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Coordinate transformations of cubic force constants and transferability of anharmonic force constants in internal coordinates

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A general approach to transforming cubic anharmonic force constants from the Cartesian coordinates to an arbitrary set of nondegenerate internal coordinates is presented and a computer program performing the transformation is described. It allows one to study the transferability of the cubic anharmonic force constants between similar molecules. The harmonic and anharmonic force constants are calculated at the Hartree–Fock level for the $C_2H_{6-n}F_n$ series. The diagonal cubic force constants for the bond stretching are found to be transferable to the same extent as the quadratic (harmonic) ones. The force constants for the bendings are not directly transferable. The present approach makes it possible to construct anharmonic force fields by fitting parametric functions to the *ab initio* anharmonic force constants in the internal coordinates.

INTRODUCTION

The study of molecular vibrations has traditionally depended on a representation of the molecular potential energy expanded about equilibrium in a Taylor series. Different coordinate systems have been used in this expansion, each with distinct properties. In this paper we discuss the importance of these representations in the calculation of anharmonic force constants and their relationship to transferability of force fields used in molecular dynamics.

The harmonic approximation truncates the Taylor series expansion of the potential energy at the second order and is appropriate only for small nuclear displacements.[1] Within this approximation, normal coordinates correspond to molecular eigenstates and form the basis of irreducible representations.[2] This greatly simplifies calculations for symmetric molecules and has been used extensively in the study of molecular spectra. Harmonic force constants in internal coordinates are the most amenable to physical interpretation, representing a change in energy associated with stretching, bending, and torsional displacements. Expressed in the internal coordinates, harmonic force constants are often transferable between similar molecules and have been used extensively in molecular mechanics[3] and dynamics.[4] Quantum-chemical programs usually calculate force constants in Cartesian coordinates. Harmonic force constants are easily transformed between coordinate systems.[2]

Insight into dynamic processes involving large amplitude motions requires that higher order (anharmonic) terms be included in the series expansion of the potential energy. Of particular interest to us are nonlinear interactions involved in the transport of vibrational energy in polymers and molecules, especially biomolecules. Since the most general case has no local symmetry, and for reasons which we later discuss, only the general nondegenerate valence internal coordinates are considered here, as opposed to the symmetric and pseudosymmetric internal coordinates proposed

by Pulay.[5] If necessary, the force constants in the latter coordinates can be readily calculated as linear combinations of those in valence internal coordinates.

By fitting the *ab initio* potential energy surface of the formate ion with different series expansions in internal coordinates, Maple, Dinur, and Hagler[6] have identified the two most significant amendments to a diagonal, harmonic force field. In order of increasing effectiveness and complexity they are (1) the addition of a diagonal cubic force field, and (2) the addition of cubic cross terms. Anharmonic force constants calculated by quantum-chemical programs are typically more dependable than those determined experimentally; for large molecules *ab initio* calculations are the only way anharmonic force constants can be obtained. Pulay[7] has noted that cubic force constants calculated at the Hartree–Fock (HF) level of approximation are typically within only 1% of those calculated at the correlated level. In contrast, harmonic force constants are usually overestimated by ~ 10% unless the effects of electron correlation are included. Improvements in accuracy and efficiency can be obtained by using higher order analytic derivatives instead of finite difference schemes in the calculation of anharmonic force constants. The calculation of analytic second derivatives, first introduced (among others) by Pople,[8] is commonly available at the HF level of approximation. Analytic third derivatives at the HF level are a standard feature of the CADPAC suite of programs,[9] while analytic fourth derivatives are being developed.[10] As previously mentioned, these derivatives are usually calculated in Cartesian coordinates; their computation is aided by the efficient evaluation of derivatives of the molecular integrals involving Cartesian Gaussian basis functions.[8,11]

Unlike harmonic force constants, the transformation of anharmonic force constants from one coordinate system to another is much more involved. Anharmonic force constants may be converted from the internal coordinates into the Cartesian ones,[12] but the inverse transformation is nontrivial and cannot be used in a general way. To get anharmonic force constants in internal coordinates, force con-

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stants in Cartesian coordinates may first be transformed into normal coordinates, and then into internal coordinates as recently described by Green et al.[13] This procedure uses the **Y** tensor, or the inverse **L** tensor of Hoy, Mills, and Strey.[14] In addition to being circuitous, the **L** tensor used in this transformation has only been tabulated for the special case of torsion from a planar geometry.[14] This precludes the calculation of anharmonic force constants in internal coordinates for several molecules of common interest.

In the present paper we address this problem by introducing a direct transformation of the cubic Cartesian force constants into the internal ones, including general torsional coordinates. Then, using the example of the $C_2H_{6-n}F_n$ molecules, we attempt to demonstrate the transferability of cubic diagonal force constants in internal coordinates and the importance of cubic off-diagonal cross terms.

METHODS

Formulas relating force constants in Cartesian and internal coordinates were originally given by Pariseu, Suzuki, and Overend,[12] and follow directly from the chain rule. The transformation from the internal to the Cartesian harmonic force constants is given by

$$F_{ij}^x = B_i^m B_j^n F_{mn}^s, \tag{1}$$

where

$$F_{mn}^s = \frac{\partial^2 E}{\partial s_m \partial s_n}, \quad F_{ij}^x = \frac{\partial^2 E}{\partial x_i \partial x_j}, \quad B_i^m = \frac{\partial s_m}{\partial x_i}. \tag{2}$$

Here and in the following the Einstein summation convention is used.

For a given molecule with N nuclei, the internal coordinates $(s_i, \ 1 \leqslant i \leqslant 3N-6)$ are explicitly defined analytic functions of the Cartesian coordinates $(x_i, \ 1 \leqslant i \leqslant 3N)$. The terms B_i^m are elements of Wilson's **B** matrix and have been systematically tabulated for all types of internal coordinates.[1] The inverse transformation of Eq. (1) is

$$F_{ij}^s = I_i^m I_j^n F_{mn}^x, \tag{3}$$

where the terms I_i^m are elements of the inverse **B** matrix. Because the **B** matrix is rectangular its inverse transpose $\widetilde{\mathbf{B}}^{-1}$ must be found using the formula

$$\widetilde{\mathbf{B}}^{-1} = (\mathbf{B} \mathbf{M} \widetilde{\mathbf{B}})^{-1} \mathbf{B} \mathbf{M}, \tag{4}$$

where **M** is any matrix that does not cause $\mathbf{B} \mathbf{M} \widetilde{\mathbf{B}}$ to become singular.[15-17]

The transformation of cubic force constants from the internal coordinates into the Cartesian ones is given by

$$F_{ijk}^x = B_i^l B_j^m B_k^n F_{lmn}^s + F_{mn}^s (B_{ij}^m B_k^n + B_{ik}^m B_j^n + B_{jk}^m B_i^n), \tag{5}$$

again a result of the chain rule. The **B** tensor has the elements

$$B_{ij}^m = \frac{\partial^2 s_m}{\partial x_i \partial x_j}, \tag{6}$$

which may be found by straightforward differentiation of the internal coordinates. These terms have been given for stretching and bending,[12] but to our knowledge have never been tabulated for torsion. Furthermore, despite extensive literature searches we have been unable to find the inverse transformation of Eq. (5).

The problem with finding an analytic form for the second derivatives of torsion is purely mechanical; the resulting equations for the **B** tensor require 78 distinct tensor elements, each highly complicated. The potential for mistakes and the inherent tedium of this task make it unattractive. The difficulty in implementing the inverse of Eq. (5) lies in evaluating

$$I_{ij}^m = \frac{\partial^2 x_m}{\partial s_i \partial s_j}, \tag{7}$$

the "inverse **B** tensor" by analogy with Eq. (3). Since the Cartesian coordinates are not uniquely defined in terms of internal coordinates, no general analytic form for these elements is available. Further, we know of no numerical method for their calculation.

To circumvent these difficulties we have made extensive use of the computer algebra program MATHEMATICA.[18] To derive the inverse of Eq. (5), the expansions in both coordinate systems of the total electronic energy relative to that at the equilibrium were compared through the third order of the Taylor series

$$E = (1/2) \sum_{ij} F_{ij}^x \Delta x_i \Delta x_j + (1/6) \sum_{ijk} F_{ijk}^x \Delta x_i \Delta x_j \Delta x_k$$

$$= (1/2) \sum_{ij} F_{ij}^s \Delta s_i \Delta s_j + (1/6) \sum_{ijk} F_{ijk}^s \Delta s_i \Delta s_j \Delta s_k. \tag{8}$$

The symbolic manipulation features of MATHEMATICA were used to differentiate both sides of Eq. (8) three times with respect to the unique permutations of x_i, x_j, and x_k. Assuming an equilibrium geometry, each Δx and Δs was then set to zero resulting in equations for the matrix elements of the tensor F^s. Solving this system of equations for each element F_{ijk}^s led to the following general formula [cf. Eq. (3)]:

$$F_{ijk}^s = I_i^l I_j^m I_k^n F_{lmn}^x - B_{mn}^l$$

$$\times (F_{il}^s I_j^m I_k^n + F_{jl}^s I_i^m I_k^n + F_{kl}^s I_i^m I_j^n). \tag{9}$$

MATHEMATICA was also used to derive explicit FORTRAN statements for the **B** matrix and the **B** tensor for the stretching, bending, and torsional internal coordinates. We used the following standard analytic functions defining internal coordinates:

$$s_{IJ} \equiv r_{IJ} = (\mathbf{r}_{IJ} \cdot \mathbf{r}_{IJ})^{1/2}, \tag{10a}$$

$$s_{IJK} \equiv \phi_{IJK}, \quad \cos \phi_{IJK} = -r_{IJ}^{-1} r_{JK}^{-1} (\mathbf{r}_{IJ} \cdot \mathbf{r}_{JK}), \tag{10b}$$

and

$$s_{IJKL} \equiv \tau_{IJKL},$$

$$\sin \tau_{IJKL} = (r_{IJ} r_{JK} r_{KL} \sin \phi_{IJK} \sin \phi_{JKL})^{-1}$$

$$\times (\mathbf{r}_{IJ} \times \mathbf{r}_{JK}) \cdot \mathbf{r}_{KL}, \tag{10c}$$

where the difference Cartesian coordinates,

$$\mathbf{r}_{IJ} \equiv (r_{IJ,1}, \ r_{IJ,2}, \ r_{IJ,3}) = \mathbf{R}_J - \mathbf{R}_I, \tag{11}$$

are given in terms of the $3N$ Cartesian coordinates,

$$\mathbf{R}_I \equiv (R_{I,1}, \ R_{I,2}, \ R_{I,3}) \equiv (x_{3I-2}, \ x_{3I-1}, \ x_{3I}),$$

$$\text{for} \ 1 \leqslant i \leqslant N. \tag{12}$$

As a sample of our results, we list here the second element of the **B** tensor for torsion which reads

$$\frac{\partial^2 \tau_{IJKL}}{\partial R_{I,1} \partial R_{I,2}} = \frac{r_{IJ,1} r_{IJ,2} \tan \tau_{IJKL}}{r_{IJ}^4 \sin^2 \phi_{IJK}} + \tan \tau_{IJKL} \frac{\partial \tau_{IJKL}}{\partial R_{I,1}} \frac{\partial \tau_{IJKL}}{\partial R_{I,2}} + \frac{r_{IJ,2}}{r_{IJ}^2} \frac{\partial \tau_{IJKL}}{\partial R_{I,1}} + \frac{r_{IJ,1}}{r_{IJ}^2} \frac{\partial \tau_{IJKL}}{\partial R_{I,2}}$$
$$+ \frac{\tan \tau_{IJKL}}{\sin^2 \phi_{IJK}} \frac{\partial \phi_{IJK}}{\partial R_{I,1}} \frac{\partial \phi_{IJK}}{\partial R_{I,2}} - \cot \phi_{IJK} \left(\frac{\partial \tau_{IJKL}}{\partial R_{I,1}} \frac{\partial \phi_{IJK}}{\partial R_{I,2}} + \frac{\partial \tau_{IJKL}}{\partial R_{I,2}} \frac{\partial \phi_{IJK}}{\partial R_{I,1}} \right), \tag{13}$$

where the first partial derivatives are just the elements of the B matrix. The FORTRAN statements defining the B matrix and the B tensor together comprise approximately 1800 lines of code.

On the surface this may appear to be an inefficient method for evaluating the B tensor, compared with the numerical differencing schemes of Gwinn[19] or Hilderbrandt.[20] However, in checking our results we found that using the fourth order central differences was about 3 orders of magnitude slower and also less accurate (we compared the numerics with an analytic test using MATHEMATICA).

We have implemented these developments in the program ANHTRAX.[21] ANHTRAX reads the geometry, harmonic and cubic force constants in the Cartesian coordinates together with the molecular connectivity from a GAUSSIAN 88[22] checkpoint file. Alternatively, the user can redefine the connectivity. ANHTRAX then calculates the harmonic and cubic force constants in the chosen set of internal coordinates. Due to the assumption of an equilibrium geometry in the derivation of Eq. (9), the geometry used to calculate the force constants must come from a well converged optimization.

After the B matrix is constructed and its inverse is computed, it is contracted with the B tensor as its elements are calculated. The product of the resulting intermediate tensor with the quadratic force constants is then summed over three permutations to generate the last term in Eq. (9). This approach allows us to take full advantage of all permutational symmetry in matrices and tensors, resulting in an optimal usage of memory and savings in the CPU time.

In order to test the transferability of diagonal cubic force constants and to demonstrate the performance of our approach, we calculated the harmonic and cubic force constants in internal coordinates for the molecular series of C_2H_6, $1,2$-$C_2H_4F_2$, $1,1,1$-$C_2H_3F_3$, $1,1,2,2$-$C_2H_2F_4$, and C_2F_6. The ab initio calculations were carried out at the HF/6-311G** level of approximation with the GAUSSIAN 88 suite of programs[22] running on a CRAY Y-MP4/32 supercomputer. Each minimum energy conformation was optimized with very tight convergence criteria, followed by calculation of the harmonic and cubic force constants in the Cartesian coordinates (note that GAUSSIAN 88 calculates the cubic force constants as numerical derivatives of the quadratic force constants). The force constants were transformed to the internal coordinates by ANHTRAX, using the molecular connectivity displayed in Fig. 1.

RESULTS AND DISCUSSION

For each of the five molecules discussed in this paper, 153 harmonic and 969 cubic force constants were calculated. Running each force constant transformation took only 3 ms on a CRAY Y-MP4/32 supercomputer.

The bond lengths and bond angles, together with the respective diagonal harmonic (quadratic) and anharmonic (cubic) force constants are shown in Tables I–V. The variation in both the harmonic and anharmonic constants for the C–C stretching is of the order of 13% (Table I). The variation is reduced to 6% for the C–H stretching (Table II), whereas for the C–F stretching, it is as large as 20% (Table III). This means that although the force constants are not strictly transferable, they can be approximated using parametric functions that are often employed in the construction of force fields. In particular, we find that with the knowledge of the corresponding bond lengths and the harmonic force constants, it is possible to approximate the anharmonic force constants using simple formulas

$$F^s_{CC,CC,CC} = -7.6 r^{-1}_{CC} F^s_{CC,CC}, \tag{14a}$$

$$F^s_{CH,CH,CH} = -6.1 r^{-1}_{CH} F^s_{CH,CH}, \tag{14b}$$

and

$$F^s_{CF,CF,CF} = -7.9 r^{-1}_{CF} F^s_{CF,CF}. \tag{14c}$$

These equations yield values of the diagonal cubic force constants within 1% of error, which indicates that although the cubic force constants for the bond stretching are not directly transferable, the respective ratios of force constants and bond lengths are.

A different picture is presented by the diagonal cubic force constants for the C–C–H and C–C–F bendings (Tables IV and V). They are about 1 order of magnitude smaller than the force constants for bond stretchings, and there is no apparent correlation between the cubic and quadratic force constants, and the bond lengths. This is not surprising since all nonbonded interactions, expected to be large for molecules with fluorine atoms, are implicit in these force constants. While no general trends emerge regarding these parameters, they certainly characterize the molecules in question and may be used in fitting potential energy functions.

Except for the $1,2$-$C_2H_4F_2$ and $1,1,2,2$-$C_2H_2F_4$ mole-

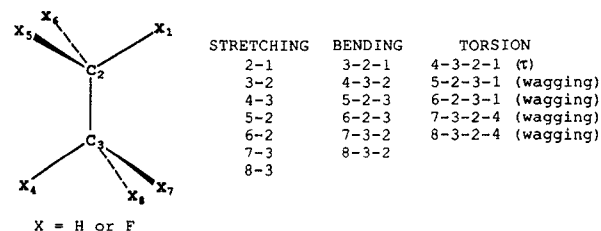| STRETCHING	BENDING	TORSION	
2-1	3-2-1	4-3-2-1	(τ)
3-2	4-3-2	5-2-3-1	(wagging)
4-3	5-2-3	6-2-3-1	(wagging)
5-2	6-2-3	7-3-2-4	(wagging)
6-2	7-3-2	8-3-2-4	(wagging)
7-3	8-3-2		
8-3			

X = H or F

FIG. 1. The atomic connectivity used in the definition of internal coordinates. Note that in the $C_2H_4F_2$ molecule $X_1 = X_4 = F$, whereas in $C_2H_2F_4$ $X_1 = X_4 = H$.

TABLE I. The C–C bond lengths and the diagonal quadratic and cubic force constants for the C–C stretching.[a]

Molecule	r_{CC}	$F^s_{CC,CC}$	$F^s_{CC,CC,CC}$
C_2H_6	2.8857	0.3165	− 0.8279
$1,2$-$C_2H_4F_2$	2.8547	0.3343	− 0.8997
$1,1,1$-$C_2H_3F_3$	2.8290	0.3511	− 0.9477
$1,1,2,2$-$C_2H_2F_4$	2.8572	0.3414	− 0.9227
C_2F_6	2.8902	0.3429	− 0.9059

[a] All values in atomic units.

TABLE II. The C–H bond lengths and the diagonal quadratic and cubic force constants for the C–H stretching.[a]

Molecule	r_{CH}	$F^s_{CH,CH}$	$F^s_{CH,CH,CH}$
C_2H_6	2.0526	0.3624	− 1.0823
$1,2$-$C_2H_4F_2$	2.0447	0.3742	− 1.1129
$1,1,1$-$C_2H_3F_3$	2.0447	0.3768	− 1.1046
$1,1,2,2$-$C_2H_2F_4$	2.0398	0.3855	− 1.1388

[a] All values in atomic units.

TABLE III. The C–F bond lengths and the diagonal quadratic and cubic force constants for the C–F stretching.[a]

Molecule	r_{CF}	$F^s_{CF,CF}$	$F^s_{CF,CF,CF}$
$1,2$-$C_2H_4F_2$	2.5824	0.4311	− 1.3073
$1,1,1$-$C_2H_3F_3$	2.4972	0.4839	− 1.5443
$1,1,2,2$-$C_2H_2F_4$	2.5167	0.4806	− 1.5031
C_2F_6	2.4683	0.5263	− 1.6808

[a] All values in atomic units.

TABLE IV. The C–C–H bond angles and the diagonal quadratic and cubic force constants for the C–C–H bending.[a]

Molecule	ϕ_{CCH}	$F^s_{CCH,CCH}$	$F^s_{CCH,CCH,CCH}$
C_2H_6	111.191	0.2514	− 0.0730
$1,2$-$C_2H_4F_2$	110.899	0.2708	− 0.0822
$1,1,1$-$C_2H_3F_3$	109.254	0.2455	− 0.1127
$1,1,2,2$-$C_2H_2F_4$	112.022	0.2932	− 0.0432

[a] Bond angles in degrees, force constants in atomic units.

TABLE V. The C–C–F Bond angles and the diagonal quadratic and cubic force constants for the C–C–F bending.[a]

Molecule	ϕ_{CCF}	$F^s_{CCF,CCF}$	$F^s_{CCF,CCF,CCF}$
$1,2$-$C_2H_4F_2$	108.049	0.3983	− 0.4005
$1,1,1$-$C_2H_3F_3$	111.707	0.5569	− 0.2284
$1,1,2,2$-$C_2H_2F_4$	108.685	0.4585	− 0.4242
C_2F_6	109.803	0.5243	− 0.3421

[a] Bond angles in degrees, force constants in atomic units.

TABLE VI. Off-diagonal quadratic and cubic force constants coupling the C–C stretching with the C–C–H bending.[a]

Molecule	$F^s_{CC,CCH}$	$F^s_{CC,CCH,CCH}$	$F^s_{CC,CC,CCH}$
C_2H_6	0.0331	− 0.0804	− 0.0229
$1,2$-$C_2H_4F_2$	0.0298	− 0.0789	− 0.0209
$1,1,1$-$C_2H_3F_3$	0.0252	− 0.0584	− 0.0061
$1,1,2,2$-$C_2H_2F_4$	0.0215	− 0.0642	− 0.0116

[a] All values in atomic units.

cules, all diagonal cubic force constants for wagging are equal to zero by symmetry. Likewise, all force constants involving odd derivatives with respect to torsion vanish. The off-diagonal force constants coupling the the C–C stretching with C–C–H bending appear in Table VI. Table VII shows the off-diagonal force constants linking the C–C stretching with the C–C–F bending. In Table VIII the off-diagonal force constants coupling the torsion (τ, Fig. 1) with stretching and bending are given.

One of the interesting results of this study is the presence of the large off-diagonal force constants in Tables VI–VIII. In particular, one should note the relative size of the quadratic and cubic force constants linking the bending with the C–C stretching. In Table VIII, the $F^s_{CC,\tau,\tau}$ column contains the largest of these force constants and $F^s_{CF,\tau,\tau}$ changes sign for C_2F_6. These cubic force constants represent the first order coupling of torsion with other internal degrees of freedom. The importance of this coupling in dynamical systems has been experimentally verified with the examples of IVR in the ground state of trans-stilbene[23] and the S_1 excited state of p-fluorotoluene.[24] In a recent letter, Ozkabak and Goodman[25] describe the pointwise evaluation of fully relaxed ab initio torsional potentials for several small dimethyl molecules. They conclude that steric hindrance generated by methyl rotation leads to skeletal flexing of valence angles. Our results suggest that, for the $C_2H_{6-n}F_n$ series, deformation of the C–C bond is as significant as flexing of the valence angles upon torsion.

CONCLUSIONS

Our general method for calculating cubic force constants in the general valence internal coordinates has made it possible to study their transferability between similar molecules. We have shown that, within the series of $C_2H_{6-n}F_n$ molecules, the cubic diagonal force constants are as transfer-

TABLE VII. Off-diagonal quadratic and cubic force constants coupling the C–C stretching with the C–C–F bending.[a]

Molecule	$F^s_{CC,CCF}$	$F^s_{CC,CCF,CCF}$	$F^s_{CC,CC,CCF}$
$1,2$-$C_2H_4F_2$	0.0191	− 0.1342	− 0.0291
$1,1,1$-$C_2H_3F_3$	0.0390	− 0.1677	− 0.0589
$1,1,2,2$-$C_2H_2F_4$	0.0279	− 0.1603	− 0.0443
C_2F_6	0.0296	− 0.1706	− 0.0473

[a] All values in atomic units.

TABLE VIII. Off-diagonal cubic force constants coupling the 4-3-2-1 (Fig. 1) torsion (τ) with stretching and bending.[a]

Molecule	$F^s_{CC,\tau,\tau}$	$F^s_{CH,\tau,\tau}$	$F^s_{CF,\tau,\tau}$	$F^s_{CCH,\tau,\tau}$	$F^s_{CCF,\tau,\tau}$
C_2H_6	-0.0461	0.0037	$\cdots$	-0.0169	$\cdots$
$1,2$-$C_2H_4F_2$	-0.0493	0.0024	-0.0116	-0.0088	-0.0575
$1,1,1$-$C_2H_3F_3$	-0.0524	0.0037	-0.0033	-0.0130	-0.0300
$1,1,2,2$-$C_2H_2F_4$	-0.0799	0.0029	-0.0021	-0.0066	-0.0533
C_2F_6	-0.0983	$\cdots$	0.0019	$\cdots$	-0.0530

[a] All values in atomic units.

able as the harmonic force constants. While our test molecules have a high degree of symmetry, we have not expressed our results in the internal symmetry[5] or degenerate valence coordinates. The methodology described here can be generalized to include these coordinates after trivial modifications in the ANHTRAX program.

Although the other force constants are not directly transferable, they may be used to parameterize a variety of analytic functions for different functional groups and structural motifs; in this way anharmonic force fields can be built up even for large molecules. The ability of program ANHTRAX to redefine the molecular connectivity is a particular advantage in probing anharmonic effects. For instance, the influence of torsion on hydrogen bonding could be studied by redefining the connectivity to include hydrogen bonds. Also, for large amplitudes certain choices of internal coordinates may be more appropriate than others.[6]

The programming techniques used in ANHTRAX make it capable of interfacing with any quantum-chemical program producing third derivatives of the energy in Cartesian coordinates. Moreover, the algebraic methods used in our MATHEMATICA programming can easily be extended to the fourth order. Finally, the derived analytic form of the **B** tensor may have a general utility in conjunction with the Newton–Raphson algorithm, used for finding minima and transition states on the molecular potential energy hypersurfaces.[3,4,20]

ACKNOWLEDGMENTS

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