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Reaction-Path Dynamics in Redundant Internal Coordinates

Yao-Yuan Chuang and Donald G. Truhlar*

*Department of Chemistry and Supercomputer Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431**Received: July 23, 1997*

This paper presents a general method for reaction-path calculations with redundant curvilinear internal coordinates. Following Pulay and Fogarasi, the generalized inverse of the Wilson \mathcal{G} matrix is used to remove the redundancy of the curvilinear internal coordinates. An illustrative application to $\text{HBr} + \text{HCCH} \rightarrow \text{H}_2\text{CCHBr}$ is presented, and the results with the new algorithm are compared to calculations with rectilinear coordinates.

1. Introduction

Expressing the potential energy for a chemical reaction in terms of a harmonic expansion around a reaction path has a long history and has established itself as an important practical approach in theoretical and computational dynamics.^{1–13} Our own interest in this approach has centered on its use for variational transition state theory and multidimensional tunneling calculations.^{3,6,10,11,14–17} It is known that the harmonic frequencies depend on the coordinate system, in particular, on the definition of the reaction coordinate for points off the reaction path.^{18,19} (The frequencies are actually ambiguous not only along reaction paths but any time that the gradient does not vanish, for example when *ab initio* force constants are evaluated at an experimental geometry.^{20,21}) We have established that curvilinear internal coordinates provide more physical values for the frequencies along reaction paths than are obtained with rectilinear coordinates.^{19,22–24} (Rectilinear coordinates are any coordinates that can be written as linear combinations of atomic Cartesians, and curvilinear coordinates are any coordinates that cannot so be written.) It has also been pointed out that valence coordinates provide a more rapidly convergent series representation of the anharmonicity than rectilinear coordinates and that they minimize coupling terms.^{10,25,26} (Valence coordinates^{31–33} are the most useful curvilinear internal coordinates; they consist of A–B bond stretches, bending angles between two bonds sharing an atom, e.g., A–B and B–C, and torsions. Proper torsions are dihedral angles between A–B–C and B–C–D planes where an A–B–C–D bonding pattern exists. In some molecules, one needs improper torsions which are more general dihedral angles.) Other workers^{27–30} have also found curvilinear internal coordinates useful for reaction-path calculations, although most work reported to date is based on rectilinear coordinates.

In recent papers, we have presented a general formalism for using nonredundant valence coordinates for calculating reaction-path frequencies.^{22–24} In the present paper we turn to the question of redundant valence coordinates. Redundant valence coordinates arise naturally because the number of valence coordinates for systems with five or more atoms that do not constitute a simple chain usually exceeds $3N - 6$, where N is

the number of atoms. Since only $3N - 6$ coordinates are required to span the vibrational degrees of freedom, the valence coordinates are not unique in such cases. For typical cases in organic chemistry the number of redundancies equals the number of carbon atoms with four bonds (called 4-fold star centers) plus at least one redundancy for each ring. For hypervalent systems and transition states there may be additional redundancies. Usually, one can obtain correct results by arbitrarily omitting one bend coordinate at each 4-fold star center and for each ring; however, there are many reasons why it is preferable to work directly in redundant coordinates. For example,

(1) Omitting one bend coordinate arbitrarily destroys the symmetry in high-symmetry situations.

(2) In complicated cases, it is not always clear which subsets of $3N - 6$ coordinates properly span the vibrational space and which do not.

(3) Redundant coordinates may lead to force fields that are easier to interpolate or more transferable.

(4) For calculations along a reaction path, including all the valence coordinates necessary for a complete description of both reactants and products may lead to redundancies at the transition state. Some chemical reactions (e.g., $\text{HBr} + \text{HCCH} \rightarrow \text{H}_2\text{CCHBr}$) simply cannot be described correctly all along the reaction path with a single set of nonredundant valence coordinates.

Redundant valence coordinates have been used at stationary points since the early days of vibrational spectroscopy,³² and, more recently, general and fully automatic procedures for using redundant coordinates at stationary points and in optimization algorithms have appeared in the literature.^{34,35} The present paper gives a fully automatic general algorithm for using redundant curvilinear coordinates to calculate frequencies along a reaction path. Section 2 presents the theory, and section 3 presents an application to the reaction $\text{HBr} + \text{C}_2\text{H}_2$.

2. Theory

2.1. General. Our algorithm is a combination of the nonredundant reaction-path formulation of Jackels et al.²² and the redundant-coordinate stationary-point formalism of Pulay and Fogarasi.³⁴

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Consider a system with N atoms, and let V denote the potential energy. Following our previous notation,²² the potential energy can be expressed as a Taylor expansion in terms of the displacement of atomic Cartesian coordinates R_i from the reference structure

$$V = V_0 + \sum_i^{3N} G_i(R_i - R_i^0) + \frac{1}{2} \sum_{ij}^{3N} F_{ij}(R_i - R_i^0)(R_j - R_j^0) + \dots \quad (1)$$

or in terms of displacements of curvilinear internal coordinates q_i from the reference structure

$$V = V_0 + \sum_i^F g_i(q_i - q_i^0) + \frac{1}{2} \sum_{ij}^F f_{ij}(q_i - q_i^0)(q_j - q_j^0) + \dots \quad (2)$$

where F is the number of internal coordinates ($\geq 3N - 5$ for linear molecules, and $\geq 3N - 6$ for general polyatomic molecules). A curvilinear coordinate can be written as a power series in the Cartesian displacement coordinates:

$$q_i = \sum_j^{3N} B_{ij}(R_j - R_j^0) + \frac{1}{2} \sum_{j,k}^{3N} C_{jk}^i(R_j - R_j^0)(R_k - R_k^0) + \dots; \quad i = 1, \dots, F \quad (3)$$

in which B_{ij} is an element of the Wilson B matrix³²

$$B_{ij} = \left(\frac{\partial q_i}{\partial R_j} \right) \bigg|_{\{R_k\}=\{R_k^0\}}; \quad i = 1, \dots, F; j = 1, \dots, 3N \quad (4)$$

and C_{jk}^i is an element of the tensor C^i representing the quadratic term

$$C_{jk}^i = \left(\frac{\partial^2 q_i}{\partial R_j \partial R_k} \right) \bigg|_{\{R_k\}=\{R_k^0\}}; \quad i = 1, \dots, F; j, k = 1, \dots, 3N \quad (5)$$

Note that C^i is sometimes³⁶ called B^i .

2.2. Transformation of Gradient Vector and Force Constant Matrix. The Cartesian gradient vector G and force-constant matrix F are given in terms of their curvilinear counterparts g and f by

$$G = B^T g \quad (6)$$

$$F = B^T f B + \sum_i^F g_i C^i \quad (7)$$

As before, the generalized inverse of the Wilson B matrix is^{21,22,34,37,38}

$$A = u B^T (B u B^T)^{-1} \quad (8)$$

where

$$B A = I \quad (9)$$

I is the unit matrix, and u is a diagonal matrix with the reciprocals of the atomic masses on the diagonal. (Any symmetric positive definite matrix would be suitable at this stage of the development, but in order to identify $B u B^T$ with G in the next subsection and to provide a formalism that correctly transforms vector properties such as dipole moments and laboratory-frame reaction-path curvature components we

require this more specific form for u .^{21,39}) With these definitions

$$g = A^T G \quad (10)$$

$$f = A^T F A - \sum_i^F g_i A^T C^i A \quad (11)$$

2.3. The Vibrational Frequencies. In the Wilson \mathcal{GF} matrix method,^{32,40}

$$\mathcal{GF}\mathcal{L} = \mathcal{L}\Lambda \quad (12)$$

where \mathcal{L} is the matrix of the generalized normal mode eigenvectors, Λ is the eigenvalue matrix, \mathcal{G} is $B u B^T$, and \mathcal{F} is the force constant matrix. To compute the vibrational frequencies in the subspace orthogonal to a curvilinear reaction coordinate, \mathcal{F} is the projected Hessian f^P , which is given in curvilinear coordinates by²²

$$f^P = \{1 - p(s)[B u B^T]\} f(s) \{1 - [B u B^T]p(s)\} \quad (13)$$

where $p(s)$ is the nonorthogonal coordinate projection operator given by

$$p(s) = \frac{g g^T}{g^T [B u B^T] g} \quad (14)$$

The vibrational frequencies are given by

$$\omega_m = (\Lambda_{mm})^{1/2} \quad (15)$$

2.4. Transformation of Vibrational Eigenvectors. The eigenvectors obtained from (12) are not normalized. The normalized eigenvector matrix is defined as^{22,32,40}

$$\hat{\mathcal{L}} = \mathcal{L} W \quad (16)$$

where

$$W_{ij} = \sqrt{C_{ij}} \delta_{ij} \quad (17)$$

$$C = \mathcal{L}^{-1} \mathcal{G} (\mathcal{L}^{-1})^T \quad (18)$$

The matrix of Cartesian displacement normal-mode eigenvectors is²²

$$\chi = u B^T \mathcal{G}^{-1} \hat{\mathcal{L}} = A \hat{\mathcal{L}} = A \mathcal{L} W \quad (19)$$

The elements of the normalized generalized normal-mode direction vectors in mass-scaled Cartesian displacement vectors, as needed for the multidimensional tunneling calculations,^{12,14-17} are given by

$$L_{ij} = \frac{(m_i/\mu)^{1/2}}{\left[\sum_k (m_k/\mu) \chi_{kj}^2 \right]^{1/2}} = \frac{m_i^{1/2} \chi_{ij}}{\left[\sum_k m_k \chi_{kj}^2 \right]^{1/2}} \quad (20)$$

Following Pulay and Fogarasi³⁴ the generalized inverse \mathcal{G}^- of the \mathcal{G} matrix required for eq 19 is obtained by solving the following eigenvalue equation.

$$\mathcal{G}(\mathbf{K} \quad \mathbf{K}') = (\mathbf{K} \quad \mathbf{K}') \begin{pmatrix} \Gamma & 0 \\ 0 & 0 \end{pmatrix} \quad (21)$$

where \mathbf{K} consists of the eigenvectors of \mathcal{G} corresponding to

nonzero eigenvalues (denoted by G), and the K' consists of the redundant eigenvectors. This yields

$$\mathcal{G}^- = (K \quad K') \begin{pmatrix} \Gamma^{-1} & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} K^T \\ (K')^T \end{pmatrix} \quad (22)$$

The \mathcal{G}^- matrix is also used to calculate the matrix A required for eqs 10 and 11. In particular, it follows from the development of Pulay and Fogarasi³⁴ that

$$A = uB^T \mathcal{G}^- \quad (23)$$

2.5. Practical Procedures. With the theoretical framework given by eqs 1–23, the calculation at a given point along the reaction path proceeds as follows:

1. Calculate the B matrix and C' tensor using formulas given elsewhere.^{22–24,32,36} (See also the treatment of Miller,⁴¹ although we have not used his formulas.)

2. Calculate \mathcal{G} by

$$\mathcal{G} = BuB^T \quad (24)$$

\mathcal{G}^- by eq 22 and A by eq 23.

3. Calculate the gradient and Hessian in redundant coordinates by eqs 10 and 11.

4. Project the gradient and force constants from redundant internal to nonredundant internal coordinates, with the projector P .

$$P = \mathcal{G} \mathcal{G}^- \quad (25)$$

$$\tilde{f} = P f P \quad (26)$$

$$\tilde{g} = P g \quad (27)$$

Project out the reaction coordinate by plugging \tilde{g} and \tilde{f} into eqs 13 and 14. Obtain the frequencies from eqs 12 and 15.

5. Transform the eigenvectors to the mass-scaled Cartesian coordinate system by eqs 16–20. The inverse of the eigenvector matrix required for eq 18 is obtained by singular value decomposition using a standard algorithm.⁴²

6. Remove the zero eigenvalues and the corresponding eigenvectors and store the remaining eigenvalues and eigenvectors in canonical order (largest to smallest eigenvalue). As a check, we calculate the scalar products of the eigenvectors to confirm that they are orthonormal.

3. Calculations

For several reactions we checked that the new algorithm using redundant coordinates gives frequencies identical with the previous^{22–24} nonredundant-coordinate algorithm. These test cases included $H + H_2$, $H + O_2$, $H + CH_4$, $H + N_2H_2$, $NH_2 + PH_3$, $NH_2 + CH_4$, and $NH_2 + SiH_4$. The first three examples were carried out with potentials given elsewhere,^{43–45} and the last three were calculated by direct dynamics^{46,47} using the AM1⁴⁸ and MNDO⁴⁹ methods. In all cases, the results computed with redundant and nonredundant valence coordinates agree with each other, although they disagree with the results obtained with rectilinear coordinates, which are less physical.

Consider the reaction $NH_2 + CH_4$ as an example. In this case $N = 8$ and $3N - 6 = 18$. However, there are 7 stretches, 10 bends, and 2 torsions. (Usually it is not necessary to include an A–B–C–E torsion if A–B–C–D is already included, and it is this fact that reduces the number of torsions from 5 to 2.) Dropping one H–C–H bend of the spectator methyl group reduces F to 18 in a physically reasonable way (since it is the

TABLE 1: Valence Coordinates for $HBr + HCCH \rightarrow H_2CCHBr$

	reactant	reaction path		product
		before ring formation	after ring formation	
stretches	4	5	6	6
bends, nonlinear	0	6	8	8
bends, linear	4 ^a	0	0	0
torsions	0	1	6	4
total	8	12	20	18
vibrational degrees of freedom	8 ^b	12 ^c	12 ^c	12 ^c

^a Two doubly degenerate linear bends. ^b $3N_{HBr} - 5 + 3N_{HCCH} - 5$. ^c $3N_{total} - 6$.

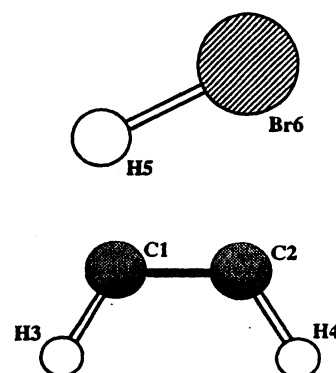


Figure 1. Atom numbering scheme.

4-fold star center that generated the redundancy in the first place), and this calculation agrees with using all 19 internal coordinates. However, dropping either torsion gives smaller frequencies or even zero for low-frequency modes, as expected since the torsional modes are not the modes that generate the redundancy.

Next we considered a more complicated case, namely $HBr + HCCH \rightarrow H_2CCHBr$. This system has $N = 6$ and $3N - 6 = 12$. The number of each type of valence coordinate at various points along the reaction path is summarized in Table 1. Because our goal is to illustrate the calculation of physically meaningful results for a given potential energy function, we did not attempt to obtain a quantitatively accurate potential energy function, but rather we employed direct dynamics calculations based on AM1. AM1 yields a classical barrier height of 51.8 kcal/mol and a classical exoergicity of –26.3 kcal/mol, in qualitative agreement with previous modeling,⁵⁰ which used a potential surface with a barrier height of 48.2 kcal/mol and a classical exoergicity of –33.7 kcal/mol.

In Figure 1 we specify a labeling scheme for the atoms at an arbitrary point along the reaction path, and in Table 2 we list three possible sets of redundant coordinates. Using any of these sets gives the same frequencies along the reaction path, and furthermore the frequencies tend to the correct values for reactants and products (the reactant and product values are unambiguous since the gradient vanishes). However, any attempt to further reduce the number of bends or torsions as compared to sets B or C results in incorrect frequencies. We conclude that no set of nonredundant valence coordinates is sufficient.⁵¹ Furthermore, the use of rectilinear coordinates results in an artifactual imaginary frequency (which is a frequently encountered occurrence for rectilinear coordinates). The frequencies obtained with rectilinear and redundant curvilinear coordinates (set A, B, or C) are compared in Table 3. In this table, s denotes the value of the reaction coordinate, which

TABLE 2: Sets of Valence Coordinates for H₂CCHBr

set	type	no.	specifications
A	stretches	6	1-2 1-3 1-5 2-4 2-6 5-6
	bends	6	12-6 1-5-6 2-1-5 2-6-5 3-1-5 4-2-6
	torsions	6	1-2-6-5 1-5-6-2 2-1-5-6 3-1-5-6 4-2-6-5 5-1-2-6
	total	18	
B	stretches	6	same as A
	bends	6	same as A
	torsions	3	3-1-5-6 4-2-6-5 5-1-2-6
	total	15	
C	stretches	6	same as A
	bends	6	same as A
	torsions	3	1-5-6-2 3-1-5-6 4-2-6-5
	total	15	

TABLE 3: Frequencies along the Reaction Path for HBr + HCCH → H₂CCHBr

mode	reactant	$s = -1.0$	$s = -0.5$	$s = 0.0$	$s = 0.5$	$s = 1.0$	product
1	3475 ^a	3447	3410	3370	3346	3322	3205
2	3422	3387	3362	3336	3310	3261	3172
3	2438	2344, 2295	2068, 2048	1941	1965, 1944	2832, 2791	3151
4	2182	2111, 2108	1865, 1818	1660	1784, 1836	1818, 1824	1810
5	928	933, 925	935, 940	939	1129, 1117	1407, 1404	1397
6	928	926, 903	921, 887	903	967, 1075	1015, 1052	1220
7	805	831, 827	828, 842	863	946, 953	992, 1015	1064
8	804	828, 795	826, 793	804	790, 803	800, 837	1019
9		412, 402	369, 372	629	707, 614	739, 741	939
10		317, 312	348, 356	447	595, 574	678, 464	625
11		280, 230i	332, 317	334	405, 387	398, 391	560
12				2507i			345

^a When a single value is given, it indicates that we obtain the same value using either redundant valence coordinates or rectilinear coordinates. When two values are given, the first value is obtained with redundant valence coordinates and the second value with rectilinear coordinates.

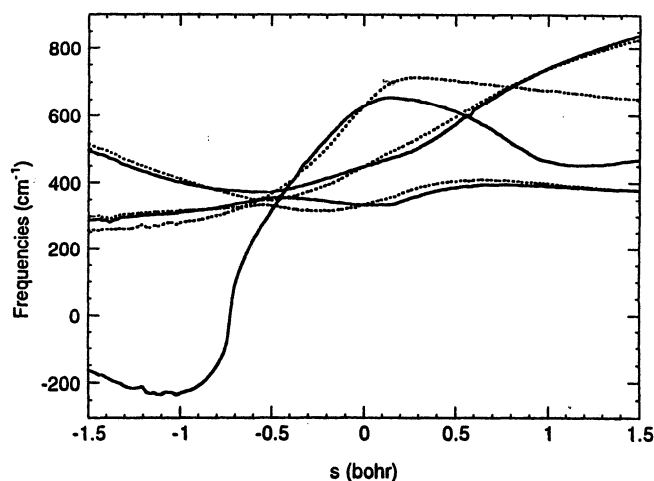


Figure 2. Frequencies of modes 9, 10, and 11 as calculated with redundant curvilinear coordinates (dashed curves) and rectilinear coordinates (solid curves). Imaginary frequencies are plotted as negative numbers for illustrative purposes. The slight oscillatory noise in the curves is due to the numerical nature of the reaction-path calculation.

is defined to be zero at the saddle point. Nonzero values of s may be interpreted as the signed distance in $\text{amu}^{1/2} a_0$ along the minimum energy path in mass-weighted coordinates³² or as the signed distance in a_0 along the minimum energy path in mass-scaled coordinates^{14,15} where all coordinates are scaled to a reduced mass of 1 amu. Note that for nonstationary points along the reaction path, there are only 11 frequencies, not 12, because the reaction coordinate is projected out.

The nonphysical imaginary frequency obtained with rectilinear coordinates shows up in Table 3 in mode 11 at $s = -1.0$. We also see a particularly large deviation between rectilinear

TABLE 4: Rate Constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for HBr + HCCH → H₂CCHBr

T (K)	CVT/ZCT	CVT/LCT	CVT/SCT
Rectilinear			
250	1.5(-50)	2.1(-48)	8.2(-48)
300	2.6(-45)	8.3(-45)	3.9(-44)
400	6.1(-39)	7.0(-39)	1.8(-38)
1000	1.2(-23)	1.2(-23)	1.2(-23)
2400	1.3(-16)	1.3(-16)	1.3(-16)
Curvilinear			
250	8.5(-50)	1.2(-48)	4.3(-48)
300	1.8(-45)	5.5(-45)	2.4(-44)
400	5.4(-39)	6.2(-39)	1.5(-38)
1000	1.2(-23)	1.2(-23)	1.2(-23)
2400	1.2(-16)	1.2(-16)	1.2(-16)
Curvilinear ÷ Rectilinear ^a			
250	0.57	0.55	0.53
300	0.69	0.66	0.62
400	0.89	0.88	0.82
1000	0.97	0.97	0.97
2400	0.94	0.94	0.94

^a Ratios were calculated before rounding the rate constants to two significant figures.

and curvilinear coordinates for mode 10 at $s = +1.0$. If we identify the modes diabatically, this is actually the same mode as mode 10 at $s = -1.0$. This is illustrated in Figure 2 which shows modes 9, 10, and 11 for $-1.5 \leq s \leq 1.5$. The high-frequency modes show smaller percentage errors, but the absolute errors can be very significant. For example, mode 3 shows deviations between the two coordinate systems of 49 cm^{-1} at $s = -1.0$ and 41 cm^{-1} at $s = +1.0$; these would affect the local zero-point energy by 0.06–0.07 kcal/mol. And mode 4 shows deviations between the two coordinate systems of 47 cm^{-1} at $s = -0.5$ and 52 cm^{-1} at $s = 0.5$ in Table 3. The

deviations in all the modes grow rapidly as one leaves $s = 0$; in particular $d\omega/ds|_{s=0}$ is not the same in the two coordinate systems.

Table 4 gives thermal rate constants using canonical variational theory^{6,14,15} (CVT) with three different methods for the tunneling contribution: zero-curvature tunneling^{3,14,15} (ZCT, also called MEPSAG), small-curvature tunneling^{17,52} (SCT, also called CD-SCSAG), and large-curvature tunneling^{15-17,53,54} (LCT, also called LCG3). The rates are small because the reaction barrier is high, 51.8 kcal/mol, for the present example. The most accurate results are expected to be obtained by the microcanonical optimized multidimensional tunneling⁵⁴ (μ OMT) approximation, which selects the greater of the SCT and LCT tunneling results at each energy. For the present problem, the μ OMT results are the same as the SCT results. The table shows that the calculated rate constants are smaller when using curvilinear coordinates. This occurs because the zero-point-corrected barrier profile is wider in curvilinear coordinates, especially for negative s (i.e., on the reactant side of the saddle point).

4. Concluding Remarks

One essential element of calculating the reaction rates with variational transition state theory (VTST) or other reaction-path-based methods is the evaluation of the vibrational frequencies along the reaction path. Our previous studies have shown that using the physically intuitive valence internal coordinates leads to more physical generalized normal-mode frequencies. However, in order to maintain the symmetry of the system studied, permit automatic generation of coordinates, or treat a system along a reaction path with a single set of coordinates, the number of valence coordinates will often be greater than the degrees of freedom of the system. Using different subsets of the valence internal coordinates will sometimes result in different frequencies. The use of redundant valence coordinates alleviates these problems. To permit automatic calculations in the presence of redundancies, the algorithm based on a generalized inverse of the \mathcal{G} matrix, proposed by Pulay and Fogarasi,³⁴ is generalized to treat reaction-path frequencies at locations where the gradient is nonzero, using the formalism of Jackels et al.²² The resulting algorithm is stable and is illustrated for the reaction $\text{HBr} + \text{HCCH} \rightarrow \text{H}_2\text{CCHBr}$. The redundant-valence-coordinate algorithm has been included in versions 7.4 of the computer programs POLYRATE,^{17,55,56} MORATE,^{53,57,58} and GAUSS-RATE,⁵⁹ which are available to interested researchers through the World Wide Web.

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