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# GLOBAL OPTIMIZATION USING AUTOMATIC DIFFERENTIATION: APPLICATION TO QUANTUM CHEMISTRY

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We present a new optimization method and one of its applications in quantum chemistry. The problem is to find the most stable configurations of sodium clusters. We have to minimize a weighted sum of eigenvalues of the Hamiltonian operator which corresponds to the energy of the molecules. According to the Rellich theorem, the eigenvalues/eigenvectors are analytic when the matrix follows an analytic path. Using automatic differentiation, we compute higher-order derivatives of the matrix. The eigenvalue/eigenvector derivatives are calculated by solving several factorized linear systems. The higher-order derivative method is used to obtain an explicit solution of the cost function (Taylor's expansion).

This approach leads to a new global optimization algorithm whose idea is as follows: if we apply the optimality condition to the approximated cost function, we obtain a polynomial equation. We find its roots. The "best" zeros are used to restart the algorithm with a new search direction. This algorithm presents a natural way of parallelization: computation of Taylor's expansion and its minima in many directions can be performed independently.

This method applied to our chemical problem gives very promising results. All the lowest energies of small sodium clusters have been found. This optimization algorithm can also be applied in dynamics of mechanical structures.

## 1. Introduction

The Automatic Differentiation (AD) was introduced (Griewank, 1989; Speelpenning, 1980) in order to compute first- and second-order derivatives needed by optimization algorithms. AD and the higher-order derivatives method can be used to obtain an explicit expression (Taylor's expansion, Pade's approximation, etc.) of the cost function (Guillaume and Masmoudi, 1994; Masmoudi *et al.*, 1995). This method was applied to a shape optimization problem involving Maxwell equations yielding very promising results.

The aim of this paper is to apply this method to an eigenvalue problem. We first describe in Section 2 the higher-order derivative method and its application to an eigenvalue problem. This method leads to the resolution of several linear systems.

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In Section 3 we give an efficient method to solve them. We describe the application of AD to our problem in Section 4. This approach suggests a new global optimization algorithm which we present in Section 5. This method is applied to a chemical problem giving very satisfying results (Section 6).

## 2. Higher-Order Derivative Method and Its Application to an Eigenvalue Problem

### 2.1. Higher-Order Derivative Method in the Linear Case

We first recall an application of the parametrization method (Guillaume and Masmoudi, 1994; Masmoudi *et al.*, 1995) to the linear system

$$H(u)\,Y_u = B(u) \tag{1}$$

depending on a parameter $u \in \mathbb{R}$ (shape, material properties, etc.).

We assume that $H(u)$ is an invertible matrix and that the maps $u \to H(u)$ and $u \to B(u)$ are regular (analytic).

We differentiate eqn. (1) with respect to $u$ and obtain the following systems:

$$\begin{aligned} &H(u)\,Y_u' = B'(u) - H'(u)\,Y_u \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ &H(u)\,Y_u^{(N)} = B^{(N)}(u) - \sum_{j=1}^{N} C_N^j H^{(j)}(u)\,Y_u^{(N-j)} \end{aligned} \tag{2}$$

where $Y_u^{(N)}$ denotes the $N$-th order derivative of $Y_u$ with respect to $u$ $(N > 0)$.

The higher-order derivatives of $Y_u$ are obtained by solving the linear systems (2). The terms $H^{(N)}(u)$ and $B^{(N)}(u)$ $(N > 0)$ appearing on the right-hand side of (2) can be computed by AD. The derivatives of $Y$ can be calculated efficiently applying LU factorization of $H$. This method can also be generalized to non-linear problems. The aim of this paper is to apply it to eigenvalue problems.

### 2.2. Differentiability of Eigenvalue with Respect to a Parameter

Let

$$\begin{cases} H(v)\,q = \lambda\,q \\ q \neq 0 \end{cases}$$

be an eigenvalue problem where $H$ is a symmetric matrix which depends on a parameter $v = (v_1, \ldots, v_k) \in \mathbb{R}^k$ $(k > 0)$.

We know that the map $v \in \mathbb{R}^k \to \lambda(v) \in \mathbb{R}$ is not differentiable with respect to $v$ $(k > 1)$. In fact, let us consider e.g.

$$H(v_1, v_2) = \begin{pmatrix} v_1 & v_2 \\ v_2 & -v_1 \end{pmatrix}$$

It is easy to see that the eigenvalue

$$\lambda(v_1, v_2) = \sqrt{v_1^2 + v_2^2}$$

is not differentiable (Fig. 1) at $v = 0$ with respect to $(v_1, v_2)$.

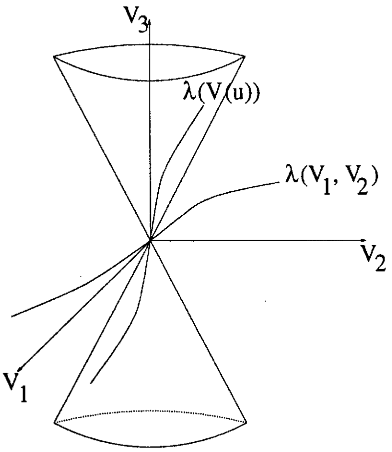


Fig. 1. Eigenvalues of $H$.

We assume now that $v$ depends analytically on a parameter $u \in \mathbb{R}$. According to the Rellich theorem (Kato, 1966), the map $u \to \lambda(u) = \lambda(v(u))$ is analytic with respect to $u$.

From now on, we can talk about derivatives of eigenvalues/eigenvectors with respect to a real parameter and characterize them.

### 2.3. Eigenvalue and Eigenvector Derivatives with Respect to a Real Parameter

Let us denote by

$$\Lambda = \operatorname{diag}(\lambda_1, \ldots, \lambda_n)$$

the diagonal matrix of eigenvalues and let $Q = (q_1, \ldots, q_n)$ be the corresponding orthogonal matrix of eigenvectors. We have

$$H = Q \Lambda Q^T$$

For a given $1 \leq i_1 \leq n$, the couple $(q_{i_1}, \lambda_{i_1})$ is the solution of the non-linear system

$$\begin{cases} H(u)\, q_{i_1} = \lambda_{i_1}\, q_{i_1} \\ \|q_{i_1}\|^2 = 1 \end{cases} \tag{3}$$

where $u$ is a real parameter.

Let us differentiate (3) with respect to $u$, calling $z'$ the first derivative of $z$ with respect to $u$:

$$\begin{cases} H(u)\, q_{i_1}^{'} - \lambda_{i_1}\, q_{i_1}^{'} = \lambda_{i_1}^{'}\, q_{i_1} - H'(u)\, q_{i_1} \\ q_{i_1}^T\, q_{i_1}^{'} = 0 \end{cases}$$

$$\Longleftrightarrow \begin{pmatrix} H - \lambda_{i_1} I & -q_{i_1} \\ -q_{i_1}^T & 0 \end{pmatrix} \begin{pmatrix} q_{i_1}^{'} \\ \lambda_{i_1}^{'} \end{pmatrix} = - \begin{pmatrix} H'\, q_{i_1} \\ 0 \end{pmatrix}$$

where $I$ is the identity matrix.

**Proposition 1.** *If $q_{i_1}$ and $\lambda_{i_1}$ are of class $C^N$ $(N > 0)$, the N-th order derivatives of $q_{i_1}$ and $\lambda_{i_1}$ with respect to the scalar $u$ are solutions of the system*

$$\begin{pmatrix} H - \lambda_{i_1} I & -q_{i_1} \\ -q_{i_1}^T & 0 \end{pmatrix} \begin{pmatrix} q_{i_1}^{(N)} \\ \lambda_{i_1}^{(N)} \end{pmatrix} = \sum_{i=1}^{N-1} \begin{pmatrix} -C_N^i (H^{(i)} - \lambda_{i_1}^{(i)} I) q_{i_1}^{(N-i)} \\ C_{N-1}^i (q_{i_1}^{(i)})^T q_{i_1}^{(N-i)} \end{pmatrix} - \begin{pmatrix} H^{(N)} q_{i_1} \\ 0 \end{pmatrix} \tag{4}$$

The recurrent approach is used to prove this proposition.

In the following section, we give an efficient method to solve the successive systems.

## 3. How to Solve the Linear Systems?

The successive systems to be solved in order to obtain the derivatives of $q_{i_1}$ and $\lambda_{i_1}$ can be written in the same form

$$\tilde{H}\, U = B \tag{5}$$

where

$$\tilde{H} = \begin{pmatrix} H - \lambda_{i_1} I & -q_{i_1} \\ -q_{i_1}^T & 0 \end{pmatrix} \in \mathbb{R}^{(n+1)\times(n+1)}$$

$U = \begin{pmatrix} u_1 \\ u_2 \end{pmatrix}$ is the unknown vector ($u_1 \in \mathbb{R}^n$, $u_2 \in \mathbb{R}$), and $B = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix}$ stands for the right-hand side vector of eqn. (4) ($b_1 \in \mathbb{R}^n$, $b_2 \in \mathbb{R}$).

**Proposition 2.** *If* $\lambda_{i_1}$ *is a single eigenvalue of* $H$, *then*

- $\tilde{H}$ *is invertible;*
- *The solution of the linear system* $\tilde{H}\,U = B$ *is given by*

$$\begin{cases} u_1 = Q\,v \quad \text{with} \quad \begin{cases} v_k = \frac{q_k^T b_1}{\lambda_k - \lambda_{i_1}}, & k \neq i_1 \\ v_{i_1} = -b_2 \end{cases} \\ u_2 = -q_{i_1}^T\, b_1 \end{cases}$$

*Proof.* System (5) can be written as

$$\begin{cases} (H - \lambda_{i_1} I)u_1 - u_2\, q_{i_1} = b_1 & \text{(6a)} \\ -q_{i_1}^T\, u_1 = b_2 & \text{(6b)} \end{cases} \qquad (6)$$

Using the decomposition $Q^T H Q = \Lambda$, we obtain

$$H - \lambda_{i_1} I = Q(\Lambda - \lambda_{i_1} I)Q^T$$

From (6a), we have

$$(\Lambda - \lambda_{i_1} I)v = Q^T(b_1 + u_2 q_{i_1}) \qquad (7)$$

where $v = Q^T u_1$, $v \in \mathbb{R}^n$. The $i_1$-th equation of system (7) gives, using $Q^T Q = I$,

$$(\lambda_{i_1} - \lambda_{i_1})v_{i_1} = (Q^T b_1)_{i_1} + u_2(Q^T q_{i_1})_{i_1}$$
$$\Longleftrightarrow u_2 = -(Q^T b_1)_{i_1} = -q_{i_1}^T b_1$$

The other equations give $v_k$ for $1 \leq k \leq n$ and $k \neq i_1$

$$(\lambda_k - \lambda_{i_1})v_k = (Q^T b_1)_k = q_k^T b_1$$

We assume that $\lambda_{i_1}$ is a single eigenvalue, hence we have

$$v_k = \frac{q_k^T b_1}{\lambda_k - \lambda_{i_1}}, \qquad 1 \leq k \leq n, \; k \neq i_1$$

We use eqn. (6b) in order to calculate $v_{i_1}$

$$\begin{aligned} \text{(6b)} \quad &\Longleftrightarrow \quad -q_{i_1}^T\, u_1 = b_2 \\ &\Longleftrightarrow \quad q_{i_1}^T\, Q\, v = -b_2 \\ &\Longleftrightarrow \quad v_{i_1} = -b_2 \end{aligned}$$

Thus, we have proved that if $\lambda_{i_1}$ is a single eigenvalue, then the linear system (5) has a unique solution, i.e. $\tilde{H}$ is invertible. ■

**Remarks.**

- The analyticity of the map $u \rightarrow \lambda(u)$ can be obtained as a consequence of the *implicit function theorem* using the invertibility of $\tilde{H}$.
- In order to find the solution of system (5), we do not invert the matrix $\tilde{H}$. The cost of this search is only the cost of a matrix-vector product.

The linear system is very easy to solve, but how to build its right-hand side? We give the answer in the following section.

## 4. Application of the Automatic Differentiation to an Eigenvalue Problem

The knowledge of higher-order derivatives of eigenvalues and eigenvectors of $H$ with respect to $u$ requires computation of successive derivatives of the matrix $H$ with respect to $u$. In order to generate these derivatives, we use AD software as a black box. This one uses operators' overloading (redefinition of $*$, $+$, etc.), the technique which is available in modern languages, e.g. C++, FORTRAN90, etc.

AD permits differentiation of a function defined by its program (in Fortran or C). The resultant derivative is exact whereas the derivative obtained by finite differences is not.

It follows from the classic results of Strassen (1990) and Morgenstern (1985) that if a differentiable function can be evaluated using $m$ operations, its derivative can be computed in only $5m$ operations.

How to use the AD software? Let

$$\begin{array}{rccc} g: & \mathbb{R}^{k_1} & \longrightarrow & \mathbb{R}^{k_1} \\ & u & \longmapsto & v = g(u) \end{array}$$

be a differentiable function defined by a program named *prog.c* which computes $v = g(u)$. To perform AD, we have just to modify the declarative part of the program *prog.c*. We define

- the independent variables (a subset of $u$ components),
- the dependent variables (a subset of $v$ components),
- the active section of the program, i.e. its part to differentiate.

Using AD, we create a new program *PROG-DIFF.c* which provides successive derivatives of the function $g$ for an arbitrary order. The AD process can be represented by the scheme shown in Fig. 2. In the case considered, we used the AD software called Adogen (Rochette, 1994).

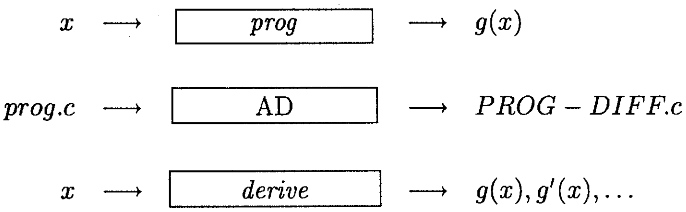


Fig. 2. The AD scheme.

## 5. Global Optimization Algorithm

In the following, we shall minimize the energy of sodium clusters in quantum chemistry. The goal of this application is to find the most stable configurations of the molecule. The energy to be minimized is a function of eigenvalues. We explain this chemical problem in Section 6. For this reason, we are interested in the solution of the following generic problem:

How to find the "lowest" minima of an analytic cost function

$$\begin{array}{rcl} J : \mathbb{R}^n & \longrightarrow & \mathbb{R} \\ x & \longrightarrow & J(x) \end{array} ?$$

Various minimization algorithms are used in quantum chemistry (Liotard, 1992):

1. Local algorithms such as the conjugate gradient one (Preuss *et al.*, 1986). They lead to the nearest minimum of the initial configuration. This means that the chemist must have good intuition of the most stable geometry of the molecule.

2. Global algorithms which do not require *a priori* knowledge of the shape of the most stable geometry. The most popular method used in quantum chemistry software is the simulated annealing algorithm (Kirkpatrick *et al.*, 1983).

We introduce a new global optimization method which is detailed in what follows. Given an initial guess $x_0$ and a search direction $d_0$, we compute Taylor's expansion of the cost function

$$j(t) = J(x_0 + t\, d_0), \qquad t \in [t_{\min}, t_{\max}]$$

The approximated optimality condition is a polynomial equation. Using an improved *Weierstrass method* (Bellido, 1992), we compute all the roots of this equation and we retain the best ones $x_1, \ldots, x_m$.

From each selected point, we start again the algorithm computing Taylor's expansion in a new direction. This direction is e.g. the conjugate gradient one allowing for local convergence of the process.

This method is a recursive algorithm with exponential increase of the memory required. For this reason, we keep in the memory at most $p$ points. Before introducing a new point, we discard another point using the following rules:

- If the new point is too close to an existing one, we discard the latter;
- Otherwise, we discard a point with high level of energy.

Let us denote by $\tilde{J} = \sum_{i=1}^{p} J(x_i)$ the global energy of the population $x_1, \ldots, x_p$. We stop our process if $\tilde{J}$ cannot be improved after a given number of iterations.

This algorithm gives a set of local minima corresponding to stable configurations of clusters (this set may include the global solution). Those minima are obtained with good accuracy owing to the local convergence of the conjugate gradient method.

The proposed algorithm suggests a natural way of parallelization: computations of Taylor's expansion and its minima in many directions can be performed independently of one another.

## 6. Application to Quantum Chemistry

Minimization algorithms are important tools in quantum chemistry, mainly in the study of structural properties of molecules. Before introducing some technical aspects related to the function we want to minimize, it seems necessary to review briefly the usual vocabulary and the associated physical background of quantum chemists (Atkins, 1983; Karplus and Porter, 1970; Szabo and Ostlund, 1982).

In what follows, we always assume that the nuclei have fixed positions, i.e. we work with the so-called Born-Oppenheimer approximation. Information about the electronic structure and chemical bonding is obtained through the analysis of a function called the wavefunction and usually written as $\psi(r_1, r_2, \ldots, r_n)$, where $r_i$ represents the coordinates of the $i$-th electron. The wavefunction must be antisymmetric, because electrons are fermions (this is known as the Pauli principle), and it is usually normalized:

$$\int_{\mathbb{R}^{3n}} \psi^*(r_1, r_2, \ldots, r_n)\psi(r_1, r_2, \ldots, r_n)\, \mathrm{d}r_1 \mathrm{d}r_2 \ldots \mathrm{d}r_n = \int_{\mathbb{R}^{3n}} |\psi|^2\, \mathrm{d}r_1 \mathrm{d}r_2 \ldots \mathrm{d}r_n = 1$$

The quantity $|\psi|^2$ is the density probability that the $n$ electrons are respectively localized at the coordinates $r_1, \ldots, r_n$. The wavefunction $\psi$ which describes the electronic system and its associated electronic energy $E$ are solutions of the time-independent Schrödinger equation $\hat{H}\psi = E\psi$. The quantity $\hat{H}$ is the Hamiltonian operator: $\hat{H} = \hat{T} + V$, where $\hat{T}$ is the kinetic operator and $V$ includes the nuclei-electrons and electron-electron interactions.

Many methods have been developed for finding the solutions to the Schrödinger equation. They are based upon approximations that are more or less justified physically. The usual methods consist in searching the solutions of the Schrödinger equation using a finite basis set of functions $(\chi)$. These functions are localized on $N$

atoms. They are called atomic wavefunctions or atomic orbitals. Thus, the electronic wavefunction $\psi$ is developed upon this basis set of size $N$:

$$\psi = \sum_{p=1}^{N} c_p \, \chi_p$$

The Hamiltonian is a matrix and solving the Schrödinger equation consists in the diagonalization of the Hamiltonian operator in the space spanned by the atomic orbitals. Because we work in a finite basis set, the Hamiltonian operator $\hat{h}$ is an approximation to the exact operator $\hat{H}$. The energies and wavefunctions are the eigenvalues and eigenvectors of the Hamiltonian operator $\hat{h}$, respectively. Here $\hat{h}$ is a hermitian operator (self-adjoint), thus the eigenvalues are real.

The $N$ eigenvectors $\psi_i$ are called molecular orbitals. Their analysis leads to the understanding of the chemical bond between atoms. The $N$ eigenvalues $\varepsilon_i$ are the energies of the molecular orbitals. The electrons occupy the lowest energy levels: two electrons per orbital, only one in the last occupied orbital for an odd number of electrons. The total electronic energy $E$ of the molecule is the sum of the lowest eigenvalues $\varepsilon_i$:

$$E = \sum_{i \in occupied} n_i \varepsilon_i, \qquad n_i = 1 \text{ or } 2$$

A minimum of the energy $E$ corresponds to a stable structure of the molecule. The molecule can adopt many geometries, but the most stable of them will correspond to the lowest minimum of the energy.

The reliability of the minimization method will be checked using the Hamiltonian operator. In particular, we shall study alkali clusters (Poteau and Spiegelmann, 1992; Spiegelmann and Poteau, 1995). This is an improvement of one of the simplest theory in quantum chemistry, namely the Hückel method (Heilbronner and Bock, 1976). Clusters of atoms have an intermediate size between the atom and the solid state, and they may reveal specific properties. They were the subject of numerous studies, both experimental and theoretical (Bonacic-Koutecky *et al.*, 1991; Haberland, 1987; Koutecky and Fantucci, 1986). Alkali clusters are usually called prototypes of metallic clusters. From a theoretical point of view, they are quite interesting because their study requires less computational efforts than other metallic clusters, such as transition metal ones. As a matter of fact, only one atomic orbital per atom is sufficient for a good description of the metallic bond between two alkali atoms. Thus, the size of the matrix to be diagonalized is equal to the number of atoms. The elements of the matrix are dependent on the distance between atoms. The diagonal elements are the sum of repulsive functions between two atoms:

$$h_{ii} = \sum_{\substack{k=1 \\ k \neq i}}^{N} \rho_{ss}(R_{ik})$$

The off-diagonal terms are interaction functions called transfer integrals between two atoms $i$ and $j$:

$$h_{ij} = t_{ss}(R_{ij}) - \sum_{\substack{k=1 \\ k \neq i,j}}^{N} \frac{t_{s\sigma}(R_{ik}) t_{s\sigma}(R_{jk})}{\Delta E} \frac{R_{ik}.R_{jk}}{R_{ik} R_{jk}}$$

where $R_{ij}$ is the distance between atoms $i$ and $j$, and $\Delta E$ is a constant.

The Hamiltonian elements are combinations of three distance-dependent functions $\rho_{ss}$, $t_{ss}$ and $t_{s\sigma}$. These functions are constructed to reproduce some known energetic properties of sodium clusters. For practical convenience linked to the $n$-th order differentiation, we give them the following analytic form:

$$\rho_{ss}(R) = a\, e^{-\alpha R} + b\, e^{-\beta R}$$

$$t_{ss}(R) = D_e \left[ e^{-c(R-R_e)} - 2\, e^{-d(R-R_e)} \right]$$

where $t_{s\sigma}$ is the same as $t_{ss}$. The parameters of these functions are given in Table 1. Moreover, in the case of sodium, $\Delta E$ is taken as 0.077307.

Tab. 1. Values of different parameters.

| $t_{ss}$ | $t_{s\sigma}$ | $r_{ss}$ |
|---|---|---|
| $D_e = -.000262033$ | $D_e = -.001002885$ | $a = 1.286228004$ |
| $R_e = 14.920840175$ | $R_e = 13.149411127$ | $\alpha = 1.327600652$ |
| $c = 0.662022408$ | $c = 0.540246063$ | $b = 19486.594912775$ |
| $d = 0.599083352$ | $d = 0.464888416$ | $\beta = 4.430431756$ |

The problem is now formulated and we can use the global optimization algorithm. We recall that the dimension of the problem is $n = 3N$. It was shown by the use of graph theory that, for ten atoms, there are at most eleven million of stable structures. Moreover, the minima of the hypersurface are separated only by an infinitesimal amount of energy. We started to check our method within the range of size 2–20. The method was the same as used in Section 5 where we kept in each step only one point, namely the best one. This point was supposed to be the global minimum.

For three atoms, the initial structure is linear. The global minimum was found with the use of our algorithm. It is an isosceles triangle (Fig. 3). For four atoms, we start with a square. After the use of the algorithm, we find a rhomb, which is the most stable configuration (Fig. 4). Our method gives good results for five atoms. The global minimum corresponds to a plane structure (Fig. 5). For seven atoms, we observe an important decrease in energy. In the most stable configuration, five atoms are on the same plane (Fig. 6).

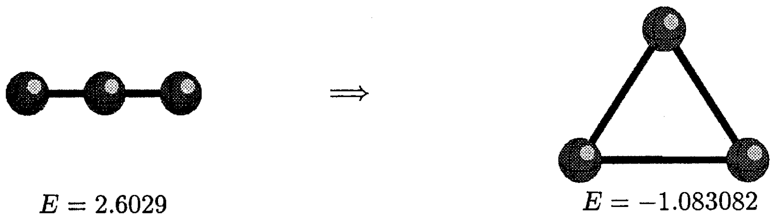


Fig. 3. The initial and the best configurations for $Na_3$. We give the corresponding energies (in eV).

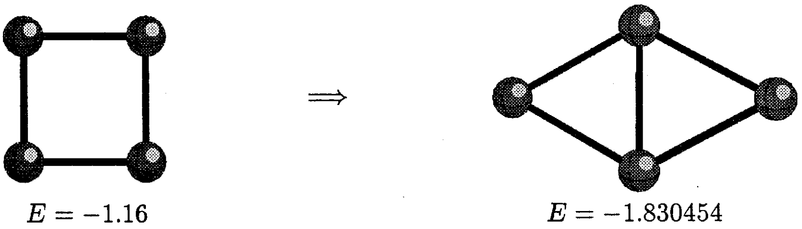


Fig. 4. The initial and the best configurations for $Na_4$. We give the corresponding energies (in eV).

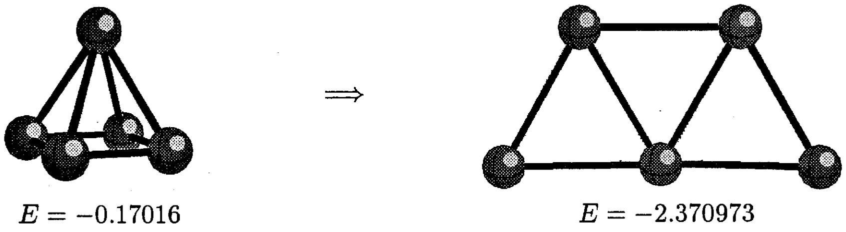
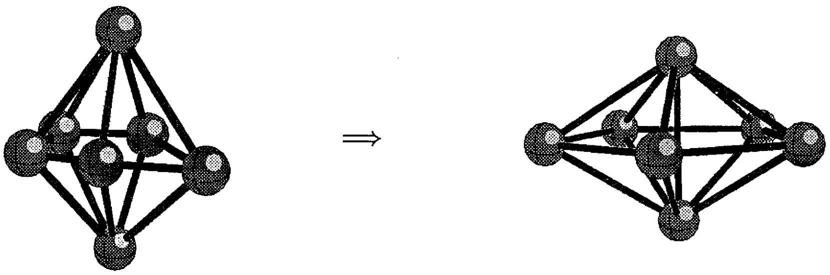


Fig. 5. The initial and the best configurations for $Na_5$. We give the corresponding energies (in eV).



$E = 2.577751$ $E = -3.791287$

Fig. 6. The initial and the best configurations for $Na_7$. We give the corresponding energies (in eV).

## 7. Conclusion

This paper describes a new global optimization method based on Taylor's expansion of the cost function. Those higher-order derivatives are calculated by automatic differentiation. The application of this algorithm in quantum chemistry gives very promising results. All the lowest energies of small sodium clusters have been found.

Our next aim is to use the natural parallelization of the algorithm and to study larger sodium clusters.

This method can be applied in structural dynamics optimization, but the domain of its applications is by far larger than eigenvalue problems.

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