S* of Fig. 1

tion of the transformation **T** may be somewhat simpler than that given by Eq. (9)ff., but the present algorithm is considerably simpler when more than two adiabatic/diabatic states are involved.

## 7 Generality

Although the described method has been formulated in the context of a full configuration space, it is readily seen to be equally applicable when the adiabatic states are given in terms of a set of configurations that do not span a full space:

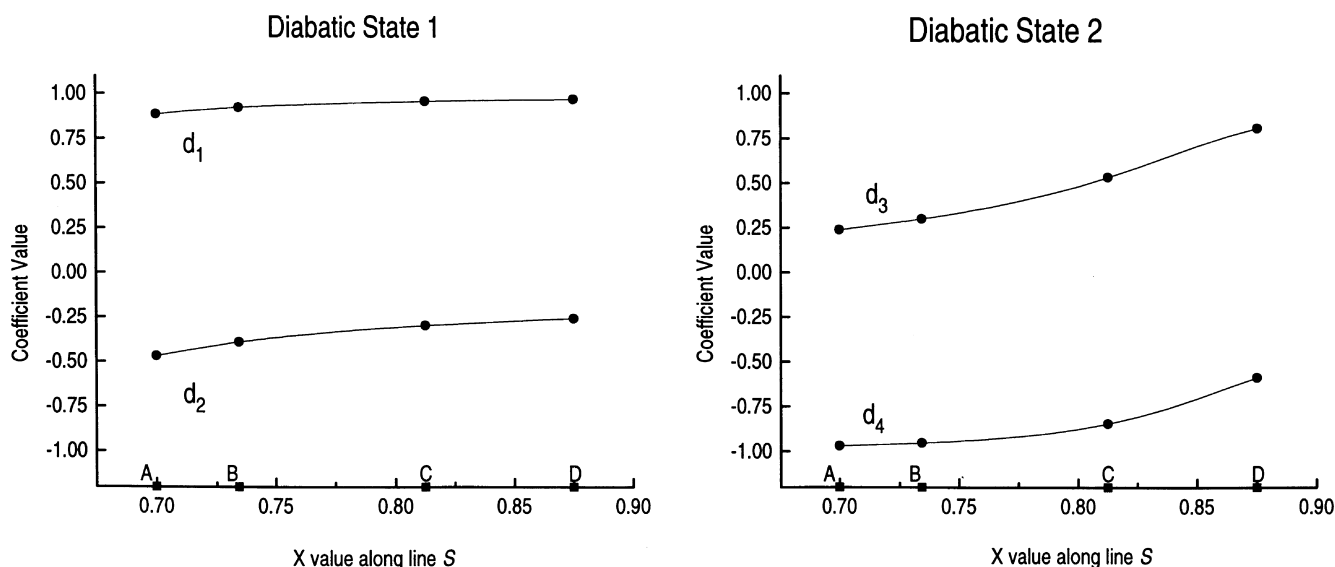
First, the construction of the diabaticization-adapted MOs requires only the first-order density matrices of the adiabatic states and it makes no difference whether the latter originate from a full configuration space or not.

Second, the construction of the diabaticization transformation **T** requires the expansion of the wavefunctions  $\psi_n$  in terms of the diabaticization-adapted configurations. While the total number of the latter may greatly exceed that of the original configurations and, indeed, possibly fill the full configuration space, *only the coefficients of the dominant configurations are required*. As mentioned at the end of Sect. 3, these can be found by direct transformation without solution of any CI problem.

**Table 4.** Comparison of the angles  $\gamma/\pi$  obtained at four points along the line *S* by the present and the previous diabaticization methods

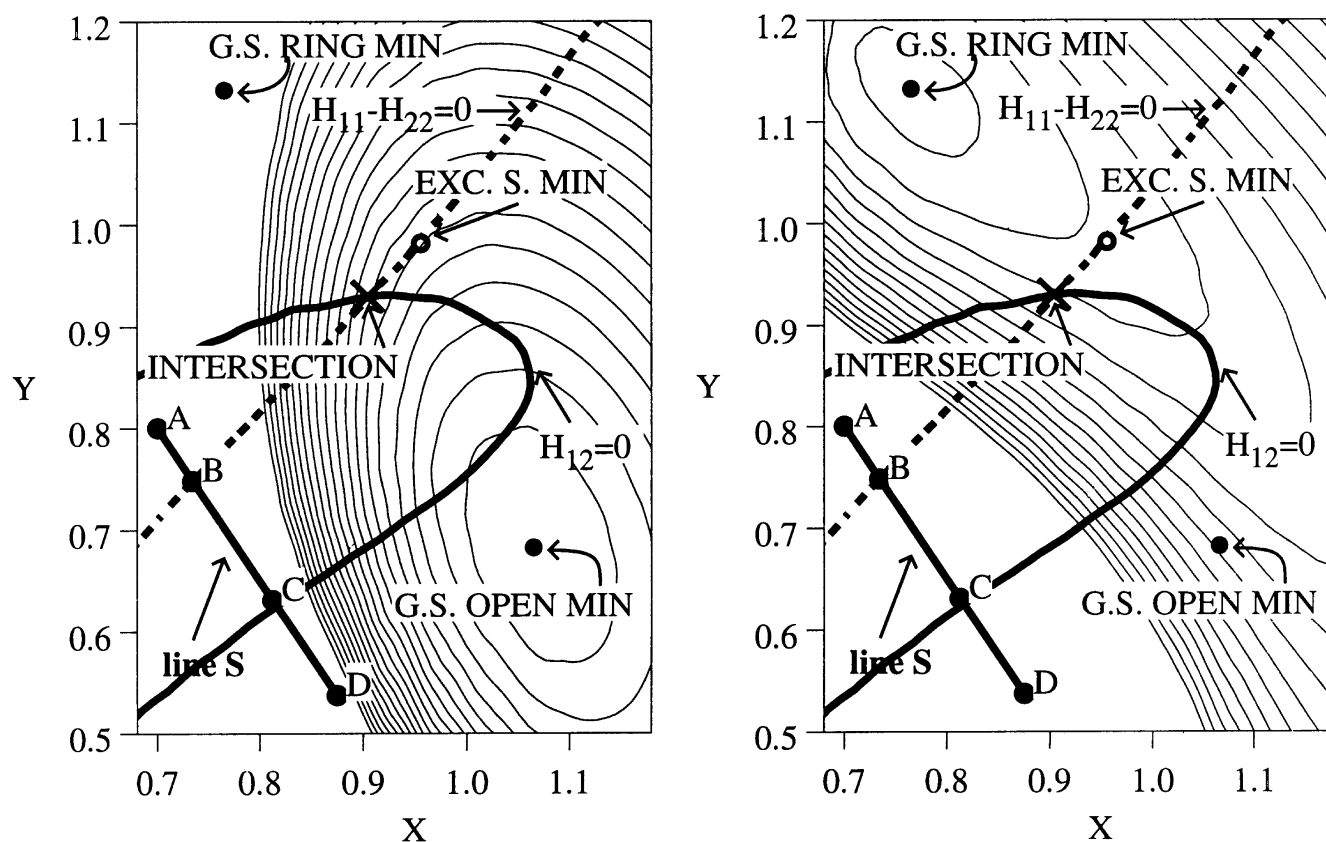
$\gamma/\pi$ from	Point A	Point B	Point C	Point D
Present method	0.49530808	0.24957514	0.00056770	-0.00709466
Previous method [12]	0.49530808	0.24957514	0.00056770	-0.00709466

## Coefficients of Dominant CSF's in the Diabatic States



**Fig. 5.** Dominant coefficients of the two diabatic states along the line *S* of Fig. 1. The labels  $d_1 - d_4$  refer to the same CSF's as in Fig. 3

## Diabatic PES of Ozone



**Fig. 6.** Contours of the diagonal Hamiltonian elements  $H_{11}$ ,  $H_{22}$  for the diabatic states. The critical points of the adiabatic surfaces are marked as in Fig. 1. A dotted line marks the curve  $H_{11} - H_{22} = 0$  and a solid line marks the curve  $H_{12} = 0$  on each panel

Third, after **T** has been calculated through the algorithm of Sect. 5, the diabatic states can be obtained by Eq. (5) from the adiabatic states in terms of the original expansions or in terms of the diabaticization-adapted configurations.

Fourth, the energy matrix between the diabatic states can be obtained directly from the adiabatic energies according to  $\langle \phi_j | \mathcal{H} | \phi_k \rangle = \sum_n E_n T_{nj} T_{nk}$ .

The described procedure is thus completely general. The only question that remains open is whether it is always possible to identify disjoint dominant configuration groups  $G_k$  that can be associated with diabatic states, as described in Sect. 2.3. A prerequisite is certainly that the orbitals and configurations must be sufficient in number for a satisfactory representation of *all* adiabatic states  $\psi_n$  under consideration. This question deserves further exploration.

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