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The Experimental Design for Computing the Harmonic and Anharmonic Force Constant Matrices of Polyatomic Molecules

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In the present work we propose a numerical approach to estimate the harmonic and anharmonic force constant matrices, supposing we are able to compute analytically the first order derivative vector of the potential energy surface with respect to the internal coordinates. We use a polynomial least square fit to interpolate this gradient in the stationary point region. The structure of the regression matrix shows that the harmonic force constant matrix may be obtained even for large molecules; the evaluation of the anharmonic contributions request slightly more labor but is possible for 5 to 7 atoms. The present work is applicable even at the CI level and the number of computations remains small. We use the experimental planification to select the geometries to be computed in order to improve the estimation of the regression coefficients i.e. this means to lower their variance.

Key words: Harmonic and anharmonic force constant matrix.

1. Introduction

The problem of computing the successive derivatives of the potential energy surface with respect to any degree of freedom (in a polyatomic molecule, around a stationary point of interest) is essential to the estimation of some molecular properties related to the nuclear motions such as: (i) the vibrational-states and transitions, (ii) the thermodynamical properties [2] and (iii), via the transition state theory, the reaction rate [3].

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In the last years different methods have been developed to compute the gradient and the force constant matrix. At the present time a purely numerical approach is feasible for not too large molecules (up to seven atoms) if we accept the harmonic approximation [4]. Nevertheless for analysing more complex chemical compounds or for extending the analysis up to the third order derivatives such an approach becomes rapidly expansive. On the other hand the analytical computation of the gradient [5] (a first order property) may be done even at the CI level [6]. The problem is more difficult for the harmonic force constant matrix (a second order property) and is only solved at the SCF level [5, 7]. For higher order derivatives and for medium size molecules this computational problem remains open. According to an idea of Pulay [8] we propose to compute analytically the gradient vector and numerically the next derivatives.

In this work we define an appropriate strategy to reach this goal. If we develop the potential energy surface as a polynome of order 2 or 3, we show that it exists point distributions particularly well suited for the gradient fitting.

2. The Regression with the Gradient

The potential energy surface (E) of a chemical system of interest can be expressed as a function of the internal coordinates (s):

$$E = E(s_1, s_2 \cdots s_k)$$

usually $k = 3N-6$ if N is the atom number.

Assuming that the limited region of immediate interest around a central point s_0 in the internal coordinate space is not too large, we develop the potential energy in Taylor's series; if S stands for the column vector of the internal displacements $s - s_0$, we have:

$$E(S) = E_0 + S'g_0 + 1/2S'H_0S + \cdots \tag{1}$$

where $E_0 = E(s_0)$, $g_0 = (\nabla E)_{s_0}$ and $H_0 = ([\nabla\nabla']E)_{s_0}$.

If we have at our disposal a method which only provides the first derivative vector of the energy with respect to the internal coordinates ($g(S)$), the problem is how to compute the next derivative matrix and/or hypermatrices. The simplest method we can use comes out by differentiating the Eq. (1):

$$g(S) = g_0 + H_0S + \cdots \tag{2}$$

If we compute the gradient vector $g(S)$ in k different (and non linearly related) points of a purely quadratic hypersurface we have:

$$[(g(S_1)|g(S_2)| \cdots g(S_k)) - g_0](S_1|S_2| \cdots S_k)^{-1} = H_0 \tag{3}$$

Nevertheless in practice such an approach leads to non symmetrical H_0 matrix; more over it cannot permit to go further than the quadratic approximation. In order to bypass those difficulties let us replace the Eq. (1) by a local polynomial expansion up to order n:

$$E(S) = (1\,|\,S^{[n]})\begin{pmatrix} b_0 \\ b^{[n]} \end{pmatrix} \tag{4}$$

The column vector b stands for the vector of the expansion coefficients:

$$b^{[n]'} = (b_1 \dots b_k, b_{11} \dots b_{kk}, b_{21} \dots b_{kk-1}, \dots) \tag{5}$$

The line vector $S^{[n]}$ is the model vector (for the simulation process), it contains the functional values of the fitting at any point of coordinates S:

$$S^{[n]} = (S_1 \dots S_k, S_1^2 \dots S_k^2, S_2S_1 \dots S_kS_{k-1}, \dots) \tag{6}$$

By differentiating the Eq. (4) with respect to any internal coordinate we have the following set of equations:

$$\left(\frac{dE}{dS_i}\right)_S = g_i(S) = \left(\frac{dS^{[n]}}{dS_i}\right)_S b^{[n]} \qquad \forall i = 1 \text{ to } k \tag{7}$$

or more simply: $g = Zb^{[n]}$. (8)

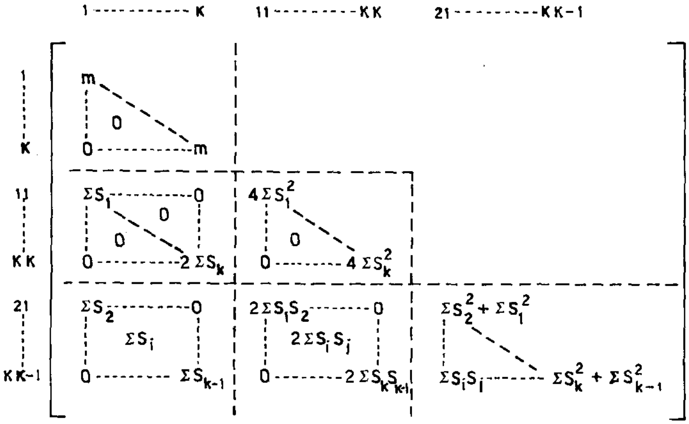
If we dispose of $m*k$ gradients for m points suitably distributed around the central point s_0 (with $1/k\binom{k+n}{n} \leq m$), the problem becomes a least square fit problem for with the solution is:

$$b^{[n]} = (Z'Z)^{-1}Z'g \tag{9}$$

It follows that the quality of the $b^{[n]}$ coefficients is closely related to the point distribution (so called experimental design) through the inverse product $(Z'Z)^{-1}$, as:

$$Var\,(b^{[n]}) = (Z'Z)^{-1}\sigma^2 \tag{10}$$

where σ^2 stands for the error variance.



Scheme 1.

3. Second Order Regression Designs ($n = 2$)

Assuming firstly a quadratic approximation for the potential energy hypersurface, we have to find an experience plane, which gives to the variance-covariance matrix $(Z'Z)^{-1}$ a good structure in order to improve the quality of the $b^{[2]}$ expected values. The $Z'Z$ matrix becomes orthogonal if:

$$\sum_P S_i(P) = 0 \qquad \forall i$$

$$\sum_P S_i(P) S_j(P) = 0 \qquad \forall i \neq j$$

In such a case all the coefficients b are independently estimated and the determinant of the matrix $Z'Z$ is maximized. The simplex [9] or the centered simplex plane meet this requirement; this trivial experimental design contains only $k+1$ or $k+2$ points which is enough to estimate the $\binom{k+2}{2} - 1$ regression coefficients of the quadratic approximation when the gradient vector is every times provided. The corresponding experience matrix is:

$$\begin{array}{c|cccc|}
1 & p_1\Delta_1 & p_2\Delta_2 & \dots & p_k\Delta_k \\
 & -q_1\Delta_1 & p_2\Delta_2 & \dots & p_k\Delta_k \\
 & 0 & -q_2\Delta_2 & \dots & p_k\Delta_k \\
p & \vdots & \vdots & & \vdots \\
 & 0 & 0 & \dots & q_k\Delta_k \\
 & \vdots & \vdots & & \vdots \\
m & 0 & 0 & \dots & 0 \\
 & l\dots & i & \dots & k
\end{array}$$

where

$$p_i = 1/(2i[i+1])^{1/2}$$

$$q_i = i p_i$$

and Δ_i stands for a scaling factor which defines the step size around the central point s_0 in each coordinate space direction ($s_i(p) = s_{i0} + \Delta_i$ times p_i, $-q_i$ or 0).

So we find the following expressions for the $b^{[2]}$ coefficients:

$$b_i = \frac{1}{m}\left\{\sum_{p=1}^{m}\left(\frac{dE}{dS_i}\right)_p\right\}$$

$$b_{ii} = \frac{p_i}{\Delta_i}\left\{\sum_{p=1}^{i}\left(\frac{dE}{dS_i}\right)_p - i\left(\frac{dE}{dS_i}\right)_{i+1}\right\}$$

$$b_{ij} = \frac{2}{\Delta_i^2 + \Delta_j^2} \left\{ p_j \Delta_j \left[\sum_{p=1}^{i} \left(\frac{dE}{dS_i} \right)_p - j \left(\frac{dE}{dS_i} \right)_{j+1} \right] \right.$$
$$\left. + p_i \Delta_i \left[\sum_{p=1}^{i} \left(\frac{dE}{dS_j} \right)_p - i \left(\frac{dE}{dS_j} \right)_{i+1} \right] \right\}$$

Then the regression program does not require the storage of any large matrix; in fact we chiefly need only one large vector as long as the first derivative number. For example for 12 atoms and 30 degrees of freedom we need only 32 gradients computations in order to evaluate 495 regression coefficients. If the chemical system of interest contains some symmetry operator the computation number may be shortened (for the benzene molecule only 11 gradients are requested [25]).

On the other hand the problems of numerical stability during the inversion are eliminated. From our experience they appear for molecules having more than 12 degrees of freedom when large and small force constants have to be simultaneously estimated [26] (in the quadratic approximation domain it is not always possible to widen enough the step size in the directions corresponding to the small forces). One advantage more in using this simplicial approach is that such a design may be translated in the k-dimensional space of the factors by recomputing only one vertex (plus one central point).

4. Third Order Regression Design ($n = 3$)

The knowledge of the third order derivative hypermatrix will become more and more interesting in vibrational analysis. Until now the success of the harmonic approximation for the vibrational analysis of the polyatomic systems is due to available level of accuracy and to the difficulties to obtain information about the anharmonicity [10]. Nevertheless for some small systems a more detailed analysis exist [11, 12] from a long time ago.

By using a regression on the gradient we only need second order design to estimate the third order derivative hypermatrix. It exists mainly two types of such designs:

- the Doehlert's planes [13];
- the composite planes [14].

As already discussed elsewhere [4] the Doehlert's planes are particularly useful to scan a certain portion of the potential energy surface. For our actual purpose it seems to be more interesting to employ the composite planes. Those designs are built up by combining the following geometrical figures in the internal factor space (see Fig. 1):

(1) a central point;
(2) a factorial plane (a square for $k = 2$, a cube for $k = 3$ or an hypercube for $k \geq 4$) with 2^k vertices (or a fractional replicate of this plane with 2^{k-p} vertices);

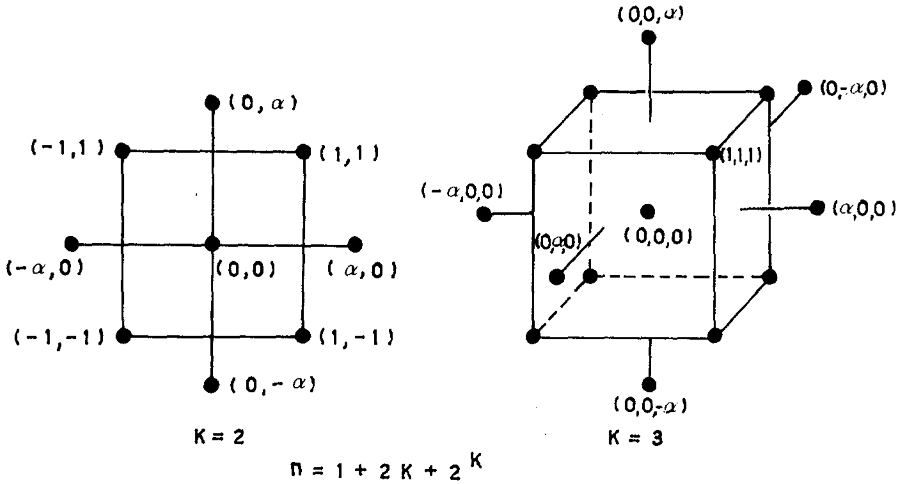


Fig. 1. The two and three dimensional composite planes

(3) a cross or a cross polytope with $2k$ vertices.

We have now to choose an appropriate value for the arm cross length (α in Fig. 1). We will be particularly interested by the orthogonality property which leads to an independent evaluation of the regression coefficients.

The composite planes have the next properties:

$$\sum_p S_i(p) = 0 \qquad \forall i \text{ from 1 to } k$$

$$\sum_p S_i(p)S_j(p) = 0 \qquad \forall i \neq j \neq \text{ from 1 to } k$$

$$\sum_p S_i(p)S_j(p)S_l(p) = 0 \qquad \forall i \neq j \neq l \text{ from 1 to } k$$

$$\sum_p S_i^2(p)S_j(p) = 0 \qquad \forall i \neq j \text{ from 1 to } k$$

$$\sum_p S_i^3(p) = 0 \qquad \forall i \text{ from 1 to } k$$

$$\sum_p S_i(p)S_j(p)S_l(p)S_m(p) = 0 \qquad \forall i \neq j \neq l \neq m \text{ from 1 to } k$$

$$\sum S_i^2(p)S_j(p)S_l(p) = 0 \qquad \forall i \neq j \neq 1 \text{ from 1 to } k$$

$$\sum S_i^3(p)S_j(p) = 0 \qquad \forall i \neq j \text{ from 1 to } k$$

It follows that the $Z'Z$ matrix at the third order regression level on the gradient has the form:

$$Z'Z = \begin{vmatrix} \mathscr{A}_1 & & 0 \\ & \ddots \, \mathscr{A}_k & \\ 0 & & \ddots \, \mathscr{B} \end{vmatrix}$$

where, if

$$B_i = \sum_p S_i^2(p) = (N_F + 2\alpha^2)\Delta_i^2$$

$$C_i = \sum_p S_i^4(p) = (N_F + 2\alpha^4)\Delta_i^4$$

$$D_{ij} = \sum_p S_i^2(p) S_j^2(p) = N_F \Delta_i^2 \Delta_j^2$$

we have for example for the block $\mathscr{A}_1$:

$$\mathscr{A}_1 = \begin{array}{r|cccccc|}
\underline{1} & m & & & & & \\
\underline{1}11 & 3B_1 & 9C_1 & & & & \\
\underline{1}22 & B_2 & 3D_{12} & 4D_{12}+C_2 & & & \\
\underline{1}33 & B_3 & 3D_{13} & D_{23} & 4D_{13}+C_3 & & \\
\vdots & \vdots & \vdots & \vdots & \vdots & & \\
\underline{1}kk & B_k & 3D_{1k} & D_{2k} & D_{3k} & \ldots & 4D_{1k}+C_k \\
\multicolumn{1}{r}{} & \underline{1} & \underline{1}11 & \underline{1}22 & \underline{1}33 & \ldots & \multicolumn{1}{c}{\underline{1}kk}
\end{array}$$

and for the remaining block $\mathscr{B}$:

$$\begin{array}{l|cccccc|}
11 & 4B_1 & & & & & \\
kk & & 4B_k & & & & \\
21 & & & B_2+B_1 & & & 0 \\
kk-1 & & & & B_2+B_{k-1} & & \\
321 & & 0 & & & 3D & \\
kk-1k-2 & & & & & & 3D \\
\multicolumn{1}{l}{} & 11\ldots kk, & & 21\ldots kk-1, & & 321\ldots & \multicolumn{1}{c}{kk-1 \quad k-2}
\end{array}$$

From the structure of $Z'Z$ we conclude that the inversion of such a matrix requests at least (if all s_i are different) to inverse independently k blocks $\mathscr{A}$($k+1$ times $k+1$) and one diagonal block $\mathscr{B}$ (r times r, if $r = k + k!/2!(k-2)! + k!/3!(k-3)!$). In order to avoid a too long discussion we here only investigate the inversion of one $\mathscr{A}$ matrix for which all the s_i terms are equal. The following results appear:

(1) The case for which $\alpha = 0$ (that corresponds to the disappearance of the cross polytope structure) does not lead to a singular $Z'Z$ matrix as it does for the regression on the energy [15]. Moreover it produces a $\mathscr{A}_i^{-1}$ matrix which may

be called quasi-orthogonal:

$$\mathscr{A}_i^{-1}(\alpha=0)=\left|\begin{array}{cccccc} a & & & & & \\ -a/3 & c & & & & \\ 0 & -e/3 & e & & & \\ 0 & -e/3 & 0 & e & & \\ \vdots & \vdots & \vdots & \vdots & & \\ 0 & -e/3 & 0 & 0 & \ldots & e \end{array}\right|$$

(2) Another kind of quasi-orthogonality may be built up by using for α:

$$\alpha=\left(\frac{\sqrt{m*N_F}-N_F}{2}\right)^{1/2}=\alpha_\perp$$

N_F: beying the number of vertices in the factorial plane.

In this case we have for $\mathscr{A}^{-1}$:

$$\mathscr{A}_i^{-1}(\alpha=\alpha_\perp)=\left|\begin{array}{cccccc} a & & & & & \\ b & c & & & & \\ d & 0 & e & & & \\ d & 0 & 0 & e & & \\ \vdots & \vdots & \vdots & \vdots & & \\ d & 0 & 0 & 0 & \ldots & e \end{array}\right|$$

In Table 1 we present the determinant of the moment matrix (det $[(1/m)\mathscr{A}'\mathscr{A}]$) corresponding to any block $\mathscr{A}$.

We see that even the point number is increasing by the addition of the cross to the factorial plane, the determinant of the moment matrix becomes higher; that corresponds to a parallel decreasing of the variance of any regression coefficients.

According to the last discussion we propose to follow a procedure which enable us to complete progressively our experience plane. First of all we start with the lowest possible fractional replicate ($(\frac{1}{2})^p$) of the complete factorial plane [16]. So

Table 1. Determinant of the matrix $(1/m\mathscr{A}'\mathscr{A})^*$ for different planes assuming that all points are in a sphere of radius 1.0

k	$\alpha=0$ (without cross)	$\alpha=\alpha_\perp$ (with cross)
3	$1.124\ 10^1$	$1.539\ 10^1$
4	$2.656\ 10^1$	$6.880\ 10^1$
5	$5.986\ 10^1$	$3.138\ 10^2$
6	$1.292\ 10^2$	$1.310\ 10^3$

* The moment matrix $(1/m)\mathscr{A}'\mathscr{A}$ let us enable to compare the efficiency of planes which have not the same number of vertices; evolution of determinant of $(1/m)Z'Z$ is strictly parallel to the one of $(1/m)\mathscr{A}'\mathscr{A}$.

we choose the smallest p value which satisfies the following inequality [17]:

$$(2^{k-p}) > \frac{1}{k}\binom{k+3}{k} - 1$$

After a first estimation of the regression coefficients $b^{[3]}$ we can increase p each time by 1, till the correlation coefficient becomes sufficiently good and the regression coefficients enough stable. A last check may be done by adding the cross polytope with an appropriate α value. We must also keep in mind that the use of an enough large second order composite plane let us enable to check the accuracy of the quadratic terms by regression on the energy only.

Finally such kind of planes may be used to evaluate some fourth order regression coefficients such as b_{ijkl} or b_{iijk}. Taking those coefficients together with the preceding one we do not disturb the structure of the regression; we only add one diagonal block in the $Z'Z$ matrix. For numerical convenience it seems to be important to inverse the $Z'Z$ matrix block after block and not to inverse it at one time.

When we are not sure to have to compute the third order regression coefficients, we can ask that our first experimental plane would be adequate for estimating the harmonic terms as well as possible and keeps the capability to be completed for estimating properly the anharmonicity contribution. In order to meet this requirement an alternate procedure may be applied. We start with the centered cross design which needs $2k+1$ computations. This old design is adequate (as well as the preceding simplex plane) to estimate the second order regression coefficients by using the gradient fitting.

The corresponding regression coefficients expressions are:

$$b_i = \frac{1}{m}\left\{\sum_p \left(\frac{dE}{dS_i}\right)_p\right\}$$

$$b_{ii} = \frac{1}{4\alpha\Delta_i}\left\{\left(\frac{dE}{dS_i}\right)_{S=\alpha\Delta_i} - \left(\frac{dE}{dS_i}\right)_{S=-\alpha\Delta_i}\right\}$$

$$b_{ij} = \frac{1}{2\alpha(\Delta_i^2+\Delta_j^2)}\left\{\Delta_j\left[\left(\frac{dE}{dS_i}\right)_{S=\alpha\Delta_j} - \left(\frac{dE}{dS_i}\right)_{S=-\alpha\Delta_j}\right]\right.$$
$$\left. + \Delta_i\left[\left(\frac{dE}{dS_j}\right)_{S=\alpha\Delta_i} - \left(\frac{dE}{dS_j}\right)_{S=-\alpha\Delta_i}\right]\right\}$$

As shown in Table 2 the cross plane remains approximately as efficient as the simplex one according to the D-optimality; if it contains more points, it can be completed by factorial plane for estimating the anharmonicity contributions. All this shows the large flexibility of such an approach which may be adapted to any purposes we have.

In the regression here presented we only use the gradient vectors for different nuclear structures well distributed; the available information concerning the total

Table 2. Comparison between simplex plane and cross plane assuming an experimental domain of radius equals to 1

	Simplex design[a]		Cross design[b]	
k	$\det(Z'Z)$	$\det(1/mZ'Z)^{c}$	$\det(Z'Z)$	$\det(1/mZ'Z)^{c}$
3	$3.596\ 10^{5}$	$1.841\ 10^{-1}$	$1.756\ 10^{5}$	$4.352\ 10^{-3}$
6	$8.958\ 10^{14}$	$3.705\ 10^{-10}$	$6.478\ 10^{14}$	$5.432\ 10^{-16}$
9	$4.867\ 10^{27}$	$2.832\ 10^{-29}$	$5.813\ 10^{27}$	$5.149\ 10^{-42}$

[a] for simplex: $\Delta_i = (2(k+1)/k)^{1/2} \forall i = 1, k$ in order to normalize the plane at radius = 1.

[b] for cross: $\alpha\Delta_i = 1 \forall i = 1, k$ in order to normalize the plane at radius = 1.

[c] the moment matrix $M = 1/mZ'Z$ let us enable to compare the efficiency of planes not having the same number of vertices.

energy is completely neglected. In fact it is possible to introduce both energy and gradient in the least square fit. Nevertheless this procedure destroy the properties of the $Z'Z$ matrix with does not remain orthogonal. Moreover even if we accept to pay the numerical inversion of the new $Z'Z$ matrix conclusion drawn from experience is that the result is less satisfactory; in particular the correlation coefficient goes down and the regression coefficients corresponding to the highest degree are badly estimated.

5. The Bias Analysis

The truncated Taylor expansion we use to represent the domain of interest in the k-dimensional potential hypersurface is not always adequate. It follows that the estimator of the regression coefficients ($\{b\}$) are biased by higher order terms not included in the expansion.

The structure of the so called "alias" matrix (A) tell us how the biased coefficients ($\{b\}$) are related to the unbiased estimates ($\{\beta\}$):

$$A = (Z'Z)^{-1}Z'\zeta$$

where ζ is the complement of the Z matrix for a more accurate Taylor expansion ($Z^{[n+r]} = (Z^{[n]} \vdots \zeta)$).

For the simplex plane (using the experimental matrix defined before with $\Delta_i = 1$ $\forall i$ from 1 to k), it appears that the first and second order regression coefficients are biased by the third order terms; i.e.

$$b_i^0 = \beta_i^0 + \frac{1}{2k+4}\sum_{l=1}^{k} (1+2\delta_{il})\beta_{ill}^0$$

$$b_{ii}^0 = \beta_{ii}^0 - \frac{3(i-1)p_i}{2}\beta_{iii}^0 + \tfrac{1}{2}\sum_{l<i} p_l\beta_{lli}^0 + \sum_{l>i} p_l\beta_{iil}^0$$

$$
\begin{aligned}
b_{ij}^{0} = \beta_{ij}^{0} + \frac{p_j}{2} \sum_{1 \le l \le j} \{1 + 2\delta_{il} + (2-j)\delta_{jl}\}\beta_{lli}^{0} \\
+ \frac{p_i}{2} \left\{ \sum_{1 \le l \le i} [1 - i\delta_{il}]\beta_{llj}^{0} \right\} \\
+ \sum_{i<l<j} \frac{p_l}{2} \beta_{ilj}^{0} + \sum_{j<l \le k} p_l \beta_{ijl}^{0} \qquad \forall i<j
\end{aligned}
$$

the superscript 0 indicates that we are referring to the normalized plane ($\Delta_i = 1$).

If the simplex design is adequate in terms of the regression coefficient variance, it becomes less efficient in terms of bias, specially for the second order terms (b_{ii} and b_{ij}). On another hand the cross plane, as efficient as the simplex one according to the coefficient variance, is less disturbed by the truncation error; the first and second order terms are respectively biased by the third and fourth order terms:

$$
\begin{aligned}
b_i^0 &= \beta_i^0 + \frac{2}{2k+1} \sum_{l=1}^{k} (1 + 2\delta_{il})\beta_{ill}^0 \\
b_{ii}^0 &= \beta_{ii}^0 + 2\beta_{iiii}^0 \\
b_{ij}^0 &= \beta_{ij}^0 + (\beta_{iiij}^0 + \beta_{ijjj}^0)/2 \qquad \forall i \ne j
\end{aligned}
$$

(the points stands at 0, +1 and −1 on each space direction).

Going now to the quasi-orthogonal third order designs:
- the complete centered factorial plane (the centered square, cube . . . , without cross, $\alpha = 0$);
- the composite plane with $\alpha = \alpha_{\perp}$; the alias matrix gives the following relations:

$$
\begin{aligned}
b_i^0 &= \beta_i^0 \\
b_{ii}^0 &= \beta_{ii}^0 + \frac{1}{1+\alpha^2/2^{k-1}} \sum_{l=1}^{k} [1 + (1 + \alpha^4/2^{k-2})\delta_{il}]\beta_{iill}^0 \\
b_{ij}^0 &= \beta_{ij}^0 + \frac{1}{1+\alpha^2/2^{k-1}} \sum_{l=1}^{k} [1 + (1 + \alpha^4/2^{k})(\delta_{il} + \delta_{jl})]\beta_{ijll}^0 \qquad \forall i \ne j \\
b_{ii'i''}^0 &= \beta_{ii'i''}^0
\end{aligned}
$$

in any case the distance between the vertices of the factorial plane and the origin is $\sqrt{k}$.

All this shows that the factorial and composite designs are not too bad; bias exists only between second and fourth order terms. As usually the stepsize (Δ) in each space direction is of about 10^{-2} Å or radian, the unnormalized regression coefficients ($\{b\}$) are related to the normalized one ($\{b^0\}$) by:

$$
b = (10^{-2})^r b^0 \quad \text{and} \quad \beta = (10^{-2})^r \beta^0
$$

where r stands for the number of indices of the considered b or β coefficient.

Table 3. Harmonic force constant matrix for same small compounds (derivatives in a.u. for energy, Å for bond lengths and radians for angles)

Molecule	H_2O				NH_2					
Plane	Simplex	Composite			Simplex	Cross	Factorial	Composite	Composite	Factorial
Regression	Gradient	Gradient	Energy	Gradient	Gradient	Gradient	Gradient	Gradient	Energy	Gradient
Order	2	2	2	3	2	2	2	2	2	3
Point number[a]	5	11	11	11	5	5	7	11	11	7
ξ	0.9999	0.9991	0.9998	0.9999	0.9999	0.9995	0.9996	0.9996	0.9999	0.9999
Second derivatives										
11	2.163	2.149	2.146	2.148	1.673	1.666	1.662	1.663	1.662	1.664
22	2.163	2.149	2.146	2.148	1.673	1.666	1.662	1.663	1.662	1.664
33	0.178	0.176	0.176	0.176	0.183	0.181	0.181	0.181	0.181	0.181
12	−0.045	−0.033	−0.033	−0.033	−0.030	−0.018	−0.018	−0.018	−0.018	−0.018
13	0.071	0.073	0.074	0.074	0.069	0.070	0.070	0.071	0.071	0.071
23	0.071	0.073	0.074	0.074	0.069	0.070	0.070	0.071	0.071	0.071
Stationary point										
d_1 (Å)	0.9497	0.9500	0.9499	0.9496	1.0146	1.0147	1.0149	1.0149	1.0147	1.0145
d_2 (Å)	0.9497	0.9500	0.9499	0.9496	1.0146	1.0147	1.0149	1.0149	1.0147	1.0145
$\measuredangle$(°)	111.43	111.64	111.61	111.54	108.54	108.58	108.64	108.63	108.58	108.53

[a] effective point number to be computed taking into account the symmetry reduction (see Ref. [27]).

Molecule		HNO							CO_2
Plane	Composite	Simplex	Cross	Factorial	Composite	Composite	Factorial	Composite	Simplex
Regression	Gradient	Gradient	Gradient	Gradient	Gradient	Energy	Gradient	Gradient	Gradient
Order	3	2	2	2	2	2	3	3	3
Point number[a]	11	5	7	9	15	15	15	15	5
ξ	0.9999	0.9999	0.9992	0.9993	0.9993	0.9998	0.9999	0.9999	0.9999
Second derivatives									
11	1.662	1.452	1.453	1.450	1.451	1.449	1.450	1.451	3.829
22	1.662	3.510	3.480	3.477	3.478	3.478	3.476	3.477	3.829
33	0.181	0.353	0.348	0.348	0.348	0.348	0.348	0.348	0.172
12	−0.018	0.148	0.160	0.160	0.160	0.160	0.160	0.160	0.453
13	0.071	0.021	0.023	0.023	0.023	0.023	0.023	0.023	−0.001
23	0.071	0.173	0.168	0.168	0.170	0.170	0.170	0.170	0.001
Stationary point									
d_1 (Å)	1.0146	1.0265	1.0267	1.0269	1.0268	1.0267	1.0265	1.0265	1.1611
d_2 (Å)	1.0146	1.1990	1.1993	1.1997	1.1995	1.1999	1.1989	1.1989	1.1611
$\measuredangle$(°)	108.52	110.81	110.85	110.91	110.90	110.85	110.80	110.80	180.00

Then we find that the bias importance is given by

for simplex design: $\beta_{ii'l}/\beta_{ii'} \simeq 10^{-1}\beta^0_{ii'l}/\beta^0_{ii'}$

for cross, factorial or composite designs: $\beta_{ii'll}/\beta_{ii'} \simeq 10^{-2}\beta^0_{ii'll}/\beta^0_{ii'}$

We conclude that the last designs, accurate in terms of the coefficient variance, remain valuable for bias. Let us also remember as explain before that the terms b_{ijll} with $i \neq j$ can be estimated in the same plane as long as the point number is larger than the regression coefficient number. In such a case only the b_{ii} terms remain biased.

6. Applications

We present here the applications of the method to some small compounds. Our purpose is to show the stability of the regression more than the accuracy of the absolute value of the successive derivatives. This last point is more depending of the level of sophistication in the theoretical method used (basis set, SCF and CI) than of the numerical method itself. All the actual computations are done with the 6-31G basis set of Pople [18] and we use the SCF-RHF or UHF method (with GAUSSIAN-70 program [19]) to solve the Hartree–Fock equations. It has been shown elsewhere that such kind of computation leads to a force constant matrix overestimated by about 10% [20]. To compute the gradient we are using the FORCE program of Schlegel [21]. In Tables 3 and 4 we present the results for the molecules H_2O, NH_2, HNO and CO_2. The program PLAN [22] is used for selecting the point distribution and MULFRA [23] is employed for the regressions. We can see that the quantities computed using gradient are in perfect agreement with the one computed by using the classical fit on the energy [4]. It exists only less than one percent of difference on the regression coefficients when we compare the different methods. The less efficient regression seems to be the simplex design. Reasons for this have been explained in the last section.

Table 4. Anharmonic force constant hypermatrix for some small compounds (same units as Table 3)

Molecule	H_2O	NH_2		HNO	
Plane	Composite	Factorial	Composite	Factorial	Composite
Regression	Gradient	Gradient	Gradient	Gradient	Gradient
Third derivatives					
111	−7.463	−5.520	−5.537	−5.144	−5.123
222	−7.463	−5.520	−5.537	−11.981	−11.994
333	−0.101	−0.107	−0.106	−0.206	−0.204
112	0.017	0.016	0.021	0.542	0.547
113	0.004	0.016	0.016	0.009	0.009
122	0.017	0.016	0.021	−1.214	−1.215
223	0.004	0.016	0.016	−0.439	−0.439
133	−0.055	−0.043	−0.042	−0.008	−0.008
233	−0.055	−0.043	−0.042	−0.629	−0.628
123	−0.134	−0.120	−0.120	−0.128	−0.128

Finally we can see that the introduction of the anharmonicity terms does not disturb the quadratic terms. The stationary point location remains insensible to the kind of regression up to 10^{-3} Å and 0.1 degree.

As we have seen a sufficiently small region (±0.015 Å on the bond lengths and ±4° on the angles) the second derivative matrix in the harmonic approximation remains stable by adding anharmonic terms. Such a property does not hold further under enlargement of the experimental domain. Our experience is that the inclusion of the third order regression coefficients let us enable to consider a domain at least three times larger than the present one without disturbing the accuracy of the second order regression coefficients. Examples exist [4] for which the quadratic approximation remains valid for very large regions.

Other works are now realized on larger molecules and super-molecules (such as transition structures [26]). The present technique always remains accurate. They will be published separately.

7. Conclusion

The here presented work let us enable by a regression on the gradient to find a local analytical surface around any stationary point of interest. In all cases the point distribution must be carefully chosen in order to be sure to lower the regression coefficient variance.

The estimation of the harmonic force constant matrix may be done by using the simplicial or the cross experimental planes. Both provides a diagonal variance-covariance matrix which guarantees an independent estimation on each coefficient and simplifies as much as possible the numerical aspect of the least square fit even for large molecules. The simplicial plane has two advantages:

(1) it contains as few points as possible and
(2) it may be translated in the k-dimensional space of the internal parameters by recomputing only one point each times.

On another hand the cross plane let us enable to further investigation for computing the anharmonic contributions; it provides also best estimation of the quadratic terms (closer to the one given by a composite plane) and can be splitted more easily when numerical stability problems are met.

Factorial plane and composite plane are adequate to obtain the cubic force constant matrix and some quartic terms. In table V we show the requested work in order to find quadratic and cubic regression coefficients from 2 up to 9 atoms in the molecular supersystem of interest. Those designs have also the basic structure for computing completely the quartic terms [24]; progress is now attempted in this direction.

The interest of such a work is also to show that everytimes an analytical derivative (at the order n) for any molecular property is available, it remains possible by a numerical approach to have at our disposal the derivatives at the order $n+1$,

Table 5. The requested work to estimate the harmonic and anharmonic force constant matrices

	Coefficient number		Point number to evaluate the gradient		
k	Order 2	Order 3	Simplex	Doehlert	Composite ([a])
3	10	20	5	13	9+6
6	28	84	8	43	17(+16)+12
9	55	220	11	91	33(+32)+18
12	91	455	14	157	65(+64)+24
15	136	816	17	241	65(+64)+30
18	190	1330	20	343	129(+128)+36
21	253	2024	23	463	257+42

[a] the first number corresponds to the lowest centered fractional replicate of the whole factorial plane, between parenthesis the possible increasing and finally the cross vertices.

$n+2$ and later $n+3$. To reach this goal we only have to choose properly the point distribution.

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15. The determinant in the energy regression is proportional to C-D which becomes zero when α disappears

16. Fractional replicate means that we select only $(1/p)$ points in the complete factorial plane. By example for $k = 3$ the fractional replicate $\frac{1}{2}$ of the complete plane (a cube) is a Tetrahedron (see also 4).
So the normalized point coordinates are $(1\ \ 11)\ (1-1-1)\ (-1\ \ 1-1)\ (-1-1\ \ 1)$ instead of the height tripled which corresponds to the cube vertices. We see that the product of all the coordinates inside each triplet always remains equal to $+1$. We note that $1 \circ 2 \circ 3 = I$ (identity). This concept may be easily generalized for more than 3 dimensions; we only request that the coordinates product of some column must be always equal to ± 1. For more details see Ref. [16] or [4]
17. Care is nevertheless to be taken in looking the alias matrix in order to keep away the influence of higher order terms from the estimation of the second and third order terms (see Ref. [4])
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27. The equivalences in nuclear structures are recognized by comparing their nuclear repulsions. We compute the inertial tensors (I_1, I_2) of the equivalent structures (C_1, C_2); after ordering the eigenvalues (λ_1, λ_2) and the eigenvectors (V_1, V_2) we are enable to find the rotation matrix R which connects C_1 and C_2: $R = V_2 V_1'$. If B stands for the well known Wilson's matrix between internal displacements (S) and cartesian displacements (ξ) such that $S = B\xi$, then the gradients for the structures C_1 and C_2 are related by:

$$g(2) = B_{(2)}^{-1} \begin{vmatrix} R & & & 0 \\ & R & & \\ & & \ddots & \\ 0 & & & R \end{vmatrix} B_{(1)} g_{(1)}$$

N diagonal R block

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