Ab initio calculation of force constants and equilibrium geometries in polyatomic molecules. I. Theory

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P. PULAY†

Hungarian Academy of Sciences, Research Group for Inorganic Chemistry,
Budapest, Hungary

The general expression for the exact forces on the nuclei (negative derivatives of the total energy with respect to the nuclear coordinates) is applied for Hartree–Fock wavefunctions. It is suggested that force constants should be calculated by differentiating the forces numerically. This method, called the force method, is numerically more accurate and requires less computation than the customary one of differentiating the energy numerically twice. It permits the quick determination of the equilibrium geometry by relaxing the nuclear coordinates until the forces vanish. The unreliability of the methods using the Hellmann–Feynman forces is re-emphasized. The question of which force constants can be best calculated *ab initio* is discussed.

1. Introduction

Recently there has been considerable interest in the *ab initio* calculation of both force constants and molecular geometries. A force constant F_{ij} is defined as the second derivative of the molecular energy E with respect to the nuclear coordinates q_i and q_j in the equilibrium configuration:

$$F_{ij} = \left(\frac{\partial^2 E}{\partial q_i \partial q_j} \right)_0. \qquad (1)$$

There are three methods of calculation which differ in the manner in which the differentiations in (1) are carried out:

(A) Numerically twice.
(B) Analytically twice.
(C) First analytically and then numerically.

Method (A) is the simplest and has been used so far almost exclusively. It consists of computing the energy at the points of a two-dimensional mesh for different values of q_i and q_j and fitting a surface to the points. Differentiating the surface equation leads to the equilibrium configuration (assuming all other coordinates q_k have their equilibrium values) and to the force constant F_{ij}. If $i = j$, only a one-dimensional mesh is necessary. As Bishop and Randić have shown [1], method (A) has several serious disadvantages: it is not economical because the wavefunction must be computed for a number of nuclear configurations, and it is numerically

† Present address: Institut für Anorganische Chemie der Universität, 7 Stuttgart, Germany.

inaccurate because of the two numerical differentiations. Bishop and Randić therefore suggested method (B), i.e. that E should be differentiated analytically twice. Their method requires the evaluation of derivatives of the form:

$$\frac{\partial \rho_m}{\partial q_i} \quad \text{or} \quad \frac{\partial^2 E}{\partial q_i \partial \rho_m} \quad \text{and} \quad \frac{\partial^2 E}{\partial \rho_m \partial \rho_n}, \qquad (2)$$

where the ρ's are variational parameters. These quantities are generally difficult to obtain. In the most important SCF–MO calculations, the ρ's are the SCF coefficients. The derivatives (2) cannot be determined analytically in this case, only numerically by carrying out a series of calculations with different nuclear coordinates. The economy of the method is thus lost. In addition, this method does not contribute to the determination of the equilibrium nuclear configuration. The latter problem is also a major problem in method (A) if there are several internal coordinates in the totally symmetric symmetry species. The number of necessary points on the energy surface varies somewhat with the strategy used to find the equilibrium configuration but becomes excessive if there are three or more coordinates. We suggest that method (C) should be used for *ab initio* calculation of force constants and equilibrium geometries. In this method the energy is first differentiated analytically, i.e. the force acting in the direction of q_i is calculated:

$$f_i = -\frac{\partial E}{\partial q_i}.$$

The equilibrium geometry is determined by allowing the nuclear coordinates to relax until the net forces on the

atoms vanish. The force constant F_{ij}, the negative derivative of the force f_i as a function of q_j (or the negative derivative of f_j with respect to q_i), is then determined numerically, carrying out calculations for different q_j's near the equilibrium configuration. We call method (C) the force method; it has the following advantages:

(1) All the force constants F_{ij} ($i = 1, 2, \ldots, n$; j fixed) can be obtained by varying only the coordinate q_j. In method (A), for each F_{ij} a two-dimensional mesh of points must be calculated. This advantage is most pronounced in molecules with several degrees of freedom in a symmetry species. If there is only one vibration in a symmetry species, the gain is small: in method (A) a minimum of three points is necessary, but in the force method two points can suffice.

(2) The method is numerically much more accurate than method (A) because only one numerical differentiation is involved.

(3) Dependence of the variation parameters on the nuclear coordinates does not enter the formulas which are therefore quite simple.

(4) The method makes possible a quick iteration procedure to determine the equilibrium nuclear configuraton (see §5). This is one of the most interesting aspects of the method.

If carried out correctly the three methods above will supply the same result except for numerical uncertainties. In contrast the methods using the Hellmann–Feynman forces or the virial theorem may yield different results with the same approximate wavefunction. Because the virial theorem method [2] is applicable only to the 'breathing' vibration, it is of very little use for polyatomics and will not be dealt with here. On the other hand, the Hellmann–Feynman force method will be discussed briefly in §3 because

(a) it has a formal similarity with the force method
(b) this method has been suggested for calculating force constants in several papers, even very recently, although it has been known for some time that it is practically of no value, at least with present-day wavefunctions.

2. The force method

Let ϕ be a normalized trial wavefunction, depending on the nuclear coordinates $q = (q_1, q_2, \ldots, q_n)^+$ and on the variational parameters $\rho = (\rho_1, \rho_2, \ldots, \rho_m)^+$. The parameters are determined so that they minimize the total energy $E = \langle \phi | H | \phi \rangle$ and are themselves functions of the q's. In the following, the symbol $\partial/\partial q$ denotes a differentiation in which the dependence of the parameters upon the nuclear coordinates has not been

taken into account, i.e. the ρ's have been regarded as constant. d/dq will denote the total derivative including the q dependence of the parameters.

As it is well known [3, 4], for the *first* derivative:

$$\frac{dE}{dq} = \frac{\partial E}{\partial q},$$

because $\partial E/\partial \rho_i = 0$. This means that it is not necessary to know how the variational parameters change with the nuclear coordinates in computing the force, which greatly simplifies the formalism.

Let us assume for the sake of simplicity that ϕ is real, then

$$f_i = -\frac{dE}{dq_i} = -\left\langle \phi \left| \frac{\partial H}{\partial q_i} \right| \phi \right\rangle - 2\left\langle \frac{\partial \phi}{\partial q_i} | H | \phi \right\rangle. \quad (2)$$

The first term in (2) is the Hellmann–Feynman force. It can be calculated very easily because $\partial H/\partial q_i$ is a one-electron operator. Calculation of the second term in equation (2), which we call the wavefunction force, requires, of course, the definition of orbital following. It seems best to assign each basis function to an atom and to let it follow that atom rigidly. In this case there must be other variational parameters (e.g. SCF coefficients or orbital exponents) to account for changes in the electronic structure during the vibration. Orbitals situated between atoms can also be handled easily. Note that a definition of orbital following is also necessary in methods (A) and (B).

Computation of all the forces acting on the atoms does not require much more numerical work than computation of the total energy. The gain of information, however, outweighs greatly the additional work. Below we deal with the very important special case of closed-shell MO–SCF calculations. A generalization to open-shells or configuration interaction is simple and will be dealt with in a subsequent paper.

The force is the negative derivative of the Hartree–Fock energy expression, which we write in the following form:

$$E = 2\sum_j (\varphi_j | H_1 | \varphi_j) + \sum_{jk} [2(\varphi_j^2 | 1/r_{12} | \varphi_k^2)$$

$$- (\varphi_j \varphi_k | 1/r_{12} | \varphi_j \varphi_k)]$$

$$= 2\sum_{mn} (m | H_1 | n) D_{mn}$$

$$+ \sum_{mnrs} (mn \mid rs)(2D_{mn}D_{rs} - D_{mr}D_{ns}). \quad (3)$$

Here H_1 is the one-electron part of the hamiltonian, the φ's are the SCF molecular orbitals, related to the basis functions χ by transformation with the rectangular matrix $\mathbf{C}^+$: $\mathbf{\varphi} = \mathbf{C}^+\chi$, and $\mathbf{D}$ is the density matrix, defined

as $\mathbf{D} = \mathbf{CC}^+$. The notations $(m|H_1|n) = (\chi_m|H_1|\chi_n)$ and $(mn \mid rs) = (\chi_m\chi_n|1/r_{12}|\chi_r\chi_s)$ have been introduced. The terms which come from differentiating the operator H_1 in (3) constitute the Hellmann–Feynman force in this special case. Its calculation is very simple and requires the evaluation of just one new integral type. The wavefunction force consists of the terms which come from differentiating the basis functions in (3). It contains integrals with the derivatives of the basis functions. These can be obtained with the same techniques used for the basis integrals themselves (see Part II of this series [23]). The only point which requires attention is that equation (3) holds only if the molecular orbitals are orthonormal. This is equivalent to the requirement that $\mathbf{D}$ must be idempotent:

$$\mathbf{DSD} = \mathbf{D}, \qquad (4)$$

where $\mathbf{S}$ is the overlap matrix, $S_{mn} = (m \mid n)$. Equation (3) must be differentiated with the condition that $\mathbf{D}$ remains idempotent, which, in turn, means that $\partial\mathbf{D}/\partial q$ enters the formulas. The derivative of equation (4) is:

$$(\partial\mathbf{D}/\partial q)\mathbf{SD} + \mathbf{D}(\partial\mathbf{S}/\partial q)\mathbf{D} + \mathbf{DS}(\partial\mathbf{D}/\partial q) = \partial\mathbf{D}/\partial q.$$

$$(5)$$

This equation has an infinite number of solutions $\partial\mathbf{D}/\partial q$. Any of them gives the same forces because the total energy must be stationary against infinitesimal changes in the density matrix if these changes do not violate the idempotency of $\mathbf{D}$. The simplest solution to equation (5) seems to be:

$$\partial\mathbf{D}/\partial q = -\mathbf{D}(\partial\mathbf{S}/\partial q)\mathbf{D}. \qquad (6)$$

It can be shown easily that (6) satisfies equation (5), making use of the idempotency condition (4). With this in mind one obtains, for the wavefunction force:

$$-\text{WFF} = 2\langle \partial\phi/\partial q|H|\phi\rangle$$

$$= 2\sum_{mn}\{[(\partial m/\partial q|H_1|n) + (m|H_1|\partial n/\partial q)]D_{mn}$$

$$+ (m|H_1|n)(\partial D_{mn}/\partial q)\} + \sum_{mnrs}\{[(\partial m/\partial qn \mid rs)$$

$$+ (m\,\partial n/\partial q \mid rs) + (mn \mid \partial r/\partial qs)$$

$$+ (mn \mid r\,\partial s/\partial q)](2D_{mn}D_{rs} - D_{mr}D_{ns})$$

$$+ (mn \mid rs)(2\partial D_{mn}/\partial qD_{rs}$$

$$+ 2D_{mn}\,\partial D_{rs}/\partial q - \partial D_{mr}/\partial qD_{ns} - D_{mr}\,\partial D_{ns}/\partial q)\}.$$

$$(7)$$

The net force in the direction of q is the sum of the Hellmann–Feynman and the wavefunction force. The forces are best calculated using the cartesian coordinates of the atoms as nuclear coordinates. In the subsequent calculation of equilibrium geometry and force constants,

however, forces in internal coordinates are more advantageous. The transformation between the two sets of forces is described in §4.

3. The Hellmann–Feynman force

It has been suggested several times that the Hellmann–Feynman force should be used to calculate force constants [5–9]. It would be a very attractive method because it requires little numerical work. Moreover, for the exact wavefunction and for several types of fully minimized wavefunctions (e.g. for the Hartree–Fock limit) the Hellmann–Feynman theorem holds [3, 4], i.e. the wavefunction force vanishes and the total force is equal to the Hellmann–Feynman force [10, 11]. However, experience indicates that even with the best wavefunctions available today the Hellmann–Feynman force differs considerably from the energy-derivative force. As Salem and Wilson have shown [12], in the case of a discrepancy the energy derivative is much more reliable. It is like the energy itself, stationary with respect to changes in the wavefunction. Therefore, the error in the wavefunction enters the energy derivative *only in second order*, but it enters the Hellmann–Feynman force in first order.

Several numerical tests have been made ([13]–[15], see also Part II of this series) which all show how extraordinarily sensitive the Hellmann–Feynman forces are. Kern and Karplus [14] calculated the Hellmann–Feynman forces for hydrogen fluoride with the quite good wavefunction of Clementi (16 Slater-type orbitals) and obtained 0.78 a.u. $= 6.42$ mdyn for the rest force on fluorine at the experimental H–F distance. This force would shift the interatomic distance by about 0.7 Å. Thus the Hellmann–Feynman force is practically of no value in determining equilibrium configurations unless very good wavefunctions are used. The better the wavefunction is, however, the more accurate is the energy derivative compared with the Hellmann–Feynman force, because of its second-order dependence on the error in the wavefunction. Considering the quickly increasing computational labour as the wavefunction is made more and more accurate, it is much more advantageous to work with a medium-accuracy function and the energy derivative than with a very accurate function and the Hellmann–Feynman force.

If the Hellmann–Feynman theorem does not hold, another difficulty arises if one tries to calculate force constants from the Hellmann–Feynman forces. Because the sum of the forces on the atoms does not necessarily vanish for the Hellmann–Feynman force as it does for the energy derivative force, the force constants will depend on how the internal coordinates are defined with respect to the external ones (translations and rotations of the molecule as a whole), e.g. force constants of

a diatomic molecule will depend on whether the force on atom A or B was used to calculate it.

We conclude that quantities derived from the Hellmann–Feynman force are generally unreliable and should not be used, unless it is assured that the Hellmann–Feynman theorem holds. Examples show that this is not true for present-day wavefunctions. An exception would be the use of floating basis functions [10].

4. Transformation from cartesian to internal forces

Let N be the number of atoms and n the number of internal coordinates in a symmetry species. $\mathbf{x} = (x_1, x_2, \ldots, x_{3N})^+$ denotes the cartesian coordinates, $\mathbf{f} = [-(\partial E/\partial x_1), \ldots, -(\partial E/\partial x_{3N})]^+$ the corresponding forces $\mathbf{q} = (q_1, q_2, \ldots, q_n)^+$ the internal coordinates and $\boldsymbol{\varphi} = [-(\partial E/\partial q_1), \ldots, -(\partial E/\partial q_n)]^+$ the internal forces. The internal displacements $d\mathbf{q}$ are related to the cartesian ones by the well-known $\mathbf{B}$ matrix of Wilson and Eliashevich [16]:

$$d\mathbf{q} = \mathbf{B}\,d\mathbf{x}.$$

Thus for the forces:

$$\mathbf{f} = \mathbf{B}^+\boldsymbol{\varphi}. \tag{8}$$

From (8), $\boldsymbol{\varphi}$ cannot be expressed directly, $\mathbf{B}^+$ being a rectangular matrix and having no inverse. We can, however, construct a set of matrices, all denoted symbolically by $\mathbf{B}^{+-1}$ for which

$$\mathbf{B}^{+-1}\mathbf{B}^+ = \mathbf{I},$$

where $\mathbf{I}$ is the n by n unit matrix. Multiplying (8) by $\mathbf{B}^{+-1}$ from the left, we obtain the internal forces:

$$\boldsymbol{\varphi} = \mathbf{B}^{+-1}\mathbf{f}.$$

The matrices $\mathbf{B}^{+-1}$ can be obtained by:

$$\mathbf{B}^{+-1} = (\mathbf{B}\mathbf{m}\mathbf{B}^+)^{-1}\mathbf{B}\mathbf{m},$$

where $\mathbf{m}$ is any $3N$ by $3N$ matrix with has the full symmetry of the molecule so that $(\mathbf{B}\mathbf{m}\mathbf{B}^+)$ is non-singular†. The fact that an infinite set of matrices $\mathbf{B}^{+-1}$

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† There are two reasonable choices for $\mathbf{m}$. First, we can choose $\mathbf{m} = \mathbf{M}^{-1}$ where $\mathbf{M}$ is a diagonal matrix consisting of triplets of the atomic masses. As Crawford and Fletcher have shown [17], the centre of gravity of the molecule as well as its orientation will be left unchanged on a displacement $d\mathbf{q}$ with this choice. However, for our purposes it seems to be more appropriate if some of the cartesians are kept unchanged. The number of cartesians which can be kept constant simultaneously is equal to the number of translations and rotations in the symmetry species; for a whole molecule it is six (five for a linear molecule). $\mathbf{m}$ is then a diagonal matrix with zeros in the diagonal for those cartesians which have to be kept constant and with arbitrary non-zero diagonal elements, usually 1's, elsewhere.

exists is a consequence of the non-uniqueness of the transformation from internal coordinates to cartesians.

5. Determination of the equilibrium geometry

In determining the equilibrium nuclear configuration we can restrict ourselves to the totally symmetric (A_1) symmetry species if the symmetry of the equilibrium configuration is known. Let $\mathbf{q}_0$ be the starting vector of internal coordinates and $\mathbf{F}_0$ a guess for the force constant matrix. To obtain a better approximation $\mathbf{q}_1$ we calculate the forces $\boldsymbol{\varphi}_0$ and form:

$$\mathbf{q}_1 = \mathbf{q}_0 + \Delta\mathbf{q} = \mathbf{q}_0 + \mathbf{F}_0^{-1}\boldsymbol{\varphi}_0.$$

It is evident that if $\mathbf{F}_0$ were equal to the calculated force constant matrix and if the forces $\boldsymbol{\varphi}$ depended linearly on the coordinates q, then $\mathbf{q}_1$ would give the final equilibrium geometry. If this is not entirely true, $\mathbf{q}_1$ will differ from its equilibrium value. Nevertheless, if the guesses $\mathbf{F}_0$ and $\mathbf{q}_0$ are not too far from the correct values, a considerable improvement can be expected in $\mathbf{q}_1$ compared with $\mathbf{q}_0$. The iteration process:

$$\mathbf{q}_{i+1} = \mathbf{q}_i + \mathbf{F}_0^{-1}\boldsymbol{\varphi}_i,$$

will then converge towards equilibrium. Experience indicates that three or four steps are usually sufficient to achieve the final configuration. Suitable guesses $\mathbf{q}_0$ and $\mathbf{F}_0$ are almost always available. Note that

(a) this process does not depend on how many coordinates fall in the A_1 species.

(b) the final equilibrium configuration does not depend on F_0. F_0 determines only the rate of convergence.

The possibility of determining economically the equilibrium geometry is one of the most attractive features of the force method.

6. Which force constants should be calculated *ab initio*?

Let us distinguish between the following types of force constants in internal valence coordinates:

(1) diagonal stretching terms F_r,
(2) interactions between stretchings F_{rr},
(3) interactions between a stretching and bending $F_{r\alpha}$,
(4) diagonal bending terms F_α,
(5) interactions between two bendings $F_{\alpha\alpha}$.

The term 'bending' includes all angle-type coordinates. It is expected that these physically different types of force constants have different sensitivity to approximations in the wave function. This means that some types are more suitable for *ab initio* calculations than others. Thus, Hartre–Fock wavefunctions generally lead to

incorrect (ionic) dissociation of bonds because of the neglect of electron correlation. This explains why most of the F_r-type constants are overestimated by Hartree–Fock calculations.

Stretching force constants are the best-known ones to spectroscopists and only their accurate *ab initio* calculation contributes to the determination of molecular force fields. Clearly, results which fail to fall in the range well known to spectroscopists do not provide any new information. Nevertheless, most of the *ab initio* calculation of force constants made so far deal with stretching constants. We suggest that effort should be concentrated on other types of force constants. Little progress has been made with the *ab initio* calculation of the F_{rr} type. A recent result shows, however, that it may also be sensitive to correlation effects [18].

The best results can be expected for $F_{r\alpha}$-type force constants. As early as 1949, Linnett determined the correct sign of $F_{r\alpha}$ in H_2O on the basis of hybridization arguments [19]. More recently, good estimates have been obtained for these constants by Mills, using a simple hybridization model, the hybrid orbital force field [20]. The semi-quantitative method of maximum overlap also led to the correct signs and orders of magnitude [21]. Thus it seems probable that the Hartree–Fock approximation can predict values of these force constants accurately enough to provide help to molecular spectroscopy. This will be tested in the subsequent papers of this series on small molecules for which $F_{r\alpha}$ is known experimentally. It is also probable that force constants of the types F_α and $F_{\alpha\alpha}$ can be calculated more accurately than stretching constants. Comparing diagonal and interaction constants generally, we feel that *ab initio* calculation of the latter is more advantageous for the following reasons:

(1) There is no *a priori* reason why the relative accuracy of interaction constants should be lower than that of the diagonal ones. Interaction constants are usually an order of magnitude smaller than the corresponding diagonal ones. This means that the absolute error in the interaction constants will be considerably lower. Moderately accurate interaction constants, together with experimental frequencies, could be of great help in determining force fields for polyatomics. Even the knowledge of the sign is important.

(2) Vibrational frequencies depend only slightly on interaction force constants if the vibrations are characteristic, i.e. if there is neither strong kinematic coupling nor near-degeneracy, and in these cases, conversely, diagonal force constants calculated from vibrational frequencies and *ab initio* interactions will be much more accurate than the interaction constants used.

(3) In the force method several interaction constants can be calculated from the same wavefunctions.

7. Comparison with the method of Gerratt and Mills

During the preparation of this report the paper of Gerratt and Mills appeared [22]. There is much similarity between the two papers; or equation (7) corresponds closely to equation (54) in Part I of their paper. The main difference in the two versions of this equation is that our method of maintaining the orthonormality of the molecular orbitals is much simpler. Their final method for calculating force constants differs, however, considerably from ours. They calculate force constants as the analytical derivative of the Hellmann–Feynman force. The problems associated with the double analytical differentiation of the energy are eliminated in this way. On the other hand, our critique in §4 applies to their method: the Hellmann–Feynman forces are much less reliable than the energy-derivative forces and their method does not help much in establishing the equilibrium geometry. This is well demonstrated by table 6, Part II of [22].

References

[1] BISHOP, D. M., and RANDIĆ, M., 1966, *J. chem. Phys.*, **44**, 2480.
[2] CLINTON, W., 1960, *J. chem. Phys.*, **33**, 1603.
[3] HELLMANN, J., 1937, *Einführung in die Quantenchemie* (Leipzig: Deuticke & Co.).
[4] FEYNMAN, R. P., 1939, *Phys. Rev.*, **56**, 340.
[5] SALEM, L., 1963, *J. chem. Phys.*, **38**, 1227.
[6] PHILLIPSON, P., 1963, *J. chem. Phys.*, **39**, 3010; 1966, *Ibid.*, **44**, 633.
[7] SCHWENDEMAN, R. H., 1966, *J. chem. Phys.*, **44**, 556.
[8] GOODISMAN, J., 1966, *J. chem. Phys.*, **44**, 2085.
[9] BADER, R. F. W., and BANDRAUK, A. D., 1968, *J. chem. Phys.*, **49**, 1666.
[10] HURLEY, A. C., 1954, *Proc. R. Soc.* A, **226**, 170, 179.
[11] STANTON, R. E., 1962, *J. chem. Phys.*, **36**, 1298.
[12] SALEM, L., and WILSON, E. B., JR., 1962, *J. chem. Phys.*, **36**, 3421.
[13] SALEM, L., and ALEXANDER, M., 1963, *J. chem. Phys.*, **39**, 2994.
[14] KERN, C. W., and KARPLUS, M., 1964, *J. chem. Phys.*, **40**, 1374.
[15] FINK, W., WHITTEN, J. L., and ALLEN, L. C., 1967, *J. chem. Phys.*, **46**, 3270.
[16] WILSON, E. B., JR., DECIUS, J. C., and CROSS, P. C., 1955, *Molecular Vibrations* (New York: McGraw-Hill).

[17] CRAWFORD, B., JR., and FLETCHER, W. H., 1953, *J. chem. Phys.*, **21,** 1229.

[18] AHLRICHS, R., and KUTZELNIGG, W., 1968, *Theor. chim. Acta*, **10,** 377.

[19] LINNETT, J. W., and WHEATLEY, P. J., 1949, *Trans. Faraday Soc.*, **45,** 33.

[20] MILLS, I. M., 1963, *Spectrochim. Acta*, **19,** 1585.

[21] MEZEI, M., and PULAY, P., 1968, *Acta chim. hung.*, **56,** 331.

[22] GERRATT, J., and MILLS, I. M., 1968, *J. chem. Phys.*, **49,** 1719, 1730.

[23] PULAY, P., *Molec. Phys.* (to be published).