

Table 2. Enumeration of the number of stacking variants for $N = 12$

Percentage of hexagonal stacking	0	16.67	33.33	50	66.67	83.33	100	
Number of solutions obtained from Pólya's (1937) <i>Hauptsatz</i>	1	6	29	50	29	6	1	
Number of solutions for divisors of 12 to be subtracted								
$N = 6$			3		2			
$N = 4$				2				
$N = 3$					1			
$N = 2$							1	
$N = 1$	1							
Number of stacking variants for $N = 12$	0	6	26	48	26	6	0	$\sum (12) = 112$

with the special solutions

$$a_2(N) = (N - 1)/2 \quad \text{and} \quad a_{N-1}(N) = 1.$$

For example, for $N = 11$ one obtains for $N_h = 2, 4, 6, 8$ and 10 the values 5, 20, 26, 10 and 1. The sum $\sum (11) = 62$ is again in agreement with *International Tables for X-ray Crystallography* (1967).

If N is a prime number and $N \geq 3$ the total number of stacking variants is given by

$$\sum(N) = \frac{2^{(N-1)/2}(2^{(N-1)/2} + N) - (N + 1)}{2N}. \quad (9)$$

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Solving Structures by Constrained Least-Squares Refinement

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Abstract

A systematic convergence test for constrained rigid-body least-squares refinement shows good possibility of convergence towards the right solution, even starting from strongly misplaced molecular models (translations of about 1.5 Å and rotations of about 30°), if an appropriate sequence of reflections and strategy is used. Consequently, a routine for solving structures with a known molecular model by *ab initio* least-squares

refinement has been written, and successfully tested with three unknown structures: inclusion of second derivatives has also been tested, with a view to improving the method. In all cases so far examined, the routine is very fast, simple to use and competitive with usual methods, even when the model is only approximately known. The inclusion of second derivatives as such is not convenient, at least if precautions are not taken to reach a true minimum: a possible way of further improvement is discussed.

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Introduction

In recent years, a considerable development of different techniques of constrained least-squares refinement has taken place (Pawley, 1970; Diamond, 1971; Birktoft & Blow, 1972; Bianchi, Pilati & Simonetta, 1978*a,b*). Some of these methods essentially imply rigid-body or segmented-rigid-body molecular models, and their substantial success derives from a drastic reduction of the number of parameters to be dealt with. In many cases, when the molecule is indeed rigid, a constrained refinement might lead to results which are more significant than the corresponding results from conventional least-squares refinement (see, for instance, Scheringer, 1963; Pawley, 1972; Bianchi, Destro, Pilati & Simonetta, 1979).

Apart from final refinement of crystal structures, one might consider a practical use of these techniques for determining the approximate position and orientation of molecules or molecular fragments of known geometry, and therefore essentially solving the phase problem. In fact, in our experience the application of conventional least-squares refinement at a very early stage was often successful, provided a reasonable limitation of $\sin \theta/\lambda$ was considered; in some cases, atomic shifts even greater than 1 Å were involved (Gramaccioli, Destro & Simonetta, 1968). However, some quite obvious difficulties arise if one wants to refine a random structure (Booth, 1947, 1949; Lenstra, 1974; Wilson 1977). Since with a constrained model the number of degrees of freedom is drastically reduced, the possibility of converging to the correct structure can be expected to be substantially higher than for an unconstrained case. Moreover, since the number of parameters is considerably smaller, we can start with an extremely limited number of reflexions (*e.g.* six reflexions only for a rigid-body molecule). These reflexions, provided some obvious rules are respected, can be chosen with the smallest possible magnitude of the scattering vector \mathbf{h} , so that the probability of converging to the right solution is further increased. Since low-angle reflexions are not particularly sensitive to the molecular shape (and, to a certain extent, also to orientation; see below), the possibility of solution is practically unaffected by inadequacies of the proposed molecular model, provided, of course, they are not too large.

Starting from these considerations, in view of the dramatic possibility of convergence of this procedure, an examination of the convergence radius for constrained least-squares refinement in several practical cases was thought to be useful. Furthermore, a possible extension was considered to obtain a reasonable method for solving unknown crystal structures with a molecular model at least partially known; such a method, if successful, might be an alternative to a systematic search of the Patterson function, or similar procedures.

Convergence tests for known structures

A preliminary convergence test was carried out for four structures of molecular crystals which had been solved in this laboratory, *i.e.* 11,11-difluoro-1,6-methano[10]annulene, or DIF (Gramaccioli & Simonetta, 1971; Pilati & Simonetta, 1976); *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne, or DINO (Destro, Pilati & Simonetta, 1977); *syn*-5,7-diformyltricyclo[9.4.1.1^{3,9}]heptadeca-2,4,7,9,11,13,15-heptaene, or DIAL (Pilati & Simonetta, 1977), and 2,4,6-trinitrophenetole or TNPE (Gramaccioli, Destro & Simonetta, 1968). The first three structures were chosen because of the relative simplicity and regularity of their rigid models (with an increasing complexity from DIF to DIAL); the last one was chosen in view of the possibility of encountering false minima due to misorientation of the groups attached to the benzene ring, and relative pseudosymmetry. Unit-cell data of these substances are reported in Table 1.

Results from the convergence tests are reported in Table 2. For each run, a systematic series of starting points was chosen, each of them derived by shifting and rotating the molecule, as found in the structure. The direction of these shifts was taken in either sense along all the crystallographic axes and their principal diagonals, such as $\{101\}$, $\{110\}$, $\{111\}$ (when a structure is polar obviously no shift component along the polar axes is considered); the magnitudes of these shifts are reported (as Δw^i) in the seventh column of Table 2.

The rotations have been made in either sense by a certain angle (indicated as $\Delta\theta^i$ in the eighth column of Table 2), around each principal axis of inertia. This virtually covers an extensive range around the solution; the number of starting points so obtained (six possibilities of rotation \times 26 possibilities of translation = 156 in a general case, or only 48 for a crystal with a polar axis) is reported in the ninth column of Table 2.

An essential difficulty for this kind of test consists in verifying whether a certain situation indeed converges towards the right solution. Apart from the usual problem of recognizing if one of the symmetrically equivalent solutions in the Cheshire group (Hirshfeld, 1968) is emerging, this difficulty is especially evident at the starting point, when often six reflexions only are dealt with (N_{\min} in Table 2). Here, in fact, too few phases are available, and no details are apparent in the refined model. For this purpose, after a virtual convergence has been reached with a certain set of reflexions, some more must be added. This can be done by increasing the maximum length of the scattering vector \mathbf{h} , until a sufficient number of data is included for a good characterization of the result.

This expansion is rather a delicate point, because if it is made too rapidly the solution may be lost. Our procedure is as follows: after convergence has been

attained for a certain set of s reflexions, the set is expanded to a number $r.s$ of reflexions and so on, until the maximum number of reflexions (N_{\max}) is reached. For all the cases here treated N_{\max} is the number of reflexions for which $|h|^2 \leq a_{k\max}$; $a_{k\max}$ has been chosen between 0.035 and 0.05 Å⁻². A reasonable value ($r = 3$) was assigned to the expansion factor, except after the first series of cycles, where r is set to 2 for additional caution. During the first series of cycles, *i.e.* when dealing with the initial number of reflexions, the possibility of refining the translational parameters only ($L = 1$ in Table 2), or both rotational and translational parameters ($L = 2$) was considered. Scale and overall temperature factors were kept fixed at the corresponding values obtained from a Wilson (1942) plot.

After each cycle, the refinement was continued or not with the same set of data, depending on the results of certain tests. First of all, the usual exit, for a well-behaved case, is that the value of $S_{H_k}^j$, *i.e.* the residual function after the j th cycle, becomes practically

stationary. For this purpose, convergence was declared if $G = |(S_{H_k}^j - S_{H_k}^{j+1})/S_{H_k}^j| \leq 0.001$. In some cases, we noticed strong oscillations, which could result in a virtual loop. An exit for these situations was provided by testing whether for every parameter p_n^j of the j th cycle $|\Delta p_n^j + \Delta p_n^{j+1}|$ did not exceed a certain amount (here 0.025 Å or rad): in practice, this test almost coincides with testing G in many instances, but it stops oscillations if there are any. In all cases, a maximum number of cycles (here usually 12) was permitted with the same set of data.

After each exit, of whatever nature, expansion to the next, larger set of reflexions took place, because we saw that in a good number of instances a solution could be reached even in this way.

During this kind of refinement, in some cases large shifts may occur. This might indicate a meaningless solution; on the other hand, owing to the particular ease of convergence of the process, a large shift, although meaningless, often has the effect of displacing the

Table 1. *Known structures on which convergence tests have been made*

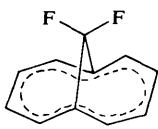
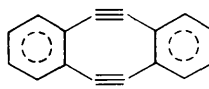
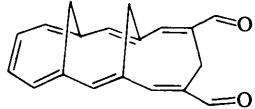
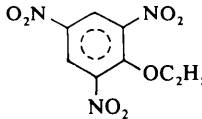
Symbol	DIF	DINO	DIAL	TNPE
Formula	C ₁₁ H ₈ F ₂	C ₁₆ H ₈	C ₁₉ H ₁₆ O ₂	C ₈ H ₇ N ₃ O ₇
				
Space group	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pca</i> 2 ₁
a (Å)	9.111	6.148	13.305	23.785
b	13.203	11.839	9.254	7.358
c	6.981	14.033	11.371	6.264
β (°)		91.02	95.89	
Z	4	4	4	4

Table 2. *Results of convergence tests on known structures*

The asterisk in the ninth column means a preliminary screening of the starting points based on packing (see text) was made.

Run	Structure	N_{\min}	N_{\max}	L	Δw^j (Å, rad)	Δw^j (Å)	$\Delta \theta^j$ (°)	Starting points	Solutions
1	DIF	6	67	2	—	1.00	30	48	36 (40)
2	DIF	6	67	2	—	1.25	30	48	30 (38)
3	DIF	6	67	2	—	1.50	30	48	23 (31)
4	DIF	6	67	1	—	1.50	45	30*	20 (23)
5	DIF	6	67	1	—	1.75	45	42*	32 (36)
6	DIF	6	67	2	—	1.50	45	30*	12 (19)
7	DIF	6	67	2	—	1.75	45	38*	21 (27)
8	DIF	6	104	1	0.5	1.50	45	48	15
9	DINO	7	99	2	—	1.00	30	156	78 (116)
10	DINO	7	99	1	—	1.50	30	114*	23 (67)
11	DINO	7	99	2	—	1.50	30	114*	40 (67)
12	DINO	7	150	1	1.0	1.50	45	108*	36
13	DINO	7	128	1	0.5	1.50	45	144*	88
14	DIAL	7	147	1	0.5	1.50	45	72*	38
15	TNPE	6	144	1	0.5	1.50	30	30*	25
16	TNPE	6	144	1	0.5	1.50	45	30*	5

molecular model from a bad point towards a more promising region, and a way out of a possible *impasse* is consequently provided. Owing to this possibility, and to the very short computing time, in most cases the refinement was continued, utilizing these shifts as they came out. In the remaining cases, the refinement was also continued, but the shifts were cut down to a maximum permitted value (Δ_{\max} in Table 2). This means that whenever any shift $|\Delta \mathbf{w}_n^j|$ or $|\Delta \theta_n^j|$ exceeded this value, it was replaced by a new shift $\Delta \mathbf{w}_n^{jj} = \Delta_{\max} \times \Delta \mathbf{w}_n^j / |\Delta \mathbf{w}_n^j|$, or $\Delta \theta_n^{jj} = \Delta_{\max} \Delta \theta_n^j / |\Delta \theta_n^j|$, *i.e.* the direction, sense, and the rotation axis were maintained.

In the last column of Table 2, the number of times a solution was reached is reported for each run. Two different criteria can be used for deciding whether or not a true solution is obtained (when, of course, a sufficient number of reflexions has been included in the refinement): the first involves a subsequent least-squares refinement, including all the data and final weights used in the paper from which the structure has been taken, and checking whether the final coordinates (or their Cheshire group symmetrically equivalent) are obtained. This criterion is obviously tedious and expensive, and for this reason it was used only partially in our tests (in Table 2, the numbers between parentheses in the last column were evaluated in this way). A second faster, although much more restrictive, criterion is to check the phase angle assigned to all the reflexions in the final set for which $F \geq F_{\max}/5$, where F_{\max} is the highest F . The situation was considered to be satisfactory when any single phase error was $< 25^\circ$: the numbers reported in the last column of Table 2 without parentheses were evaluated in this manner.

Even at a first glance, the results seem to be quite satisfactory. In fact, a considerable number of successful cases have been obtained even with shifts of the order of 1.5 Å and rotations of 30 and 45° from the correct situation. This means that we have a quite good possibility of arriving at a correct solution even starting from a grid of different points 3 Å and 60° from each other.

From the data so far obtained, on average it is difficult to see a definite advantage in having $L = 1$, or $L = 2$, *i.e.* in refining the position only, or also the molecular orientation in the first series of cycles. Similarly, cutting the shifts or not (see Δ_{\max}), as we have explained, does not seem on average to affect the possibility of convergence. Within each single case, however, the behaviour can be quite different, and this might indicate the possibility of using alternative strategies.

Applications and discussion

Based mainly on these principles and results, a program for solving an unknown crystal structure with a known

molecular model was written. The mathematical outline of the least-squares refinement is given in the Appendix: it essentially consists in a segmented-rigid-body routine, with an overall temperature factor. This parameter (and the scale factor) can be refined only in the last series of cycles, *i.e.* when the number of reflexions is the maximum (N_{\max}). The major difference with respect to the usual least-squares routines of this kind lies in considering also second derivatives: these have been taken care of, with a view to the possibility of further improving convergence, and also of testing whether a true minimum of the residual function has been reached.

The procedure is as follows: first of all, a grid of different starting positions of the molecular centres of gravity is chosen; the spacing can be assigned at will (in general about 2 Å). The origin of the grid can also be assigned: for a general case, special positions must be avoided, since convergence towards saddle points, situated between two symmetrically equivalent solutions, may result. In most cases, the packing is checked, only in order to make sure that the centres of two molecules are farther apart than a certain minimum distance (in general, about 4 Å); for molecules with a particular shape, this distance might be substantially raised, thereby resulting in a considerable saving of computing time. The extension of the grid is chosen in accordance with the requirements of symmetry (Cheshire groups and space groups).

For each point in the grid compatible with packing requirements, a structure-factor calculation on a minimum number of reflexions (N_{\min}) is performed, starting from a rotational grid of all the possible orientations; also for this grid, the spacing can be assigned at will (in general, 30°), and the extension is chosen depending on the symmetry of the molecular model. The reflexions (three only, in general, provided their indices are linearly independent) are chosen so that the scattering vector is the smallest possible. For each point in the translational grid, the orientation corresponding to the lowest value of the residuals is chosen as a starting point in the least-squares refinement. At the beginning of the refinement, a set of only N_{\min} reflexions is used (or twice as many, if also rotations are included in the first cycles, *i.e.* $L = 2$), and the procedure goes forward just as we have already indicated for the convergence tests.

As when dealing with known structures, some of the most delicate problems arise with checking whether a true solution has been achieved; since in this case no comparison with a set of standard phases can be made, only the result of a complete refinement can be taken as proof.

For testing our method, three unknown structures have been considered, *i.e.* 3,5-diformylbicyclo[5.4.1]dodeca-2,5,7,9,11-pentaene (ALD), 1,6-methano[10]annulene (MANN) and the β form of

Table 3. *Unknown structures solved by our method*

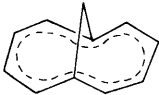
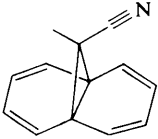
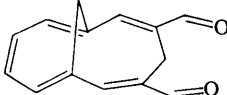
Symbol	MANN	CNME (β form)	ALD
Formula	$C_{11}H_{10}$	$C_{13}H_{11}N$	$C_{14}H_{12}O_2$
			
Space group	<i>Fdd2</i>	<i>C2/c</i>	<i>Pccn</i>
<i>a</i> (Å)	33.969	21.316	13.738
<i>b</i>	15.112	6.198	13.472
<i>c</i>	6.181	15.660	11.658
β (°)		107.54	
<i>Z</i>	16	8	8
Molecular model derived from	DIF	CNME (α form)	DIAL
\bar{D} (Å)	0.221	0.080	0.203
D_{max} (Å)	0.286	0.123	0.320

Table 4. *Results of our method for solving structures*

Run	Structure	Derivative	N_{min}	N_{max}	Starting points	Number of solutions	Computing time (CPU s)	Computing time/starting point(s)
1	MANN	I	3	35	16	3	219	13.7
2	MANN	I, II	3	35	16	1	272	17.0
3	CNME	I	3	90	15	3	150	10.0
4	CNME	I, II	3	90	15	1	229	15.2
5	CNME	I	7	90	15	3	267	17.8
6	ALD	I	3	97	10	3	215	21.5
7	ALD	I, II	3	62	10	0	259	25.9

11-methyltricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene-11-carbonitrile (CNME). A detailed report on the data collection, final refinement, geometry and discussion on these structures will be reported elsewhere (Bianchi, Pilati & Simonetta, 1980*a,b,c*). Unit-cell data of these substances are reported in Table 3. For solving these structures, molecular models have been derived from DIAL, DIF and the α form of CNME (Bianchi, Pilati & Simonetta, 1978*a*), respectively. Maximum (D_{max}) and mean (\bar{D}) variations of these coordinates (Å) between the model and the final geometry are given in the last rows of Table 3.

In Table 4, results from application of this procedure are reported. The symbols in the third column refer to inclusion or not of second derivatives in all cycles of least-squares minimization; for all these cases, translational and rotational grid spacings are 2 Å and 30°, respectively, and corresponding origins of the grids were chosen 1 Å from each crystal axis. The minimum permitted distance between molecular centres in the packing test is 4 Å; the CPU computing time is referred to a medium-fast computer (UNIVAC 1100/80).

From Table 4, several points are evident. First of all, a solution has been achieved for all these structures in a very reasonable computing time. This time could be cut down considerably (to about 1/3) if some automatic

tests for recognizing solutions are introduced, since (except when dealing with second derivatives) three symmetrically equivalent solutions are found in each case. A possible procedure for verifying the correctness of the solution is: (1) verification of the atom-atom non-bonded distances; (2) verification of second derivatives to ascertain the real presence of a minimum; (3) a reasonable *R*-factor check.

Another interesting point to notice is that inclusion of second derivatives, in spite of the substantial increase in computing time, does not lead to any improvement in finding a solution: as a matter of fact, the possibility of attaining a solution actually *decreases*. Such a situation is probably connected with the need to verify whether the refinement is going towards a real minimum, or to some sort of saddle point (or possibly even to a maximum). Since, as shown in the Appendix, our procedure is essentially a Newton-Raphson minimization of the least-squares residual, several methods are known to overcome the difficulty of not having the second-derivative matrix positive-definite, thereby ensuring that a real minimum is reached in any case (Goldfield, Quandt & Trotter, 1966).

At this stage, however, because of the essential success of the treatment including first derivatives only, we are planning to examine special mathematical

methods involving second-derivative treatment only at a later stage, for further improving convergence, in view of a Monte-Carlo-like procedure for solving structures in this way (Niggl & Fehlmann, 1965).

Assistance and advice by Dr M. Raimondi is gratefully acknowledged.

APPENDIX

Let us indicate the sum of the squares of the residuals at a certain iteration as:

$$S_{H_k}(\mathbf{p}) = \sum_{\mathbf{h} \in H_k} (I_{\mathbf{h}}^o - I_{\mathbf{h}}^c/K^2)^2, \quad (1)$$

where K is the scale factor; $I_{\mathbf{h}}^o$ is the observed intensity; $I_{\mathbf{h}}^c = |F_{\mathbf{h}}|^2$ and $F_{\mathbf{h}}$, the calculated structure factor, is

$$F_{\mathbf{h}} = A_{\mathbf{h}} + iB_{\mathbf{h}} = \sum_{n=1}^N T_n \sum_{m=1}^{M_n} d_{nm} \sum_{j=1}^J \exp(\beta_{nmj});$$

$$\beta_{nmj} = 2\pi i[\mathbf{h}_j \cdot (\mathbf{R}_n \mathbf{x}_{nm} + \mathbf{w}_n) + \alpha_j];$$

$\alpha_j = \mathbf{h} \cdot \mathbf{t}_j$; $\mathbf{h} \equiv (h_1, h_2, h_3)$ where h_i 's are the Miller indices; $\mathbf{h}_j = \mathbf{h} \mathbf{M}_j \mathbf{D}^{-1}$. Here \mathbf{M}_j and \mathbf{t}_j are the matrix and translation vector corresponding to the j th symmetry operation $\{M_j | t_j\}$; \mathbf{w}_n denotes the position in the orthogonal \hat{A} coordinate system of the mass centre of the n th molecular fragment;

$$\mathbf{R}_n = \mathbf{R}_n^3 \mathbf{R}_n^2 \mathbf{R}_n^1; \quad \mathbf{R}_n^1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta_n^1 & -\sin \theta_n^1 \\ 0 & \sin \theta_n^1 & \cos \theta_n^1 \end{pmatrix};$$

$$\mathbf{R}_n^2 = \begin{pmatrix} \cos \theta_n^2 & 0 & -\sin \theta_n^2 \\ 0 & 1 & 0 \\ \sin \theta_n^2 & 0 & \cos \theta_n^2 \end{pmatrix};$$

$$\mathbf{R}_n^3 = \begin{pmatrix} \cos \theta_n^3 & -\sin \theta_n^3 & 0 \\ \sin \theta_n^3 & \cos \theta_n^3 & 0 \\ 0 & 0 & 1 \end{pmatrix};$$

$\theta_n \equiv (\theta_n^1, \theta_n^2, \theta_n^3)$; $\theta_n^1, \theta_n^2, \theta_n^3$ are the rotation angles about orthogonal axes x_1, x_2, x_3 respectively; \mathbf{x}_{nm} designates the position of the m th atom in the n th fragment; \mathbf{D} is a transformation matrix to an arbitrary orthogonal system; J is the total number of symmetry elements; $d_{nm} = f_{nm} g_{nm}$; f_{nm} and g_{nm} are the scattering factor and the population parameter of the m th atom in the n th fragment, respectively; M_n is the total number of atoms of the n th fragment; $T_n = \exp(-B_n |\mathbf{h}|^2)$; B_n is the temperature factor for the n th fragment; N is the total number of fragments in the asymmetric unit; $H_k =$

$\{\mathbf{h}: |\mathbf{h}| < a_k\}$; a_k is a prefixed limit for $|\mathbf{h}|$ at the k th iteration in the convergence process: in any case it is kept less than an appropriate value $a_{k\max}$; $\mathbf{p} = \{\mathbf{w}_1, \dots, \mathbf{w}_N, \theta_1, \dots, \theta_N\}$.

Then our object is the iterative minimization of the function $S_{H_k}(\mathbf{p})$ with respect to \mathbf{p} .

Applying the Newton-Raphson procedure to the minimization of (1), one obtains

$$[\nabla S_{H_k}(\mathbf{p})]_{\mathbf{p}=\mathbf{p}_i^c} + \Delta \mathbf{p} [\nabla \nabla^T S_{H_k}(\mathbf{p})]_{\mathbf{p}=\mathbf{p}_i^c} = \mathbf{0};$$

where $\nabla \nabla^T S_{H_k}$ is the $6N \times 6N$ matrix of second derivatives of S_{H_k} . Hence, the normal equations may be written as

$$\sum_{v=1}^{6N} \left[\sum_{\mathbf{h} \in H_k} \left(\frac{\partial I_{\mathbf{h}}^c}{\partial p_{\mu}} \frac{\partial I_{\mathbf{h}}^c}{\partial p_v} - \frac{\partial^2 I_{\mathbf{h}}^c}{\partial p_{\mu} \partial p_v} \Delta I_{\mathbf{h}} \right)_{\mathbf{p}=\mathbf{p}_i^c} \right] \Delta p_v = \sum_{\mathbf{h} \in H_k} \Delta I_{\mathbf{h}} \left(\frac{\partial I_{\mathbf{h}}^c}{\partial p_{\mu}} \right)_{\mathbf{p}=\mathbf{p}_i^c}; \quad (2)$$

where $\mu = 1, \dots, 6N$; $\Delta I_{\mathbf{h}} = I_{\mathbf{h}}^o - I_{\mathbf{h}}^c$;

$$\frac{\partial I_{\mathbf{h}}^c}{\partial p_{\mu}} = 2 \left(A_{\mathbf{h}} \frac{\partial A_{\mathbf{h}}}{\partial p_{\mu}} + B_{\mathbf{h}} \frac{\partial B_{\mathbf{h}}}{\partial p_{\mu}} \right);$$

$$\frac{\partial^2 I_{\mathbf{h}}^c}{\partial p_{\mu} \partial p_v} = 2 \left(\frac{\partial A_{\mathbf{h}}}{\partial p_{\mu}} \frac{\partial A_{\mathbf{h}}}{\partial p_v} + A_{\mathbf{h}} \frac{\partial^2 A_{\mathbf{h}}}{\partial p_{\mu} \partial p_v} + \frac{\partial B_{\mathbf{h}}}{\partial p_{\mu}} \frac{\partial B_{\mathbf{h}}}{\partial p_v} + B_{\mathbf{h}} \frac{\partial^2 B_{\mathbf{h}}}{\partial p_{\mu} \partial p_v} \right).$$

We summarize here the derivatives of $A_{\mathbf{h}}$ with respect to the various rigid-body parameters.

$$\frac{\partial A_{\mathbf{h}}}{\partial w_n^r} = -2\pi T_n \sum_{m=1}^{M_n} d_{nm} \sum_{j=1}^J h_j^r V_{nmj};$$

$$\frac{\partial A_{\mathbf{h}}}{\partial \theta_n^r} = -T_n \sum_{m=1}^{M_n} d_{nm} \sum_{j=1}^J \gamma_{nmj}^r V_{nmj};$$

$$\frac{\partial^2 A_{\mathbf{h}}}{\partial w_n^r \partial w_n^s} = -4\pi^2 T_n \sum_{m=1}^{M_n} d_{nm} \sum_{j=1}^J h_j^r h_j^s C_{nmj};$$

$$\frac{\partial^2 A_{\mathbf{h}}}{\partial \theta_n^r \partial \theta_n^s} = -T_n \sum_{m=1}^{M_n} d_{nm} \sum_{j=1}^J \left(\gamma_{nmj}^r \gamma_{nmj}^s C_{nmj} + 2\pi \mathbf{h}_j \cdot \frac{\partial^2 \mathbf{R}_n}{\partial \theta_n^r \partial \theta_n^s} \mathbf{x}_{nm} V_{nmj} \right);$$

$$\frac{\partial^2 A_{\mathbf{h}}}{\partial w_n^r \partial \theta_n^s} = -2\pi T_n \sum_{m=1}^{M_n} d_{nm} \sum_{j=1}^J h_j^r \gamma_{nmj}^s C_{nmj}; \quad (r, s = 1, 2, 3);$$

$$C_{nmj} = \cos \beta_{nmj}; \quad V_{nmj} = \sin \beta_{nmj}; \quad \gamma_{nmj}^r = 2\pi \mathbf{h}_j \cdot \frac{\partial \mathbf{R}_n}{\partial \theta_n^r} \mathbf{x}_{nm};$$

$$\frac{\partial \mathbf{R}_n}{\partial \theta_n^1} = \mathbf{R}_n^3 \mathbf{R}_n^2 \mathbf{R}_n'^1; \quad \frac{\partial \mathbf{R}_n}{\partial \theta_n^2} = \mathbf{R}_n^3 \mathbf{R}_n'^2 \mathbf{R}_n^1;$$

$$\frac{\partial \mathbf{R}_n}{\partial \theta_n^3} = \mathbf{R}_n'^3 \mathbf{R}_n^2 \mathbf{R}_n^1;$$

$$\frac{\partial^2 \mathbf{R}_n}{(\partial \theta_n^1)^2} = \mathbf{R}_n^3 \mathbf{R}_n^2 \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\cos \theta_n^1 & \sin \theta_n^1 \\ 0 & -\sin \theta_n^1 & -\cos \theta_n^1 \end{pmatrix};$$

$$\frac{\partial^2 \mathbf{R}_n}{\partial \theta_n^1 \partial \theta_n^2} = \mathbf{R}_n^3 \mathbf{R}_n'^2 \mathbf{R}_n'^1;$$

$$\frac{\partial^2 \mathbf{R}_n}{(\partial \theta_n^2)^2} = \mathbf{R}_n^3 \begin{pmatrix} -\cos \theta_n^2 & 0 & \sin \theta_n^2 \\ 0 & 0 & 0 \\ -\sin \theta_n^2 & 0 & -\cos \theta_n^2 \end{pmatrix} \mathbf{R}_n^1;$$

$$\frac{\partial^2 \mathbf{R}_n}{\partial \theta_n^1 \partial \theta_n^3} = \mathbf{R}_n'^3 \mathbf{R}_n^2 \mathbf{R}_n'^1;$$

$$\frac{\partial^2 \mathbf{R}_n}{(\partial \theta_n^3)^2} = \begin{pmatrix} -\cos \theta_n^3 & \sin \theta_n^3 & 0 \\ -\sin \theta_n^3 & -\cos \theta_n^3 & 0 \\ 0 & 0 & 0 \end{pmatrix} \mathbf{R}_n^2 \mathbf{R}_n^1;$$

$$\frac{\partial^2 \mathbf{R}_n}{\partial \theta_n^2 \partial \theta_n^3} = \mathbf{R}_n'^3 \mathbf{R}_n'^2 \mathbf{R}_n^1;$$

$$\mathbf{R}_n'^1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\sin \theta_n^1 & -\cos \theta_n^1 \\ 0 & \cos \theta_n^1 & -\sin \theta_n^1 \end{pmatrix};$$

$$\mathbf{R}_n'^2 = \begin{pmatrix} -\sin \theta_n^2 & 0 & -\cos \theta_n^2 \\ 0 & 0 & 0 \\ \cos \theta_n^2 & 0 & -\sin \theta_n^2 \end{pmatrix};$$

$$\mathbf{R}_n'^3 = \begin{pmatrix} -\sin \theta_n^3 & -\cos \theta_n^3 & 0 \\ \cos \theta_n^3 & -\sin \theta_n^3 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The derivatives of B_n with respect to \mathbf{p} can be expressed in a similar way as for A_n .

The normal equations (2) are solved by diagonalizing the normal matrix with the Householder method.

This procedure permits also classification of the stationary points of $S_{H_n}(\mathbf{p})$.

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