

AB INITIO COMPUTATION OF FORCE CONSTANTS

Part VI. Applications of the force relaxation method for geometry optimization*

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ABSTRACT

Techniques to improve the computational efficiency of the force relaxation method are discussed. Force constants for fragments in previously computed smaller molecules can be transferred to construct a guess force constant matrix. Additional force constants that may be needed can be computed by a procedure which uses only one additional force calculation per diagonal force constant required. A scaling technique to improve convergence on the optimized geometry is discussed.

INTRODUCTION

The prediction of equilibrium geometries is one of the most successful areas of ab initio SCF-MO methods [2]. Consequently the development of accurate and efficient geometry optimization procedures is particularly important. The method most widely used at present is the axial iteration technique [3]. However, this method is relatively inefficient if the coordinates being optimized are strongly coupled, and in such cases the method may even fail to locate the minimum at all [4].

Two procedures which seem very promising are (a) the force relaxation method [5] and (b) the conjugate gradient method [6]. Both these techniques rely on the energy derivatives instead of the energies alone. It has been shown that all energy derivatives, or forces, for a molecule can be calculated as efficiently as the energy [7, 8]. Pulay and co-workers have already applied the force relaxation method to calculate the equilibrium geometry of a variety of small molecules [7]. In this paper, we wish to examine the force relaxation method with particular attention to the reduction of computational effort.

*Part V, see ref. 1.

METHOD

The force relaxation method is a variant of the Newton-Raphson algorithm. Let \vec{q}' be an approximation to the optimized geometry. The energy, E , and the forces, \vec{f} , can be expanded around \vec{q}' as, approximately

$$E(\vec{q}) = E' - \vec{f}' \cdot (\vec{q} - \vec{q}')^T + (\vec{q} - \vec{q}') F(\vec{q} - \vec{q}')^T \quad (1)$$

$$\vec{f}(\vec{q}) = \vec{f}' - F(\vec{q} - \vec{q}') \quad (2)$$

where \vec{f}' are the forces on the coordinates at \vec{q}' (i.e. $f_i = -\partial E/\partial q_i$) and F is the force constant matrix ($F_{ij} = \partial^2 E/\partial q_i \partial q_j$). At the energy minimum, the forces vanish. In the approximation of eqn. (2), the next approximation to the optimized geometry, \vec{q}'' , is given by

$$\vec{f} = \vec{f}' - F(\vec{q}'' - \vec{q}') = 0 \quad (3)$$

$$\vec{q}'' = \vec{q}' + F\vec{f}' \quad (4)$$

If F is the exact force constant for the geometry \vec{q}' , then the above iteration scheme would converge very quickly. For the computation of optimized geometry, the complete force constant matrix F is usually not known and is difficult to compute directly. However, approximations to F may be available. Provided such approximations are not too poor, the iteration outlined above will still converge, albeit more slowly. It should be pointed out that only the rate of convergence is affected by the approximation to F , but not the final optimized geometry.

In the force method [5], force constants are computed by numerical differentiation of the forces, using a central difference formula

$$F_{ij} \approx F_{ij}^0 = -(f_i(q_j + \Delta_j) - f_i(q_j - \Delta_j))/2|\Delta_j| \quad (5)$$

where $f_i(q_j + \Delta_j)$ is the force on the i -th coordinate evaluated at a displacement Δ_j of the j -th coordinate from the reference geometry, \vec{q} . While this procedure is relatively accurate [9] (error proportional to $F_{ijjj}\Delta_j^2$, where $F_{ijjj} = \partial^4 E/\partial q_i \partial q_j^3$), it requires the computation of the energy and forces at the reference geometry and two displacements, Δ_j and $-\Delta_j$, for each coordinate. An alternative, which requires less computation but is also less accurate, uses a forward or backward difference formula

$$F_{ij} \approx F_{ij}^+ = -[f_i(q_j + \Delta_j) - f_i(q_j)]/\Delta_j \quad (6)$$

$$F_{ij} \approx F_{ij}^- = -[f_i(q_j) - f_i(q_j - \Delta_j)]/\Delta_j \quad (7)$$

$$F_{ij}^0 = [F_{ij}^+ + F_{ij}^-]/2 \quad (8)$$

The error is proportional to $F_{ijjj}\Delta_j$ where $F_{ijjj} = \partial^4 E/\partial q_i \partial q_j^3$. To reduce the discrepancy between F_{ij}^0 , F_{ij}^+ and F_{ij}^- , one need only choose Δ_j small enough. However, if Δ_j is too small, there will be a loss of computational accuracy because the differences will be between two nearly equal quantities. There is also an inherent error in the computed forces, due to the finite level of

TABLE 1

Force constants for NH_3 , con

Force constants ^{a,b,c}	Step size
	0.05 Å
F_{rr}^0	9.079
F_{rr}^+	7.891
F_{rr}^-	10.267
$F_{r'r}^0$	-0.255
$F_{r'r}^+$	-0.248
$F_{r'r}^-$	-0.262
$F_{\alpha r}^0$	0.288
$F_{\alpha r}^+$	0.280
$F_{\alpha r}^-$	0.296
$F_{\alpha'r}^0$	0.120
$F_{\alpha'r}^+$	0.114
$F_{\alpha'r}^-$	0.127
	2.5°
$F_{\alpha\alpha}^0$	1.022
$F_{\alpha\alpha}^+$	0.993
$F_{\alpha\alpha}^-$	1.051
$F_{\alpha'\alpha}^0$	-0.087
$F_{\alpha'\alpha}^+$	-0.088
$F_{\alpha'\alpha}^-$	-0.086

^aUnits: stretching force constants, mdyn/Å; bend force constants, mdyn/Å; ^climit of the density matrix of

convergence during the computation of force constants is inversely proportional to the step size, a trade-off between the

Table 1 contains a summary of force constants computed according to eqns. (5)–(8) performed with the GAUSSIAN basis set [11]. Forces with step sizes of the order of 0.05 Å and F_{ij}^0 are almost coincident with convergence. Similar results are obtained. Thus, by using F_{ij}^+ , the convergence is of order 2.

Another device that has been used for the force constant method is the use of force constants of A–H and I

TABLE 1

Force constants for NH_3 , computed with various step sizes

Force constants ^{a,b,c}	Step size						
	0.05 Å	0.01 Å	0.005 Å	0.001 Å	0.0005 Å	0.0001 Å	0.00005 Å
F_{rr}^0	9.079	8.980	8.976	8.976	8.976	8.976	8.976
F_{rr}^+	7.891	8.744	8.857	8.952	8.964	8.973	8.975
F_{rr}^-	10.267	9.216	9.095	9.000	8.988	8.978	8.977
F_{rr}^0	-0.255	-0.255	-0.255	-0.255	-0.255	-0.255	-0.255
F_{rr}^+	-0.248	-0.254	-0.254	-0.255	-0.255	-0.255	-0.255
F_{rr}^-	-0.262	-0.256	-0.256	-0.255	-0.255	-0.255	-0.255
$F_{\alpha r}^0$	0.288	0.288	0.288	0.288	0.288	0.288	0.288
$F_{\alpha r}^+$	0.280	0.287	0.287	0.288	0.288	0.288	0.288
$F_{\alpha r}^-$	0.296	0.290	0.289	0.289	0.288	0.288	0.288
$F_{\alpha' r}^0$	0.120	0.120	0.120	0.120	0.120	0.120	0.120
$F_{\alpha' r}^+$	0.114	0.119	0.119	0.120	0.120	0.120	0.120
$F_{\alpha' r}^-$	0.127	0.122	0.121	0.121	0.120	0.120	0.120
	2.5°	0.5°	0.25°	0.05°	0.025°	0.005°	0.0025°
$F_{\alpha\alpha}^0$	1.022	1.022	1.022	1.022	1.022	1.022	1.022
$F_{\alpha\alpha}^+$	0.993	1.016	1.019	1.021	1.021	1.022	1.022
$F_{\alpha\alpha}^-$	1.051	1.028	1.025	1.022	1.022	1.022	1.022
$F_{\alpha'\alpha}^0$	-0.087	-0.087	-0.087	-0.087	-0.087	-0.087	-0.087
$F_{\alpha'\alpha}^+$	-0.088	-0.087	-0.087	-0.087	-0.087	-0.087	-0.087
$F_{\alpha'\alpha}^-$	-0.086	-0.087	-0.087	-0.087	-0.087	-0.087	-0.087

^aUnits: stretching force constants, $\text{mdyne } \text{Å}^{-1}$; bending force constants, mdyne-Å ; stretch-bend force constants, mdyne . ^bSee eqns. (5)–(7). ^cForces computed with a convergence limit of the density matrix of $5 \cdot 10^{-5}$.

convergence during the SCF iteration. The resulting error in the force constants is inversely proportional to Δ_j . Thus, the optimum Δ_j is the result of a trade-off between the two sources of error.

Table 1 contains a survey of the force constants for NH_3 computed according to eqns. (5)–(7) with varying step sizes. SCF computations were performed with the GAUSSIAN 70 series of programs [10] using the STO-3G basis set [11]. Forces were computed with the program FORCE [8]. For step sizes of the order of 0.00005–0.0005 Å or 0.0025–0.025°, F_{ij}^+ , F_{ij}^- and F_{ij}^0 are almost coincident, with no degradation due to the limited SCF convergence. Similar results have been obtained for CH_4 , H_2O and H_2S . Thus, by using F_{ij}^+ , the cost of computing F is reduced by almost a factor of 2.

Another device that further reduces the computational cost of the guess for the force constant matrix of a molecule A–B is the use of the force constants of A–H and H–B for all the values concerning the two fragments

A and B. The force constant for the stretching along the A—B bond axis can be computed with the procedure previously outlined as well as other force constants that are estimated to be important.

A poor approximation to the force constant matrix, when used in eqn. (4), can predict a geometry that is further from the optimized geometry and higher in energy than the previous step. This can be remedied by locating the minimum along the direction of the predicted change in geometry and scaling the change in geometry accordingly. Let the predicted change in geometry be $\Delta\vec{q} = \vec{q}'' - \vec{q}'$; let the force at the initial geometry be \vec{f}' and at the predicted geometry, \vec{f}'' . Then the components of the force along the direction $\Delta\vec{q}$ are

$$f'_q = \vec{f}' \cdot \Delta\vec{q}^T / |\Delta\vec{q}|; \quad f''_q = \vec{f}'' \cdot \Delta\vec{q}^T / |\Delta\vec{q}| \quad (9)$$

Along $\Delta\vec{q}$ the energy is at a minimum when this component of the force vanishes. Let σ be the fraction of the distance along $\Delta\vec{q}$ at which the minimum occurs

$$\sigma = f'_q / (f'_q - f''_q) \quad (10)$$

Then the corrected prediction of the geometry is

$$\vec{q} = \vec{q}' + \sigma\Delta\vec{q} \quad (11)$$

With such a technique, any tendency towards divergence can be rectified.

APPLICATIONS

To demonstrate the techniques outlined above, we have carried out various test calculations on hydroxylamine, H_2NOH , and methylamine, H_3CNH_2 . Guess force constant matrices were constructed using the appropriate force constants of CH_4 , NH_3 and H_2O . Force constants for the N—O and C—N bond stretching, and interaction force constants involving these bond stretches were computed according to eqn. (6) (this required only one additional calculation of the energy and forces for each molecule). For both molecules we have used two different starting points (see Tables 2 and 3). Starting from the initial geometry A (built from the optimized geometrical parameters of the two CH_4 , NH_3 , H_2O component fragments and with the joining bond at the standard value [12]), the optimization procedure required 5 independent computations of the forces for hydroxylamine and methylamine, respectively to reduce all the forces below $0.006 \text{ m dyn } \text{\AA}^{-1}$. If the experimental geometries [13] (initial geometries B) are used as a starting point, 5 steps are required for hydroxylamine and 6 for methylamine. The final optimized geometries are almost identical to those reported by Pople and co-workers [2].

In these applications the present procedure is found to require a computational time of the order of magnitude of that required by a single optimization of all geometrical parameters with the axial iteration technique. However, at this stage, the geometry obtained with the present procedure is

TABLE 2

Geometry optimization of h

Parameter ^a	Initial
r(N—O)	1
r(O—H)	0
r(N—H)	1
∠NOH	100
∠HNO	104
∠HNH	104
Total energy (a.u.)	-129

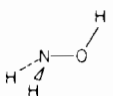
^aConformation 

TABLE 3

Geometry optimization of m

Parameter ^a	Initial
r(C—N)	1
r(C—H ₁)	1
r(C—H ₂)	1
r(N—H)	1
∠H ₁ CN	109
∠H ₂ CN	109
∠H ₁ NC	104
∠H ₂ CH ₁	109
∠H ₂ NH ₁	104
Total energy (a.u.)	-94

^aThe numbering scheme is

much more accurate. It is faster, and more reliable than the "Modified DF"

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TABLE 2

Geometry optimization of hydroxylamine by the force relaxation method

Parameter ^a	Initial (A)	Initial (B)	Optimized	Literature ^b
r(N—O)	1.360	1.453	1.428	1.427
r(O—H)	0.989	0.962	0.995	0.995
r(N—H)	1.032	1.016	1.044	1.044
∠NOH	100.1	101.4	101.4	101.4
∠HNO	104.2	103.3	104.5	104.5
∠HNH	104.2	107.1	103.9	103.3
Total energy (a.u.)	-129.25686	-125.25910	-129.26306	-129.26306

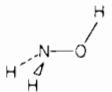
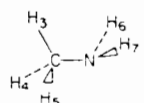
^aConformation . ^bValues optimized by Pople and co-workers [2].

TABLE 3

Geometry optimization of methylamine by the force relaxation method

Parameter ^a	Initial (A)	Initial (B)	Optimized	Literature ^b
r(C—N)	1.470	1.474	1.486	1.486
r(C—H ₃)	1.083	1.093	1.093	1.093
r(C—H ₄)	1.083	1.093	1.089	1.089
r(N—H)	1.032	1.011	1.034	1.033
∠H ₃ CN	109.47	113.0	113.7	113.7
∠H ₄ CN	109.47	107.6	109.1	109.2
∠H ₆ NC	104.2	112.1	107.2	107.3
∠H ₄ CH ₃	109.47	109.5	108.3	108.2
∠H ₆ NH ₇	104.2	105.87	104.3	104.4
Total energy (a.u.)	-94.02238	-94.03044	-94.03286	-94.03286

^aThe numbering scheme is . ^bValues optimized by Pople and co-workers [2].

much more accurate. It follows also that the present procedure is significantly faster, and more reliable, than the method suggested by Payne [14] and than the "Modified DFP Procedure" used by Pople and co-workers [15].

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CYANOGEN ISOCYANATE STUDIES OF GEOMETRY

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ABSTRACT

Complete geometry of the cyanogen isocyanate molecule is applied to the recently-proposed structure of dicyanoether [NCOCN]. The structure is compared with the computed barrier to inversion of the OCN linkages away from the plane of the OCN a fairly rigid molecule, with the barrier to have planar *trans* bent HCNCO—HOCN isomers. Complete electronic structures of the molecule are given by population analysis.

INTRODUCTION

Isocyanates have been studied in the past few years as they exhibit interesting spectroscopic features. The structure of the cyanogen isocyanate has been studied spectroscopically by Rosenberg et al. [2]: Detailed spectroscopic data are given in ref. 3). The substituted cyanogen isocyanate, for example, methyl isocyanate, has been studied in the microwave region. The case of chlorine isocyanate has been studied. Isocyanic acid, its tautomer fulminic acid, have been studied. The transitions of HCNO have been studied. A quasilinear model for the linear configuration of the cyanogen isocyanate energy surface which

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