Updated Hessian Matrix and the Restricted Step Method for Locating Transition Structures

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ABSTRACT

A family of the updated Hessian matrices for locating transition structures is presented. An analysis and improvement of the restricted step algorithm described by Culot et al. is proposed. The efficiency of the latter method is compared with other well-established methods for locating transition structures. © 1994 by John Wiley & Sons, Inc.

Introduction

In recent years, new algorithms have been proposed for locating transition structures in an efficient way. The latter are stationary points on the potential energy hypersurface in which the Hessian has one and only one negative eigenvalue while all others are positive. These stationary points are also known as first-order saddle points. The eigenvector associated to the negative eigenvalue, the so-called transition vector, is crucial to ensure that the transition structure corresponds to the elementary reaction under consideration. The problem of locating transition structures with a selected transition vector has been studied recently by Cerjan and Miller,[1] Bell and Crighton,[2] and Simon et al.[3,4] A good recent review about methods for locating first-order saddle points is given by Schlegel.[5]

The different types of algorithms for locating transition structures are based on four methods: grid search, reaction coordinate, conjugate gradients, and quasi-Newton techniques. From a theoretical point of view, both grid search and reaction coordinate methods consist in a simple exploration of the potential energy hypersurface. The methods based on the conjugate gradients technique, for instance, those proposed by Sinclair and Fletcher[6] and more recently by Fischer and Karplus,[7] are appropriate for large problems (e.g., hundreds or thousands of variables) and require the storage of only a few vectors. The drawback of these methods is that the transition vector never is checked; thus, if the initial transition vector is not correct the method converges to a wrong structure or does not converge at all. Bell et al.[8] proposed a method that

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is a mix of the conjugate gradients and quasi-Newton techniques. Among the algorithms that use the quasi-Newton technique, the first one was proposed some time ago by McIver and Komornicki.[9] This method minimizes the Euclidean norm of the potential energy gradient rather than the energy directly and, therefore, is computationally expensive. More recently Schlegel,[10] Culot et al.,[11] and particularly Baker[12] proposed efficient quasi-Newton algorithms that are applied directly to the energy function. Baker uses a rational function rather than a normal function. All these methods need only the computation of the energy and its gradient. The main difference between these methods is in the way the Hessian matrix is corrected from iteration to iteration.

The purpose of this article is to present a family of updated Hessian matrices for locating transition structures, as well as equilibrium structures, using a quasi-Newton technique. Also, the algorithm of the Culot et al.[11] is discussed and some small changes are presented to improve it. This algorithm has been implemented in the semiempirical program package MOPAC[13] and in the *ab initio* system of programs GAMESS.[14]

Presentation of the Formalism

Let us consider an energy function, $E(\mathbf{x})$, that depends of N real variables and is at least twice continuously differentiable. The quasi-Newton method consists first in using the quadratic model for the expansion of $E(\mathbf{x})$ about $\mathbf{x}^k$:

$$E(\mathbf{x}^k + \boldsymbol{\delta}^k) \approx q^k(\boldsymbol{\delta}^k) = E(\mathbf{x}^k) + (\mathbf{g}^k)^T\boldsymbol{\delta}^k + \frac{1}{2}(\boldsymbol{\delta}^k)^T\mathbf{H}^k\boldsymbol{\delta}^k \quad (1)$$

where $\boldsymbol{\delta}^k = \mathbf{x}^{k+1} - \mathbf{x}^k$, $\mathbf{g}^k$ is the gradient vector, $\mathbf{H}^k$ is the Hessian matrix, and $q^k(\boldsymbol{\delta}^k)$ is the quadratic approximation of $E(\mathbf{x})$ for iteration k. Second, the Hessian matrix $\mathbf{H}^k$ of eq. (1) is substituted by a symmetric nonsingular matrix $\mathbf{B}^k$, which is corrected or updated from iteration to iteration. In each iteration, the correction $\boldsymbol{\delta}^k$ optimizes $q^k(\boldsymbol{\delta}^k)$. Thus, the iterative procedure to locate a stationary point of any order can be summarized[15] in the following way:

1. solve $\mathbf{B}^k\boldsymbol{\delta}^k = -\mathbf{g}^k$;
2. set $\mathbf{x}^{k+1} = \mathbf{x}^k + \boldsymbol{\delta}^k$;
3. update the approximate Hessian $\mathbf{B}^{k+1}$ from $\mathbf{B}^k$. (2)

For convenience, this section is divided into two parts, one presenting the updated Hessian matrix and other the restricted step method.

FAMILY OF UPDATED HESSIAN MATRICES FOR LOCATING SADDLE POINTS

The updating formulae allow $\mathbf{B}^{k+1}$ to be evaluated from $\mathbf{B}^k$. From a mathematical point of view, normally two restrictions are imposed in the updating formula of $\mathbf{B}^{k+1}$. The first restriction is the symmetry because the true Hessian is symmetric at each iteration. The second is the so-called quasi-Newton condition, which is defined as

$$\mathbf{B}^{k+1}\boldsymbol{\delta}^k = \boldsymbol{\gamma}^k \quad (3)$$

where $\boldsymbol{\gamma}^k = \mathbf{g}^{k+1} - \mathbf{g}^k$. Expression (3) comes from the fact that $\mathbf{B}^k$ does not relate $\boldsymbol{\delta}^k$ and $\boldsymbol{\gamma}^k$ correctly in the quadratic sense, e.g., $\mathbf{B}^k\boldsymbol{\delta}^k \approx \boldsymbol{\gamma}^k$. Thus, $\mathbf{B}^{k+1}$ is calculated such that $\boldsymbol{\delta}^k$ and $\boldsymbol{\gamma}^k$ are related correctly in the quadratic approximation. A simple procedure for updating $\mathbf{B}^{k+1}$ consists in writing

$$\mathbf{B}^{k+1} = \mathbf{B}^k + \mathbf{E}^k \quad (4)$$

where $\mathbf{E}^k$ is the matrix correction, which is taken symmetric and of some rank. Often, the rank-two matrix is used because it has support from a variational principle.[15] We will take a matrix of rank two constructed from the vectors $\boldsymbol{\delta}^k$ and $\boldsymbol{\xi}^k$. The last vector is defined as

$$\boldsymbol{\xi}^k = \mathbf{E}^k\boldsymbol{\delta}^k = \boldsymbol{\gamma}^k - \mathbf{B}^k\boldsymbol{\delta}^k \quad (5)$$

and is related to the quasi-Newton condition. A more general formula that fulfills this conditions is

$$\mathbf{E}^k = a_k\boldsymbol{\delta}^k(\boldsymbol{\delta}^k)^T + b_k(\boldsymbol{\xi}^k(\boldsymbol{\delta}^k)^T + \boldsymbol{\delta}^k(\boldsymbol{\xi}^k)^T) + c_k\boldsymbol{\xi}^k(\boldsymbol{\xi}^k)^T \quad (6)$$

Using the relationship in eq. (5) and equating terms in $\boldsymbol{\delta}^k$ and $\boldsymbol{\xi}^k$, one obtains the following two equations:

$$0 = a_k(\boldsymbol{\delta}^k)^T\boldsymbol{\delta}^k + b_k(\boldsymbol{\xi}^k)^T\boldsymbol{\delta}^k$$
$$1 = b_k(\boldsymbol{\delta}^k)^T\boldsymbol{\delta}^k + c_k(\boldsymbol{\xi}^k)^T\boldsymbol{\delta}^k \quad (7)$$

Assigning $b_k = \phi_k/(\boldsymbol{\delta}^k)^T\boldsymbol{\delta}^k$, then a_k and c_k take the values $a_k = -\phi_k(\boldsymbol{\delta}^k)^T\boldsymbol{\xi}^k/((\boldsymbol{\delta}^k)^T\boldsymbol{\delta}^k)^2$ and $c_k = (1 - \phi_k)/(\boldsymbol{\delta}^k)^T\boldsymbol{\xi}^k$. The parameter ϕ_k is the single degree of freedom of the set of eq. (7). Substituting the last

results into (6) and after this into (4), one gets an updating formula for $\mathbf{B}^{k+1}$:

$$\begin{aligned}\mathbf{B}_{\phi}^{k+1} &= \mathbf{B}^{k} - \phi_k \frac{(\boldsymbol{\delta}^k)^T\boldsymbol{\xi}^k}{((\boldsymbol{\delta}^k)^T\boldsymbol{\delta}^k)^2}\,\boldsymbol{\delta}^k(\boldsymbol{\delta}^k)^T \\ &\quad + \phi_k \frac{1}{(\boldsymbol{\delta}^k)^T\boldsymbol{\delta}^k}\,(\boldsymbol{\xi}^k(\boldsymbol{\delta}^k)^T + \boldsymbol{\delta}^k(\boldsymbol{\xi}^k)^T) \\ &\quad + (1 - \phi_k)\frac{1}{(\boldsymbol{\delta}^k)^T\boldsymbol{\xi}^k}\,\boldsymbol{\xi}^k(\boldsymbol{\xi}^k)^T \\ &= \mathbf{B}^{k} + \frac{1}{(\boldsymbol{\delta}^k)^T\boldsymbol{\xi}^k}\,\boldsymbol{\xi}^k(\boldsymbol{\xi}^k)^T - \phi_k((\boldsymbol{\delta}^k)^T\boldsymbol{\xi}^k)\mathbf{w}^k(\mathbf{w}^k)^T\end{aligned} \tag{8}$$

where

$$\mathbf{w}^k = \frac{\boldsymbol{\delta}^k}{(\boldsymbol{\delta}^k)^T\boldsymbol{\delta}^k} - \frac{\boldsymbol{\xi}^k}{(\boldsymbol{\delta}^k)^T\boldsymbol{\xi}^k} \tag{9}$$

Equation (8) defines a family of updated Hessian matrices generated by the parameter ϕ. It can also be written in short form as

$$\mathbf{B}_{\phi}^{k+1} = (1 - \phi_k)\mathbf{B}_{\mathrm{MS}}^{k+1} + \phi_k\mathbf{B}_{\mathrm{P}}^{k+1} \tag{10}$$

where $\mathbf{B}_{\mathrm{MS}}^{k+1}$ is the updating formula proposed by Murtagh and Sargent[16] (MS)

$$\mathbf{B}_{\mathrm{MS}}^{k+1} = \mathbf{B}^{k} + \frac{1}{(\boldsymbol{\delta}^k)^T\boldsymbol{\xi}^k}\,\boldsymbol{\xi}^k(\boldsymbol{\xi}^k)^T \tag{11}$$

and $\mathbf{B}_{\mathrm{P}}^{k+1}$ is the formula proposed by Powell[17] (P)

$$\begin{aligned}\mathbf{B}_{\mathrm{P}}^{k+1} &= \mathbf{B}^{k} - \frac{(\boldsymbol{\delta}^k)^T\boldsymbol{\xi}^k}{((\boldsymbol{\delta}^k)^T\boldsymbol{\delta}^k)^2}\,\boldsymbol{\delta}^k(\boldsymbol{\delta}^k)^T \\ &\quad + \frac{1}{(\boldsymbol{\delta}^k)^T\boldsymbol{\delta}^k}\,(\boldsymbol{\xi}^k(\boldsymbol{\delta}^k)^T + \boldsymbol{\delta}^k(\boldsymbol{\xi}^k)^T)\end{aligned} \tag{12}$$

The family (10) includes the rank-one formula of MS ($\phi = 0$) and the rank-two formula of P ($\phi = 1$). Because both MS and P updating formulae do not keep definite positive the updated Hessian matrices, this family is appropriated for locating saddle points of any order. Now, the question is which is the best ϕ_k to accelerate the convergence of the iterative procedure. If ϕ_k lies in the range [0, 1], the updating formula is confined in the so-called convex class, the extreme elements of which are the MS and P formulae. As shown later, setting

$$\phi_k = 1 - \frac{((\boldsymbol{\delta}^k)^T\boldsymbol{\xi}^k)^2}{((\boldsymbol{\delta}^k)^T\boldsymbol{\delta}^k)((\boldsymbol{\xi}^k)^T\boldsymbol{\xi}^k)} \tag{13}$$

it turns out to be a good choice of this parameter. We note that in our algorithm ϕ_k changes at each iteration, but optionally it can be kept constant along the whole process. There are two theoretical reasons that justify eq. (13). First, defined in this way ϕ_k is equal to square sine of the angle formed by the vectors $\boldsymbol{\delta}^k$ and $\boldsymbol{\xi}^k$, so the values of this function are in accord with the domain of ϕ_k. Second, because one of the extreme values of this family is the MS and becomes unstable when the scalar product $(\boldsymbol{\delta}^k)^T\boldsymbol{\xi}^k$ is small,[15] eq. (13) avoids this problem because ϕ_k tends to 1 and, therefore, $\mathbf{B}_{\phi}^{k+1}$ tends to $\mathbf{B}_{\mathrm{P}}^{k+1}$, which is more stable in this situation.

RESTRICTED STEP METHODS FOR LOCATING SADDLE POINTS

In this subsection, we will comment on the restricted step methods for locating saddle points, recently proposed by Culot et al.[11] These methods work well with the updated Hessian matrix described above.

To improve the quasi-Newton methods, the latter authors suggest modifying $\boldsymbol{\delta}^k$ [the vector found in step 1 of the algorithm described shortly in (2)]. There are different manners of modifying this vector; one is giving a bias toward the steepest descent vector $-\mathbf{g}^k$. This is obtained by solving the set of equations

$$(\mathbf{B}^k + \nu_k\mathbf{M})\boldsymbol{\delta}^k = -\mathbf{g}^k \tag{14a}$$

$$(\boldsymbol{\delta}^k)^T\mathbf{M}\boldsymbol{\delta}^k = R_k^2 \tag{14b}$$

These equations are just the conditions of the stationary point with respect to $\boldsymbol{\delta}^k$ and $\nu_k \neq 0$ of the Lagrangian function

$$L(\boldsymbol{\delta}^k, \nu_k) = q^k(\boldsymbol{\delta}^k) + \frac{1}{2}\,\nu_k((\boldsymbol{\delta}^k)^T\mathbf{M}\boldsymbol{\delta}^k - R_k^2) \tag{15}$$

The latter can be seen as an optimization of the quadratic function (1) subjected to the restriction on the length of the step $\boldsymbol{\delta}^k$ such that $(\boldsymbol{\delta}^k)^T\mathbf{M}\boldsymbol{\delta}^k = R_k^2$ and where $\mathbf{M}$ is in principle any square and symmetric matrix. For this reason, the method is known as the *restricted step method*.[15] The Lagrange multiplier ν_k is chosen so that the modified matrix $\mathbf{B}^k + \nu_k\mathbf{M}$ has the correct number of negative and positive eigenvalues and $\boldsymbol{\delta}^k$ satisfies eq. (14). The $\mathbf{M}$ matrix is chosen diagonal in the eigenvector representation of $\mathbf{B}^k$. Normally, $\mathbf{M}$ is selected as the unit matrix in this representation. In the particular case of searching first-order saddle points, Culot

et al.[11] proposed this restricted step method but using the following **M** matrix:

$$\mathbf{M} = \begin{pmatrix} -1 & & & & \\ & 1 & & & \\ & & \cdot & & \\ & & & \cdot & \\ & & & & 1 \end{pmatrix} \tag{16}$$

The position of -1 is in the place of the transition vector. In general, the matrix **M** will have as many -1 as the order of the saddle point that one is interested in locating. Here, we will comment on the method for locating first-order saddle points only, but the generalization is straightforward.

Let us assume that the eigenvalues of $\mathbf{B}^k$ are $\{b_i^k\}$ and the orthonormal eigenvectors $\{\mathbf{v}_i^k\}$, one of them, say $\mathbf{v}_t^k$, being the transition vector and b_t^k the corresponding eigenvalue. The gradient vector can be expressed as $\mathbf{g}^k = \Sigma_i \alpha_i^k \mathbf{v}_i^k$, where $\alpha_i^k = (\mathbf{v}_i^k)^T \mathbf{g}^k$. Substituting the **M** matrix (16) into eq. (14a), one gets

$$\boldsymbol{\delta}(\nu_k) = -\frac{\alpha_t^k}{(b_t^k - \nu_k|)} \mathbf{v}_t^k - \sum_{i \neq t} \frac{\alpha_i^k}{(b_i^k + \nu_k)} \mathbf{v}_i^k \tag{17}$$

If the vector $\boldsymbol{\delta}^k$ satisfies eq. (14), then according to eq. (17) $\boldsymbol{\delta}^k = \boldsymbol{\delta}(\nu_k)$. The latter relationship is eq. (22) of ref. 11. The square of the Euclidean norm of $\boldsymbol{\delta}^k$, $\|\boldsymbol{\delta}^k\|^2$, in the space defined by the set of eigenvectors $\{\mathbf{v}_i^k\}$, is given by

$$\|\boldsymbol{\delta}(\nu_k)\|^2 = \frac{(\alpha_t^k)^2}{(b_t^k - \nu_k)^2} + \sum_{i \neq t} \frac{(\alpha_i^k)^2}{(b_t^k + \nu_k)^2} \tag{18}$$

The value of $\|\boldsymbol{\delta}^k\|^2$ decreases monotonically from ∞ to 0 as ν_k increases from $\max\{b_t^k, -b_{\min}^k\}$ to ∞, where $b_{\min}^k = \min\{b_i^k;\ i \neq t;\ i = 1, \ldots, N\}$, using the convention of Culot et al.[11] Therefore, it is possible to find a unique value of ν_k in this interval for which $\|\boldsymbol{\delta}(\nu_k)\|^2 = R_k^2$. Also, $\nu_k \geq \max\{b_t^k, -b_{\min}^k\}$ ensures that $(\mathbf{B}^k + \nu_k \mathbf{M})$ has the correct number of negative and positive eigenvalues and $\nu_k \neq 0$ that the constraint $((\boldsymbol{\delta}^k)^T \mathbf{M} \boldsymbol{\delta}^k - R_k^2)$ is active. To calculate ν_k, Hebden[18] has given the iteration formula

$$\nu_k^{i+1} = \nu_k^i + \left(1 - \frac{\|\boldsymbol{\delta}(\nu_k^i)\|}{R_k}\right) \frac{\|\boldsymbol{\delta}(\nu_k^i)\|}{\|\boldsymbol{\delta}(\nu_k^i)\|'} \tag{19}$$

where $\|\boldsymbol{\delta}(\nu_k^i)\|'$ is the derivative of $\|\boldsymbol{\delta}(\nu_k^i)\|$ with respect to ν_k at iteration i. A good starting point for this iterative process is to choose

$$\nu_k^0 = \frac{\|\mathbf{g}^k\|}{R_k} + \max\{b_t^k, -b_{\min}^k\} \tag{20}$$

Normally the process needs about four iterations and is computationally inexpensive.

In the restricted step algorithms, it is important to define the *trust region* or, in other words, the choice of R_k. The latter is defined as the set of the points $\mathbf{x}^{k+1} = \mathbf{x}^k + \boldsymbol{\delta}^k$, where $\mathbf{B}^k$ has the correct number of negative and positive eigenvalues, $(\boldsymbol{\delta}^k)^T \boldsymbol{\delta}^k \leq R_k^2$ and $\boldsymbol{\delta}^k$ optimizes $q^k(\boldsymbol{\delta}^k)$. To prevent the restriction of the step, R_k should be of a length subjected to a measure of agreement between the quadratic model $q^k(\boldsymbol{\delta}^k)$ and the real function energy $E(\mathbf{x}^k + \boldsymbol{\delta}^k)$. This is obtained defining the ratio

$$r_k = \frac{E(\mathbf{x}^k + \boldsymbol{\delta}^k) - E(\mathbf{x}^k)}{q^k(\boldsymbol{\delta}^k) - E(\mathbf{x}^k)} \tag{21}$$

Basically, this type of algorithm changes R_k at each iteration to obtain a ratio as close as possible to one. Fletcher[15] proposed one of these algorithms, but it is designed for minimizing functions only. In Fletcher's algorithm,[15] R_k is reduced only when r_k is lower than some preestablished bound; otherwise, it is increased or remains constant. With the aim of applying this technique for locating saddle points, Culot et al.[11] proposed a little modification of Fletcher's[15] algorithm. The value of R_k is decreased when r_k is out of some predefined domain; otherwise, it is increased or kept constant. In this manner, the appropriated number of negative and positive eigenvalues of the Hessian is conserved in each step. In pathological cases (e.g., Hessian with small eigenvalues, Hessian with more than a single negative eigenvalue, etc.), after the calculation of the selected step $\boldsymbol{\delta}^k$ the perturbed Hessian $(\mathbf{B}^k + \nu_k \mathbf{M})$ sometimes still has an incorrect number of negative and positive eigenvalues, which is equivalent to say that ν_k is lower than $\max\{b_t^k, -b_{\min}^k\}$. If this is the case, the method undergoes a deterioration due to the incorrect spectra of the Hessian and the algorithm does not converge to the correct point. To overcome this problem, we propose the following modification to the algorithm of Culot et al.[11]

(a) given $\mathbf{x}^1$, R_1, calculate $E(\mathbf{x}^1)$, $\mathbf{g}^1$, and $\mathbf{B}^1$, set $k = 1$;

(b) check the eigenvalue spectra of $\mathbf{B}^k$ and select the transition vector. If $\|(\mathbf{B}^k)^{-1}\mathbf{g}^k\| > R_k$ or $\mathbf{B}^k$ has not the correct eigenvalue spectra or if it is correct but the selected transition vector is positive defined then,

(c) solve eq. (14) and set up the **M** matrix with the correct structure using eq. (19) and the starting point given by eq. (20);

(d) if $\nu_k \leq \max\{b_1^k, -b_{\min}^k\}$, then

(e) $R_k = R_k/(Sf)^2$ and go to (c);

else take $\boldsymbol{\delta}^k = -(\mathbf{B}^k)^{-1}\mathbf{g}^k$ as step;

(f) evaluate $E(\mathbf{x}^k + \boldsymbol{\delta}^k)$, $q^k(\boldsymbol{\delta}^k)$, and hence r_k using eqs. (1) and (21);

(g) if $r_k \notin (r_l, r_u)$, set $R_{k+1} = R_k/Sf$;

(h) if $r_k \in (r_l, r_u)$ and $\|\boldsymbol{\delta}^k\| = R_k$, set $R_{k+1} = R_k(Sf)^{1/2}$;

(i) if $r_k > Ub$ or $r_k < Lb$, then

(j) set $\mathbf{x}_{k+1} = \mathbf{x}_k$, $\mathbf{g}^{k+1} = \mathbf{g}^k$, $\mathbf{B}^{k+1} = \mathbf{B}^k$, $E(\mathbf{x}^{k+1}) = E(\mathbf{x}^k)$, and $k = k + 1$, go to (c);

else check the convergence criteria and if it is fulfilled stop;

(k) set $\mathbf{x}^{k+1} = \mathbf{x}^k + \boldsymbol{\delta}^k$, compute $\mathbf{g}^{k+1}$, update $\mathbf{B}^{k+1}$ using eq. (8), set $k = k + 1$, and go to (b). (22)

The values of the parameters r_l and r_u lie in the range $[Lb, Up]$ with the condition $r_l < r_u$ and Sf is a scaling factor. All these parameters are arbitrary and the algorithm is insensitive to their change. Suggested values are $Lb = 0$, $Ub = 2$, $r_l = 0.25$, $r_u = 1.75$, $Sf = 2$, and $R_1 = 0.15$ Å/rad. Steps b and h are different from those proposed by Culot et al.[11] Conditions of d and e ensure both the correct spectra of the perturbed Hessian ($\mathbf{B}^k + \nu_k\mathbf{M}$) and avoid the decrease in absolute value of the eigenvalues of $\mathbf{B}^k$. The selection of the transition vector in each iteration, step b, is done following the idea of Simons et al.[3] Also, condition b is a little more restricted than in ref. 11.

Results and Discussion

This section is divided into two parts: One gives some examples of applications of the method and the other presents an example of Hebden's iteration procedure. Two calculations were carried out with the AM1[19] semiempirical Hamiltonian and the other at the *ab initio* SCF level of theory with the 3-21G basis set.[20] The appropriate wave function, (e.g., RHF, UHF, . . .), was taken in each case. The Hessian matrices at the starting geometries were computed either by numerical differentiation (AM1) or by finite differences of analytic gradients (3-21G). In the case of AM1 calculations, the convergence criteria were taken on the maximum component of $\boldsymbol{\delta}$ and its rms ($\sqrt{\boldsymbol{\delta}^T\boldsymbol{\delta}/N}$), as well as the maximum component of $\mathbf{g}$ and its rms ($\sqrt{\mathbf{g}^T\mathbf{g}/N}$), with the values 9×10^{-4} Å, 6×10^{-4} Å, 5×10^{-1} kcal/mol Å, 3×10^{-1} kcal/mol Å, respectively, which are the units used in the MOPAC program. In the case of *ab initio* calculations, the standard convergence criteria of the GAMESS program were used.

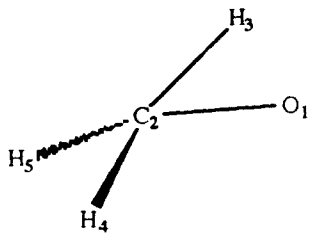
EXAMPLES OF APPLICATIONS OF THE METHOD

Methoxy Radical Isomerization

The calculations were carried out with the AM1 UHF wave function. The starting geometry used was taken from the article of Culot et al.[11] The Hessian at this point is positive defined, and its lowest eigenvalue is 103.99692. This eigenvalue corresponds to the transition vector. At the saddle point, the eigenvalue is −1036.84609. The geometric description is given in Table I. The behavior of the method is presented in Table II. This case shows the fact that far from the solution the third term of eq. (8) is important. The parameter ϕ_k represents the portion of the Powell Hessian that contributes to the iteration k [see eq. (10)]. It is interesting that near to the convergence a 99% of the Hessian comes from the Powell[17] updating formula and 1% from the Murtagh and Sargent[16] one.

The other geometry optimization methods implemented in the MOPAC program for locating saddle points, which are based on the minimization of the gradient norm,[9] fail to locate the transition state because they converge to a local minimum.

TABLE I.
Methoxy Radical Rearrangement within C_s Symmetry.



Parameter	Starting	Final
C_2O_1	1.423	1.354
C_2H_3	1.484	1.323
C_2H_4	1.087	1.103
$H_3C_2O_1$	42.7	59.1
$H_4C_2O_1$	117.5	117.4
$H_4C_2O_1H_3$	106.4	106.8

Distances in Å, angles in degrees.

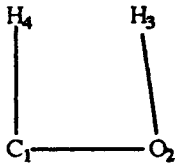
TABLE II.
Behavior of the Optimization Process for the Methoxy Radical Isomerization.

	Updated Hessian using eq. (12)	Updated Hessian using eqs. (10) and (13)	
Iteration	rms Gradient	rms Gradient	ϕ_k
1	65.35	63.35	0.69
2	40.29	40.56	0.63
3	39.37	38.70	0.40
4	28.14	47.51	0.94
5	70.01	53.16	0.81
6	322.15	80.33	0.98
7	Diverge	27.74	0.86
8		18.26	0.40
9		8.09	0.90
10		3.02	0.99
11		0.74	0.95
12		0.11	—

Hydrogenation of Carbon Monoxide

This example shows the behavior of the method when the starting point is close to the final solution. The calculations were carried out by using the AM1 Hamiltonian. The starting and final geometries are given in Table III. The initial geometry was taken from the work of Schröder et al.[21] At this point, the Hessian has one negative eigenvalue, −1416.00286, and its associated eigenvector corresponds to the true transition vector. This eigenvalue at the saddle point is −2855.82809. The iteration process is described in Table IV. As shown in this table, using eq. (10) the value of the parameter ϕ_k is around one in all iterations except the first one, in which there is strong contribution of the Murtagh–Sargent[16] Hessian. Also, in this case close to the convergence the rms displacement decreases monotonically. This is a particular characteristic of the algorithm.

TABLE III.
Hydrogenation of Carbon Monoxide within C_s Symmetry.



Parameter	Starting	Final
C_1O_2	1.255	1.280
O_2H_3	1.470	1.330
C_1H_4	1.293	1.370
$C_1O_2H_3$	77.2	74.1
$H_4C_1O_2$	92.7	96.4
$H_4C_1O_2H_3$	0.0	0.0

Distances in Å, angles in degrees.

Ring Opening of Cyclopropyl Radical

A detailed theoretical study of this reaction has been reported recently by Olivella et al.[22] The calculations were carried out at the UHF/3-21G level of theory. The AM1-optimized geometry of cyclopropyl radical, conveniently distorted, was taken as the starting geometry. At this point, the Hessian matrix has one negative eigenvalue, −0.279065, and its associated eigenvector corresponds to the true transition vector. In the positive part of its spectrum, the Hessian presents a small eigenvalue, 0.004808, associated to the $H_8C_2C_3C_1$ torsion angle. The starting and final geometries are given in Table V. In Table VI, the performance of the present method is compared with that of the method proposed by Baker,[12] as implemented in the GAMESS program. While the Baker method needs 36 iterations to achieve the convergence, the method presented here needs only 19 iterations. It is interesting that in iteration 17 the Lagrangian multiplier ν_{17} is lower than $\max\{b_i^{17}, -b_{\min}^{17}\}$. By using the reduction of R_k according to step e of (22), the Hessian recovers the correct number of negative and positive eigenvalues, so convergence is accelerated. This technique is lacking in the algorithm proposed by Culot et al.[11]

Thermal Ring Opening of Bicyclo[1.1.0]Butane to 1,3-Butadiene

According to a detailed AM1 study,[23] this reaction occurs in two steps, so there are two saddle points. The calculations were carried out at the GVB/3-21G level of theory taking the HOMO and LUMO as the orbital pair. The AM1-optimized transition structures were taken as the starting geometries in both saddle points searches. The starting and final geometries of the first saddle point are given in Table VII. At the initial point, the Hessian matrix has one negative eigenvalue, −0.040238, and its associated eigenvector corresponds to the true transition vector. In Table VIII,

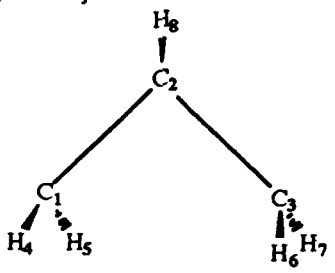
TABLE IV.
Behavior of the Method for the Hydrogenation of Carbon Monoxide.

	Updated Hessian using eq. (12)		Updated Hessian using eqs. (10) and (13)		
Iteration	rms Gradient	rms Displacement	rms Gradient	rms Displacement	ϕ_k
1	92.09	0.06708	92.09	0.06708	0.63
2	40.65	0.01186	40.65	0.01186	1.00
3	16.69	0.01677	16.20	0.01677	1.00
4	5.60	0.01448	4.55	0.01414	1.00
5	2.48	0.00365	1.66	0.00464	0.98
6	1.27	0.00591	0.74	0.00183	0.89
7	0.62	0.00124	0.31	0.00048	
8	0.25	0.00030			

the performance of the present method using the proposed updated Hessian formula is compared with Baker's method,[12] using Powell's updated Hessian formula.[17] In this case, the method presented is only a little more efficient than Baker's method by a few iterations. Rigorously, this is not totally true because according to algorithm (22) iterations 7 and 8 are not strictly complete iterations. In this situation, no gradients, updated Hessian, and new geometry are computed.

The geometries concerning the second saddle point are presented in Table IX. At the starting

TABLE V.
Cyclopropyl Radical Ring Opening within C_1 Symmetry.



Parameter	Starting	Final
C_1C_2	1.454	1.436
C_2C_3	1.454	1.484
C_1H_4	1.106	1.072
C_1H_5	1.106	1.075
C_3H_6	1.106	1.071
C_3H_7	1.106	1.071
C_2H_8	1.064	1.071
$C_3C_2C_1$	80.0	85.4
$H_4C_1C_2$	119.6	119.4
$H_5C_1C_2$	119.6	122.8
$H_6C_3C_2$	119.6	119.4
$H_7C_3C_2$	119.6	120.9
$H_8C_2C_3$	148.5	124.2
$H_4C_1C_2C_3$	40.0	76.4
$H_5C_1C_2C_3$	−160.0	−111.6
$H_6C_3C_2C_1$	108.0	95.8
$H_7C_3C_2C_1$	−108.0	−89.8
$H_8C_2C_3C_1$	−170.0	−128.8

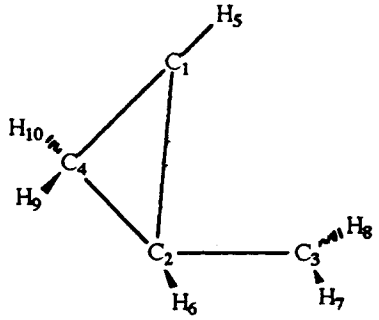
Distances in Å, angles in degrees.

TABLE VI.
Behavior of the Method for the Cyclopropyl Radical Ring Opening.

	Baker method	Updated Hessian using eq. (10)		
Iteration	rms[a] Gradient	rms[a] Gradient	ϕ_k[b]	r_k[c]
0	$5.6 \cdot 10^{-2}$	$5.6 \cdot 10^{-2}$		
1	$5.2 \cdot 10^{-2}$	$5.1 \cdot 10^{-2}$	0.38	1.00
2	$4.9 \cdot 10^{-2}$	$4.4 \cdot 10^{-2}$	0.80	0.99
3	$4.5 \cdot 10^{-2}$	$3.7 \cdot 10^{-2}$	0.89	0.99
4	$4.2 \cdot 10^{-2}$	$2.8 \cdot 10^{-2}$	0.96	0.97
5	$3.9 \cdot 10^{-2}$	$1.9 \cdot 10^{-2}$	0.99	0.95
6	$3.6 \cdot 10^{-2}$	$8.7 \cdot 10^{-3}$	0.99	0.94
7	$3.3 \cdot 10^{-2}$	$4.1 \cdot 10^{-3}$	1.00	0.95
8	$3.0 \cdot 10^{-2}$	$7.9 \cdot 10^{-3}$	0.87	0.26
9	$2.7 \cdot 10^{-2}$	$4.8 \cdot 10^{-3}$	0.87	0.51
10	$2.5 \cdot 10^{-2}$	$3.3 \cdot 10^{-3}$	1.00	0.82
11	$2.3 \cdot 10^{-2}$	$2.6 \cdot 10^{-3}$	0.98	1.16
12	$2.1 \cdot 10^{-2}$	$1.7 \cdot 10^{-3}$	0.98	0.57
13	$1.9 \cdot 10^{-2}$	$8.6 \cdot 10^{-4}$	1.00	0.99
14	$1.7 \cdot 10^{-2}$	$4.2 \cdot 10^{-4}$	0.99	1.09
15	$1.6 \cdot 10^{-2}$	$2.6 \cdot 10^{-4}$	0.88	0.47
16	$1.4 \cdot 10^{-2}$	$2.6 \cdot 10^{-4}$	0.88	4.57
17	$1.3 \cdot 10^{-2}$	$2.6 \cdot 10^{-4}$	0.88	4.19
18	$1.2 \cdot 10^{-2}$	$6.9 \cdot 10^{-4}$	1.00	1.14
19	$1.1 \cdot 10^{-2}$	$3.1 \cdot 10^{-5}$		0.97

[a] In the GAMESS program, rms = $\sqrt{\mathbf{g}^T\mathbf{g}/N}$.
[b] ϕ_k is defined in eq. (13).
[c] r_k is defined in eq. (21).

TABLE VII.
Ring Opening of Bicyclo[1.1.0]Butane within C_1 Symmetry, First Transition State.



Parameter	Initial	Final
C_1C_2	1.495	1.492
C_3C_2	1.418	1.452
C_4C_1	1.463	1.488
C_1H_5	1.093	1.065
C_2H_6	1.111	1.067
C_3H_7	1.098	1.072
C_3H_8	1.097	1.070
C_4H_9	1.110	1.074
C_4H_{10}	1.106	1.074
$C_3C_2C_1$	92.1	94.1
$C_4C_1C_2$	62.1	62.2
$H_5C_1C_2$	136.0	136.7
$H_6C_2C_1$	123.5	126.7
$H_7C_3C_2$	122.4	121.0
$H_8C_3C_2$	124.7	119.9
$H_9C_4C_1$	126.7	123.3
$H_{10}C_4C_1$	117.9	114.3
$C_4C_1C_2C_3$	−120.4	−108.2
$H_5C_1C_2C_3$	4.4	26.2
$H_6C_2C_1C_4$	108.8	111.2
$H_7C_3C_2C_1$	−107.5	−99.7
$H_8C_3C_2C_1$	84.2	75.7
$H_9C_4C_1C_2$	109.3	105.7
$H_{10}C_4C_1C_2$	−106.1	−105.9

Distances in Å, angles in degrees.

point, the Hessian matrix has one negative eigenvalue, −0.184393, and its associated eigenvector corresponds to the true transition vector. In Table X, the performance of the present method again is compared with that proposed by Baker,[12] as implemented in the GAMESS program. In this case, the present method only needs 9 iterations while Baker's method converges after 12.

1,2-Migration in β-(Formyloxy) Ethyl Radical

This reaction was studied some time ago by Saebo et al.[24] The calculations were carried out at

TABLE VIII.
Behavior of the Method for the Bicyclo[1.1.0]Butane Ring Opening, First Transition State.

	Baker method	Updated Hessian using eq. (10)		
Iteration	rms[a] Gradient	rms[a] Gradient	ϕ_k[b]	r_k[c]
0	$2.0 \cdot 10^{-1}$	$2.0 \cdot 10^{-1}$		
1	$1.8 \cdot 10^{-2}$	$1.6 \cdot 10^{-2}$	0.83	1.00
2	$1.5 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$	0.79	1.00
3	$1.3 \cdot 10^{-2}$	$6.2 \cdot 10^{-3}$	0.87	0.99
4	$1.1 \cdot 10^{-2}$	$2.2 \cdot 10^{-3}$	1.00	1.00
5	$8.9 \cdot 10^{-3}$	$7.8 \cdot 10^{-4}$	0.95	1.08
6	$7.0 \cdot 10^{-3}$	$6.2 \cdot 10^{-4}$	1.00	1.05
7	$5.3 \cdot 10^{-3}$	$6.2 \cdot 10^{-4}$	1.00	2.72
8	$3.7 \cdot 10^{-3}$	$6.2 \cdot 10^{-4}$	1.00	3.61
9	$2.3 \cdot 10^{-3}$	$1.7 \cdot 10^{-4}$	0.65	1.92
10	$1.0 \cdot 10^{-3}$	$1.1 \cdot 10^{-4}$	0.98	0.91
11	$8.8 \cdot 10^{-5}$	$2.0 \cdot 10^{-5}$		1.06
12	$3.4 \cdot 10^{-5}$			
13	$1.9 \cdot 10^{-5}$			

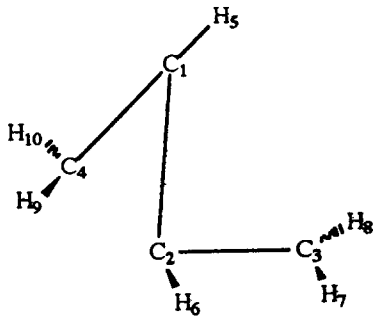
[a]In the GAMESS program, rms = $\sqrt{\mathbf{g}^T\mathbf{g}/N}$.
[b]ϕ_k is defined in eq. (13).
[c]r_k is defined in eq. (21).

the UHF/3-21G level of theory. The AM1 geometry was taken as the starting point. At this point, the Hessian matrix has one negative eigenvalue, −0.969319, corresponding at the C_1O_5 bond breaking. In the positive part of its spectrum, the Hessian presents a small eigenvalue, 0.007161, associated to the $C_4O_3C_2C_1$ torsion angle. The starting and final geometries are given in Table XI. In Table XII, the present method is compared with the method proposed by Baker.[12] While Baker's method does not converge within the default number of iterations (25), the method presented here needs only 22 iterations. As in example 3, at iterations 7 and 9 the Lagrangian multipliers ν_6 and ν_9 are lower than $\max\{b_i^7, -b_{\min}^7\}$ and $\max\{b_i^9, -b_{\min}^9\}$, respectively. Using the reduction of R_k according to step e of (22), the Hessian recovers the correct eigenvalue spectra, so convergence is accelerated.

HEBDEN ITERATION PROCEDURE

In this subsection, we present the numerical behavior of the Hebden[17] procedure, proposed above for solving eq. (14). This is shown in Table XIII, where eqs. (19) and (20) have been used. One can see the stability and efficiency of the method, not-

TABLE IX.
Ring Opening of Bicyclo[1.1.0]Butane within C_1 Symmetry, Second Transition State.



Parameter	Initial	Final
C_1C_2	1.489	1.498
C_3C_2	1.374	1.408
C_4C_1	1.384	1.426
C_1H_5	1.108	1.075
C_2H_6	1.119	1.074
C_3H_7	1.098	1.073
C_3H_8	1.097	1.072
C_4H_9	1.106	1.067
C_4H_{10}	1.114	1.076
$C_3C_2C_1$	136.3	127.4
$C_4C_1C_2$	74.5	75.2
$H_5C_1C_2$	118.7	117.2
$H_6C_2C_1$	109.3	114.7
$H_7C_3C_2$	124.9	120.6
$H_8C_3C_2$	122.4	120.1
$H_9C_4C_1$	125.5	120.4
$H_{10}C_4C_1$	126.8	122.0
$C_4C_1C_2C_3$	−94.6	−90.4
$H_5C_1C_2C_3$	150.5	155.7
$H_6C_2C_1C_4$	107.0	101.8
$H_7C_3C_2C_1$	26.9	10.1
$H_8C_3C_2C_1$	−166.0	175.7
$H_9C_4C_1C_2$	82.9	84.6
$H_{10}C_4C_1C_2$	−115.6	−112.2

Distances in Å, angles in degrees.

ing that normally in four iterations the convergence is achieved. Therefore, it is computationally inexpensive. Starting with values of ν_k different from the one given by eq. (20), the number of iterations increases. In the example presented here, $\max\{b_t^k, -b_{\min}^k\}$ is equal to zero, so the perturbed Hessian has the correct eigenvalue spectra in this case. Whenever the opposite situation occurs, we propose a reduction of the step length as described in step e of the algorithm (22).

TABLE X.
Behavior of the Method for the Bicyclo[1.1.0]Butane Ring Opening, Second Transition State.

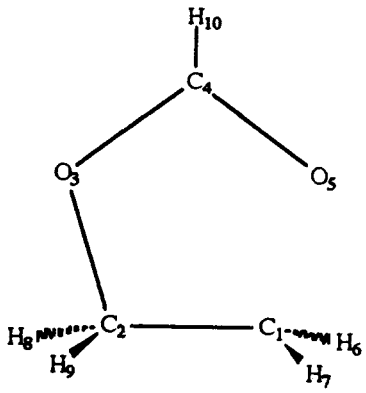
	Baker method	Updated Hessian using eq. (10)		
Iteration	rms[a] Gradient	rms[a] Gradient	ϕ_k[b]	r_k[c]
0	$1.8 \cdot 10^{-2}$	$1.8 \cdot 10^{-2}$		
1	$1.5 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	0.89	1.00
2	$1.3 \cdot 10^{-2}$	$9.5 \cdot 10^{-3}$	0.95	1.00
3	$1.1 \cdot 10^{-2}$	$3.8 \cdot 10^{-3}$	0.91	0.99
4	$9.1 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	0.99	0.99
5	$7.5 \cdot 10^{-3}$	$6.2 \cdot 10^{-4}$	0.96	1.08
6	$6.0 \cdot 10^{-3}$	$8.1 \cdot 10^{-4}$	1.00	1.03
7	$4.7 \cdot 10^{-3}$	$1.6 \cdot 10^{-4}$	0.94	1.33
8	$3.5 \cdot 10^{-3}$	$4.3 \cdot 10^{-5}$	0.72	1.21
9	$2.5 \cdot 10^{-3}$	$1.4 \cdot 10^{-5}$		0.84
10	$1.4 \cdot 10^{-3}$			
11	$4.5 \cdot 10^{-4}$			
12	$1.6 \cdot 10^{-5}$			

[a] In the GAMESS program, rms = $\sqrt{\mathbf{g}^T\mathbf{g}/N}$.
[b] ϕ_k is defined in eq. (13).
[c] r_k is defined in eq. (21).

Summary and Conclusions

Within the general problem of finding an efficient algorithm for locating transition structures on a potential energy hypersurface, this article concerns two basic aspects. One is the updating of the approximate Hessian matrix along the iterations of the optimization procedure and the other is an improvement of the algorithm proposed by Culot et al. First, a new updating Hessian matrix formula for saddle points is given, which can be considered as a mixture of the updating formulae of Powell and Murtagh-Sargent. Second, we comment on the technique of Hebden for solving the restricted step equations and propose a modification of this algorithm that avoids in part the problem arising when some eigenvalues of the Hessian matrix have small absolute values. The examples presented show that the method is capable of locating the desired saddle point even if one starts with a geometry that is far from the final solution. These examples emphasize the stability resulting from the proposed updated Hessian matrix formula. The algorithm proposed can be easily generalized for locating higher-order saddle points and minima.

TABLE XI.
1,2-Migration in β-(Formiloxy)Ethyl Radical within C_1 Symmetry.



Parameter	Initial	Final
C_1C_2	1.487	1.511
O_3C_2	1.458	1.480
C_4O_3	1.365	1.374
C_1O_5	1.812	1.890
C_1H_6	1.095	1.070
C_1H_7	1.096	1.074
C_2H_8	1.119	1.077
C_2H_9	1.120	1.077
C_4H_{10}	1.094	1.072
$O_3C_2C_1$	108.2	107.8
$C_4O_3C_2$	111.4	110.0
$O_5C_1C_2$	94.8	91.1
$H_6C_1C_2$	118.7	118.4
$H_7C_1C_2$	118.1	117.4
$H_8C_2O_3$	106.2	108.3
$H_9C_2O_3$	104.3	105.6
$H_{10}C_4O_3$	116.3	115.5
$C_4O_3C_2C_1$	8.6	18.0
$O_5C_1C_2O_3$	−20.2	−31.7
$H_6C_1C_2O_3$	−123.0	−134.8
$H_7C_1C_2O_3$	86.0	76.6
$H_8C_2O_3C_4$	−112.9	−102.1
$H_9C_2O_3C_4$	130.0	139.5
$H_{10}C_4O_3C_2$	−155.7	−134.5

Distances in Å, angles in degrees.

TABLE XII.
Behavior of the Method for the 1,2-Migration in β-(Formiloxy) Ethyl Radical.

	Baker method	Updated Hessian using eq. (10)		
Iteration	rms[a] Gradient	rms[a] Gradient	ϕ_k[b]	r_k[c]
0	$4.3 \cdot 10^{-2}$	$4.3 \cdot 10^{-2}$		
1	$3.7 \cdot 10^{-2}$	$1.3 \cdot 10^{-2}$	0.85	1.01
2	$3.3 \cdot 10^{-2}$	$7.7 \cdot 10^{-3}$	0.85	1.03
3	$3.0 \cdot 10^{-2}$	$4.5 \cdot 10^{-3}$	0.90	0.98
4	$2.7 \cdot 10^{-2}$	$5.4 \cdot 10^{-3}$	0.99	0.94
5	$2.4 \cdot 10^{-2}$	$2.8 \cdot 10^{-3}$	0.98	0.88
6	$2.1 \cdot 10^{-2}$	$2.8 \cdot 10^{-3}$	0.99	0.51
7	$1.9 \cdot 10^{-2}$	$2.8 \cdot 10^{-3}$	0.99	−1.55
8	$1.6 \cdot 10^{-2}$	$2.0 \cdot 10^{-3}$	0.70	0.60
9	$1.4 \cdot 10^{-2}$	$1.1 \cdot 10^{-3}$	0.94	0.64
10	$1.2 \cdot 10^{-2}$	$5.8 \cdot 10^{-4}$	1.00	1.01
11	$9.6 \cdot 10^{-3}$	$4.1 \cdot 10^{-4}$	0.97	1.04
12	$7.2 \cdot 10^{-3}$	$2.9 \cdot 10^{-4}$	0.99	1.05
13	$4.7 \cdot 10^{-3}$	$1.8 \cdot 10^{-4}$	0.99	0.93
14	$1.6 \cdot 10^{-3}$	$2.1 \cdot 10^{-4}$	0.99	1.00
15	$3.1 \cdot 10^{-3}$	$1.2 \cdot 10^{-4}$	1.00	1.00
16	$3.3 \cdot 10^{-3}$	$1.0 \cdot 10^{-4}$	1.00	1.00
17	$2.3 \cdot 10^{-3}$	$9.6 \cdot 10^{-5}$	1.00	1.00
18	$3.0 \cdot 10^{-3}$	$9.8 \cdot 10^{-5}$	1.00	0.99
19	$2.5 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$	1.00	0.98
20	$2.2 \cdot 10^{-3}$	$1.8 \cdot 10^{-4}$	1.00	0.95
21	$4.0 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	1.00	0.85
22	$6.1 \cdot 10^{-4}$	$2.7 \cdot 10^{-5}$		
23	$2.5 \cdot 10^{-4}$			
24	$3.6 \cdot 10^{-3}$			
25	$4.9 \cdot 10^{-4}$			

[a]In the GAMESS program, rms = $\sqrt{\mathbf{g}^T\mathbf{g}/N}$.
[b]ϕ_k is defined in eq. (13).
[c]r_k is defined in eq. (21).

TABLE XIII.
Convergence Behavior of the Hebden Iteration Procedure.

Iteration	ν_k^i	$\lvert\nu_k^{i-1} - \nu_k^i\rvert$
1	347.24121	689.41796
2	358.73959	11.49839
3	358.75041	0.01082
4	358.75041	0.00000

Initial value $\nu_k^0 = 1036.65917$, computed according to eq. (20).
Convergence criteria $\lvert\nu_k^{i-1} - \nu_k^i\rvert \leq 10^{-5}$.

Acknowledgments

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