
Calculation of Intramolecular Force Fields from Second-Derivative Tensors

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Received February 24, 1996; revised manuscript received March 13, 1996; accepted March 18, 1996

ABSTRACT

A practical procedure (FUERZA) to obtain internal force constants from Cartesian second derivatives (Hessians) is presented and discussed. It allows a systematic analysis of pair atomic interactions in a molecular system, and it is fully invariant to the choice of internal coordinates of the molecule. Force constants for bonds or for any pair of atoms in general are defined by means of the eigenanalysis of their pair interaction matrix. Force constants for the angles are obtained from their corresponding two-pair interaction matrices of the two bonds or distances forming the angle, and the dihedral force constants are similarly obtained using their corresponding three-pair interaction matrices.

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Introduction

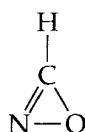
Classical molecular dynamics methods that analyze the time evolution of macroscopic systems for several thousands of time steps or conformations have become very effective tools for gaining insight into a variety of macroscopic systems and processes [1, 2]. Most of this work has involved the use of empirical force fields obtained from experimental measurements of geometries, heats of formation, vibrational frequencies, and barrier heights. However, with the increasing accuracy and availability of first-principles methods (standard *ab initio* and density functional theory), there is a growing tendency to obtain the force field data from high-level computations on the

basic molecular units [3–7]. This makes it possible to treat macroscopic systems that have not yet been investigated experimentally or that may not even exist at present.

In early molecular dynamics (MD) simulations, there was only limited use of intramolecular force fields, primarily because the time step could be increased more than twofold when molecules were constrained to having fixed bond lengths and sometimes angles (the SHAKE method [8]). However, for studying the effects of external factors, such as temperature and pressure, upon molecular properties of a fluid [9–11], e.g., shifts in vibrational spectra [12], the force field clearly must include an intramolecular component.

If the intramolecular portion of the force field is expressed in terms of force constants corresponding to molecular internal coordinates (bond lengths,

bond angles, and dihedral angles), then a significant problem that arises is that of assuring invariance of the individual internal force constants with respect to the chosen set of internals. A given molecule can be described by various sets of internal coordinates, and these may give different values for a particular internal coordinate force constant. Thus the internal force constants, and therefore their intramolecular force field, are not invariant to the choice of internal coordinates. This is due to fact that physical force constants are tensors of rank 2, but we want to use them in practical MD simulations as scalars (tensors of rank 0). An example of this problem can be visualize with the cyclic chon molecule:



A quick HF/STO-3G calculation yields a force constant for the CO bond of 0.54 a.u. if the chosen internals are the CO bond, CN bond, and NCO angle; 0.57 a.u. if we choose the CO bond, NO bond, and CON angle; and 0.26 a.u. if we choose redundant internal coordinates [13] CO, NO, CN,

CNO, NOC, and OCN (for the sake of clarity, the coordinates containing the hydrogen atom are not mentioned in this example). The choice of a value of the force constant to be used in MD calculations is therefore ambiguous. In this study, we present a procedure to compute, in an invariant fashion, the force constants corresponding to internal coordinates.

Background

The 3N component reaction force $\delta\mathbf{F}$ due to a displacement $\delta\mathbf{x}$ of the N atoms in a molecular system can be expressed exactly to second order on a Taylor series expansion as

$$\delta\mathbf{F} = -[k]\delta\mathbf{x}, \quad (1)$$

where $[k]$, the Hessian, is a tensor of rank 2 and dimension $3N \times 3N$ defined by

$$[k] = k_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}. \quad (2)$$

Explicitly, Eq. (1) can be written as

$$\begin{bmatrix} \delta F_1 \\ \delta F_2 \\ \delta F_3 \\ \vdots \\ \delta F_{3N} \end{bmatrix} = - \begin{bmatrix} \frac{\partial^2 E}{\partial x_1^2} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \frac{\partial^2 E}{\partial x_1 \partial x_3} & \cdots & \frac{\partial^2 E}{\partial x_1 \partial x_{3N}} \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2^2} & \frac{\partial^2 E}{\partial x_2 \partial x_3} & \cdots & \frac{\partial^2 E}{\partial x_2 \partial x_{3N}} \\ \frac{\partial^2 E}{\partial x_3 \partial x_1} & \frac{\partial^2 E}{\partial x_3 \partial x_2} & \frac{\partial^2 E}{\partial x_3^2} & \cdots & \frac{\partial^2 E}{\partial x_3 \partial x_{3N}} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 E}{\partial x_{3N} \partial x_1} & \frac{\partial^2 E}{\partial x_{3N} \partial x_2} & \frac{\partial^2 E}{\partial x_{3N} \partial x_3} & \cdots & \frac{\partial^2 E}{\partial x_{3N}^2} \end{bmatrix} \begin{bmatrix} \delta x_1 \\ \delta x_2 \\ \delta x_3 \\ \vdots \\ \delta x_{3N} \end{bmatrix}. \quad (3)$$

Tensor $[k]$ can be obtained by procedures available in density functional theory and ab initio programs such as deMon [14, 15] and Gaussian 94 [16].

The tensor $[k]$ represents the intramolecular force field to second order for small displacements $\delta\mathbf{x}$. The eigenvalues λ_i of $[k]$ are the 3N force

constants corresponding to the 3 translational, 3 rotational and $3N-6$ vibrational modes of the system. The eigenvectors \hat{v}_i of the Hessian $[k]$ indicate the directions of the displacements of the normal modes corresponding to each eigenvalue. If a displacement of magnitude δr occurs in the direction of one of these eigenvectors, the reaction force acts exclusively parallel or antiparallel to that

direction:

$$F_i = -[k]\hat{v}_i\delta r = -\lambda_i\hat{v}_i\delta r. \quad (4)$$

Displacements in any other direction result, in most cases, in a reaction force that is not in the direction of the displacement vector.

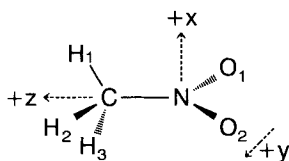
The use of the symmetric tensor $[k]$ in a molecular simulation could be cumbersome because of the large number of independent elements, $3N(3N + 1)/2$. Many of these may be relatively small in magnitude, as is shown in Figure 1 for the case of nitromethane. A more practical approach is to re-

late the force field to internal coordinates, which can generally reduce the number of terms to as few as $3N-6$. The potential energy function is then

$$V = \sum_{\text{bonds}} \frac{1}{2}k_b(b - b_0)^2 + \sum_{\text{angles}} \frac{1}{2}k_\theta(\theta - \theta_0)^2 + \sum_{\text{dihedrals}} \frac{1}{2}k_\phi(\phi - \phi_0)^2 + \sum_{\text{impropers}} \frac{1}{2}k_\omega(\omega - \omega_0)^2 \quad (5)$$

	X _N	Y _N	Z _N	X _C	Y _C	Z _C	X _{H1}	Y _{H1}	Z _{H1}	X _{H2}	Y _{H2}	Z _{H2}	X _{H3}	Y _{H3}	Z _{H3}	X _{O1}	Y _{O1}	Z _{O1}	X _{O2}	Y _{O2}	Z _{O2}
X _N	489	0	-7	-201	0	-4	9	0	-84	-1	-6	38	-1	6	38	-147	8	9	-147	-8	9
Y _N	0	1934	0	0	-164	0	0	-5	0	-1	-7	-69	1	-7	69	12	-875	-372	-12	-875	372
Z _N	-7	0	1322	1	0	-231	-1	0	-39	-6	2	-25	-6	-2	-25	9	-366	-501	9	366	-501
X _C	-201	0	1	1241	0	-27	-653	0	-151	-236	237	81	-236	-237	81	43	0	8	43	0	8
Y _C	0	-164	0	0	1389	0	0	-98	0	233	-536	-131	-233	-536	131	-4	-28	-94	4	-28	94
Z _C	-4	0	-231	-27	0	788	-158	0	-138	91	-154	-150	91	154	-150	4	-51	-60	4	51	-60
X _{H1}	9	0	-1	-653	0	-158	694	0	173	-25	-4	-8	-25	4	-8	0	2	1	0	-2	1
Y _{H1}	0	-5	0	0	-98	0	0	94	0	55	5	19	-55	5	-19	3	0	-3	-3	0	3
Z _{H1}	-84	0	-39	-151	0	-138	173	0	162	22	3	10	22	-3	10	9	0	-2	9	0	-2
X _{H2}	-1	-1	-6	-236	233	91	-25	55	22	240	-254	-91	19	-27	-14	2	-2	-3	0	-3	0
Y _{H2}	-6	-7	2	237	-536	-154	-4	5	3	-254	562	164	27	-33	-17	2	5	-3	-1	4	5
Z _{H2}	38	-69	-25	81	-131	-150	-8	19	10	-91	164	171	-14	17	10	-3	-3	-19	-4	3	3
X _{H3}	-1	1	-6	-236	-233	91	-25	-55	22	19	27	-14	240	254	-91	0	3	0	2	2	-3
Y _{H3}	6	-7	-2	-237	-536	154	4	5	-3	-27	-33	17	254	562	-164	1	4	-5	-2	5	3
Z _{H3}	38	69	-25	81	131	-150	-8	-19	10	-14	-17	10	-91	-164	171	-4	-3	3	-3	3	-19
X _{O1}	-147	12	9	43	-4	4	0	3	9	2	2	-3	0	1	-4	51	-12	-13	51	-2	-2
Y _{O1}	8	-875	-366	0	-28	-51	2	0	0	-2	5	-3	3	4	-3	-12	1117	450	2	-224	-27
Z _{O1}	9	-372	-501	8	-94	-60	1	-3	-2	-3	-3	-19	0	-5	3	-13	450	475	-2	27	104
X _{O2}	-147	-12	9	43	4	4	0	-3	9	0	-1	-4	2	-2	-3	51	2	-2	51	12	-13
Y _{O2}	-8	-875	366	0	-28	51	-2	0	0	-3	4	3	2	5	3	-2	-224	27	12	1117	-450
Z _{O2}	9	372	-501	8	94	-60	1	3	-2	0	5	3	-3	3	-19	-2	-27	104	-13	-450	475

FIGURE 1. Hessian matrix (kcal / Å² mol) for the staggered conformation of CH₃NO₂.



The pair interaction matrix that gives the reaction force on the atom N due to a displacement of atom C is given by

$$\begin{bmatrix} \delta F_{x_N} \\ \delta F_{y_N} \\ \delta F_{z_N} \end{bmatrix} = \begin{bmatrix} 201 & 0 & 4 \\ 0 & 164 & 0 \\ -1 & 0 & 231 \end{bmatrix} \begin{bmatrix} \delta x_C \\ \delta y_C \\ \delta z_C \end{bmatrix}$$

in which b , θ , ϕ , and ω correspond to the bond lengths, bond angles, dihedral angles, and improper dihedrals (out-of-plane); b_0 , θ_0 , ϕ_0 , and ω_0 are their equilibrium values; and k_b , k_θ , k_ϕ , and k_ω are the respective force constants (the indexes for bonds, angles, dihedrals, and impropers are not shown). We will now show how to obtain an invariant force constant corresponding to any internal coordinate. The same procedure can be applied for force fields that contain cross terms such as

$$\sum_{\text{bonds \& angles}} \frac{1}{2} k_{b\theta} (b - b_0)(\theta - \theta_0) \quad (6)$$

Method

BOND FORCE CONSTANTS

The essential concept is to analyze the interactions between all pairs of atoms in the molecule and to determine which ones are pairwise stable, the criterion for which shall be explained. From Eq. (3), we can get the reaction force $\delta \mathbf{F}_A = (\delta F_{x_A}, \delta F_{y_A}, \delta F_{z_A})$ on atom A due to a displacement $\delta \mathbf{r}_B = (\delta x_B, \delta y_B, \delta z_B)$ of atom B:

$$\begin{bmatrix} \delta F_{x_A} \\ \delta F_{y_A} \\ \delta F_{z_A} \end{bmatrix} = - \begin{bmatrix} \frac{\partial^2 E}{\partial x_A \partial x_B} & \frac{\partial^2 E}{\partial x_A \partial y_B} & \frac{\partial^2 E}{\partial x_A \partial z_B} \\ \frac{\partial^2 E}{\partial y_A \partial x_B} & \frac{\partial^2 E}{\partial y_A \partial y_B} & \frac{\partial^2 E}{\partial y_A \partial z_B} \\ \frac{\partial^2 E}{\partial z_A \partial x_B} & \frac{\partial^2 E}{\partial z_A \partial y_B} & \frac{\partial^2 E}{\partial z_A \partial z_B} \end{bmatrix} \times \begin{bmatrix} \delta x_B \\ \delta y_B \\ \delta z_B \end{bmatrix} \quad (7)$$

or in compact notation,

$$\delta \mathbf{F}_A = [k_{AB}] \delta \mathbf{r}_B. \quad (8)$$

The interatomic force constant matrix $[k_{AB}]$, defined including the minus sign, permits an analysis of the nature of the interaction between atoms

A and B. It has three eigenvalues λ_i^{AB} and three eigenvectors \hat{v}_i^{AB} ($i = 1, 2, 3$), which we assume to have unitary norm. An example of one interatomic force constant matrix of nitromethane molecule is also shown in Figure 1.

The physical interpretation of Eqs. (7) and (8) is as follows: If a particular eigenvalue λ_i^{AB} of $[k_{AB}]$ is positive, this means that the reaction force on A due to a displacement of B in the direction of \hat{v}_i^{AB} is in the same direction. If all three eigenvalues are positive, then for any displacement of B there is always a restoring reaction force on A that seeks to maintain the original interatomic separation. The atoms A and B are then described as pairwise stable. All pairs of formally bonded atoms belong to this category, as well as some between which there is no formal bond but such a strong interaction that the atoms can be viewed as bonded. If one or more eigenvalues are negative, then A will not feel a restoring reaction force trying to maintain unchanged the AB separation. This condition is described as a pairwise unstable interaction, and we conclude that A and B are not bonded. The same conclusion is reached when two of the three eigenvalues or eigenvectors are complex.

If one of the eigenvectors, \hat{v}_i^{AB} , is in the direction from A to B, which shall be described by the unit vector \hat{u}^{AB} , and forms an orthonormal system with the other two eigenvectors, then the force constant for the interaction between A and B, whether they are bonded or not, is,

$$k_{AB} = \lambda_i^{AB}. \quad (9)$$

When the direction from A to B does not coincide with that of any of the eigenvectors, or when the eigenvectors are not orthogonal to each other, then the force constant k_{AB} may have contributions from more than one eigenvalue of $[k_{AB}]$ in proportion to the projections of the corresponding eigenvectors upon the unit vector \hat{u}^{AB} :

$$k_{AB} = \sum_{i=1}^3 \lambda_i^{AB} |\hat{u}^{AB} \cdot \hat{v}_i^{AB}|. \quad (10)$$

Equation (9) is clearly a special case of Eq. (10). The magnitude of k_{AB} , as given by these equations, is obtained directly from the eigenvalues of the matrix $[k_{AB}]$ in Cartesian coordinates, and hence is invariant to the choice of internal coordinates. This invariance is a fundamental requirement for any physical quantity.

BOND ANGLE FORCE CONSTANTS

Consider the bonds AB and CB which have unit vectors \hat{u}^{AB} and \hat{u}^{CB} . Their interatomic matrices $[k_{AB}]$ and $[k_{CB}]$ have eigenvalues λ_i^{AB} and λ_i^{CB} , and eigenvectors \hat{v}_i^{AB} and \hat{v}_i^{CB} ($i = 1, 2, 3$). Let \hat{u}_N be a unit vector perpendicular to the plane ABC:

$$\hat{u}_N = \frac{\hat{u}^{CB} \times \hat{u}^{AB}}{|\hat{u}^{CB} \times \hat{u}^{AB}|}. \quad (11)$$

Then the unit vectors perpendicular to the bonds AB and CB on the plane ABC are

$$\hat{u}^{PA} = \hat{u}_N \times \hat{u}^{AB} \quad (12)$$

and

$$\hat{u}^{PC} = \hat{u}^{CB} \times \hat{u}_N. \quad (13)$$

They are the direction of small displacements of atoms A and C that result from opening or closing the angle ABC. If R_{AB} and R_{CB} are the length of the bonds, the bond angle force constant is then given by

$$\frac{1}{k_\theta} = \frac{1}{R_{AB}^2 \sum_{i=1}^3 \lambda_i^{AB} |\hat{u}^{PA} \cdot \hat{v}_i^{AB}|} + \frac{1}{R_{CB}^2 \sum_{i=1}^3 |\hat{u}^{PC} \cdot \hat{v}_i^{CB}|}. \quad (14)$$

DIHEDRAL ANGLE FORCE CONSTANTS

Consider the dihedral angle defined by the atoms A, B, C, and D which are linked by bonds AB, BC, and CD. The approach is similar to that used for bond angles. Unit vectors perpendicular to the planes ABC and BCD are given by

$$\hat{u}_{N_{ABC}} = \frac{\hat{u}^{CB} \times \hat{u}^{AB}}{|\hat{u}^{CB} \times \hat{u}^{AB}|} \quad (15)$$

$$\hat{u}_{N_{BCD}} = \frac{\hat{u}^{DC} \times \hat{u}^{BC}}{|\hat{u}^{DC} \times \hat{u}^{BC}|}. \quad (16)$$

The dihedral angle force constant is then

$$\frac{1}{k_\phi} = \frac{1}{R_{BA}^2 |\hat{u}_{AB} \times \hat{u}_{BC}|^2 \sum_{i=1}^3 \lambda_i^{AB} |\hat{u}_{N_{ABC}} \cdot \hat{v}_i^{AB}|} + \frac{1}{R_{CD}^2 |\hat{u}_{BC} \times \hat{u}_{CD}|^2 \sum_{i=1}^3 \lambda_i^{DC} |\hat{u}_{N_{BCD}} \cdot \hat{v}_i^{DC}|} \quad (17)$$

IMPROPER DIHEDRAL (OUT-OF-PLANE) ANGLE FORCE CONSTANTS

Let atoms B, C, and D be connected to the central atom A. Then the out-of-plane angle ω_{ABCD} is defined as the angle between planes ABC and BCD. The movement of A perpendicular to the plane BCD feels a restoring force from the bonds AB, AC, and AD. The effective force constant for the movement of A perpendicular to BCD is given by the sum of the three bond contributions:

$$k_{AN} = \sum_{i=1}^3 \lambda_i^{AB} |\hat{u}^N \cdot \hat{v}_i^{AB}| + \sum_{i=1}^3 \lambda_i^{AC} |\hat{u}^N \cdot \hat{v}_i^{AC}| + \sum_{i=1}^3 \lambda_i^{AD} |\hat{u}^N \cdot \hat{v}_i^{AD}|, \quad (18)$$

where \hat{u}^N is a unit vector perpendicular to the plane BCD. Then the out-of-plane force constant for the angle ω_{ABCD} is

$$k_\omega = k_{\omega_{ABCD}} = h_{ABCD}^2 k_{AN}, \quad (19)$$

where h_{ABCD} is the length of projection into the plane BCD of the altitude of triangle ABC (with base BC).

Applications

We have coded the preceding equations in the program FUERZA. It is presently designed to read the Cartesian Hessian tensor from the output of a Gaussian [16] program after a frequency (FREQ) or second derivative of the energy has been requested. The output format of FUERZA is compatible with the input format of the molecular modeling program CHARMM [17]. These features can, of course, be modified to be consistent with other programs.

In the applications that follow, we used a procedure based on density functional theory (DFT) available in the program Gaussian 94 [16] to optimize geometries and compute the second derivatives of the energy. The Becke 88 [18] and the Lee-Yang-Parr [19] functionals were used to represent the exchange and correlation potentials, respectively. However, our method can be implemented with any other DFT, ab initio or semiempirical technique. In the cases to be discussed, FUERZA used the force constants in the output of a frequency DFT calculation to create the intramolecular force field, which was subsequently

used in conjunction with CHARMM for a classical calculation of vibrational frequencies. The extent to which these reproduce the original DFT frequencies is a measure of the quality of the constructed force field. (The DFT procedure being used is known to be effective for vibrational frequencies [20, 21].) In the trivial case of diatomic molecules, exact agreement is obtained, as it must be, since there is only one independent internal coordinate and hence one possible force constant.

In the following, all bond lengths are in Å, angles in degrees, bond force constants in kcal/Å², angular force constants in kcal/rad², frequencies in cm⁻¹, and doubly or higher degenerate vibrational modes are listed only once.

H₂O

The DFT values for the bond length and bond angle are 0.976 and 102.7; the corresponding force constants are 1067 and 80.4, as compared to 900 and 110 in the CHARMM force field. All three eigenvalues of the interaction matrix [K_{HH}] are positive, indicating a stable HH interaction which should be included in the force field. The equilibrium HH distance is 1.249 and the force constant is 31.1. The vibrational frequencies obtained with this force field are 1555, 3674, and 3679; the DFT frequencies are 1636, 3643, and 3754 respectively.

NO₂

The DFT bond lengths and bond angle are 1.224 and 133.1, and the corresponding force constants are 1334 and 242. No stable OO interaction is found. The created force field frequencies are 703, 1201, and 1630, compared to the DFT 713, 1301, and 1586.

CH₃

For this radical in D_{3h} symmetry, the DFT bond length is 1.089 and the bond force constant is 768. The bond angle and out-of-plane force constants are 62 and 12.2. The resulting force field frequencies are 449, 1426, 2997, and 3186, while the DFT are 459, 1386, 3059, and 3236.

CH₃NO₂

It should be noted that parameters for nitro derivatives are not available in any of the standard force fields. The frequencies calculated with the

FUERZA program, with the DFT values given in parentheses, are: 577(572), 606(619), 945(866), 1000(1067), 1081(1091), 1176(1323), 1278(1370), 1294(1436), 1418(1450), 1694(1558), 2912(3014), 3033(3107), and 3064(3136). The first two frequencies are not given, since they correspond to the lowest torsional modes, in which anharmonic effects are particularly significant; accordingly, neither harmonic approximation, empirical nor DFT, is meaningful.

CIS-RH(PH₃)₂(CO)F

The results of an earlier DFT study [22] were used to make a more demanding test of the present approach. The force field frequencies obtained, with the DFT values in parentheses, are: 91(102), 91(107), 91(114), 92(115), 254(271), 260(274), 292(297), 393(403), 408(448), 419(465), 422(470), 434(477), 452(522), 782(530), 801(968), 966(993), 971(1095), 971(1095), 991(1098), 1328(1100), 1925(1935), 2315(2362), 2315(2364), 2339(2386), 2339(2388), 2348(2390), and 2361(2390). The frequencies for the lowest three torsional modes are not given, again because anharmonic effects render them useless.

Conclusion

Overall, the vibrational frequencies obtained with the FUERZA force fields are in very good agreement with those resulting from the DFT original calculations, over a wide range of values. This supports the physical validity of the approach that we have presented for obtaining an intramolecular force field in terms of force constants that are invariant to the choice of internal coordinates. The procedure can be applied to any molecular system for which Cartesian second derivatives of the energy are available.

ACKNOWLEDGMENT

We greatly appreciate the financial support of the Office of Naval Research, through contract No. N00014-95-1-0028.

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