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Direct Calculation of the Energy Gradient with Cartesian Gaussian Basis Sets

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A computer program POLYGRAD based on the POLYATOM/1 system is presented which evaluates analytically the energy gradient using the *s*-type and Cartesian *p*-type Gaussian basis functions. Model calculations on hydrogen peroxide were made to compare the accuracy and the computer time involved in the analytical and numerical determinations of the energy gradient.

Key words: Energy gradient – Differentiation of electronic integrals, analytical ~

1. Introduction

For many chemical problems the knowledge of energy hypersurfaces is of great interest. Not being able to calculate the energy hypersurface analytically one is forced to look for numerical ways of calculation. The simplest but extraordinarily time consuming approach is to compute the energy for many different geometries, i.e. to calculate many points of the hypersurface.

Another important approach requires energy calculations only for a limited set of geometries and the surroundings of the respective points being described in terms of truncated Taylor expansions. A manageable version of this procedure limits itself to the first terms of these expansions: in such a way the gradient method is reached. The energy gradient computations are inherent to the most efficient geometry optimization methods like the variable metric method [1]. Explicit evaluation of the energy gradient is also involved in the force method [2] which appears to be the most suitable method for the determination of the force constants of polyatomic molecules from both the accuracy and feasibility viewpoints. In the SCF-MO-LCAO treatments, the analytical computation of the energy gradient requires the analytical evaluation of derivatives of integrals over the basis functions with respect to all nuclear coordinates. In the semiempirical treatments based on CNDO or MINDO only overlap and two-centre electronic repulsion integrals are to be differentiated. Since the necessary derivatives of integrals are expressible in closed analytic forms [3], the computer programs [3–5] are now available for

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routine geometry optimizations. A computer program on the *ab initio* level reported by Pulay [6] makes use of the Gaussian lobe functions. Here the differentiation is simple because the derivatives of integrals over basis set *s*-type functions can be computed through the mere evaluation of the $(ps|ss)$ type integrals. In the present paper we report on the procedure based on the POLYATOM system by making use of the Cartesian Gaussian functions. We considered it expedient to develop such a computer program for two reasons. First, the *ab initio* SCF calculations are mostly performed just with the Cartesian Gaussian functions and, second, the POLYATOM system is one among the most widespread *ab initio* programs.

2. Description of the Computer Program

The expression of Moccia [7] for the derivative of energy supplemented for the nuclear repulsion term

$$\frac{\partial E}{\partial \alpha_{\mathrm{A}}}=\operatorname{tr}\left\{\left[2\frac{\partial \boldsymbol{H}}{\partial \alpha_{\mathrm{A}}}+\frac{\partial \boldsymbol{P}}{\partial \alpha_{\mathrm{A}}}\boldsymbol{D}\right]^{\dagger}\boldsymbol{D}\right\}-2\operatorname{tr}\left\{\left[\frac{\partial \boldsymbol{S}}{\partial \alpha_{\mathrm{A}}}\right]^{\dagger}\boldsymbol{B}\right\}+\frac{\partial Z}{\partial \alpha_{A}} \tag{1}$$

reduces the problem mainly to the evaluation of derivatives of all the integrals. By α_{A} we imply a Cartesian coordinate of the atom A. The matrices $\boldsymbol{H}$ and $\boldsymbol{P}$ refer to one-electron and two-electron parts of the Hamiltonian, respectively; $\boldsymbol{D}$ is the density matrix and $\boldsymbol{S}$ is the overlap matrix. $\boldsymbol{B}$ and Z are defined as follows

$$B_{ij}=2\sum_{s}\varepsilon_s C_{is} C_{js} \tag{2}$$

$$Z=\sum_{\mu>\nu}\sum\frac{z_\mu z_\nu}{r_{\mu\nu}} \tag{3}$$

Here ε_s stands for orbital energies, the summation over s goes through the occupied orbitals, z are the nuclear charges and $r_{\mu\nu}$ are interatomic distances.

We called the program POLYGRAD because it follows rather closely the philosophy and the structure of the POLYATOM/1 [8] QCPE 47.1 program. We adopted the modifications involved in the improved version [9] of the program that permits to employ contracted basis sets and avoids system-dependent file handling subroutines. POLYGRAD is thus fully system independent except for statements that assign 2 and 4 bytes to integers and 4 and 8 bytes to real numbers. The subroutines for the actual gradient computation are so written that they can be incorporated into the unmodified POLYATOM system with little effort.

The program accommodates the *s*-type and Cartesian *p*-type Gaussian functions and the geometry transformation for the local integration is performed by rehybridizing the basis set functions. This results in geometry-dependent hybridization coefficients. The integral finally is the sum of products of a local integral with a geometry-dependent coefficient which in turn is made up by the hybridization coefficients. Thus our problem breaks down into obtaining the derivatives of the local integrals and the derivatives of the geometry-dependent coefficients.

The evaluation of the derivatives of the local integrals is performed by differentiating the so-called elementary functions. This is straightforward, especially as the function FMCH can be used for the derivatives, too. The derivatives of the coefficients are evaluated by differentiation of the rotation matrix and by subsequent combination with the hybridization coefficients.

The input to the program is almost the same as to the POLYATOM/1 program. The calculation of the integral labels is done with a minor modification by the program PA20. The part PA30 of POLYATOM is replaced by PAG30, which is built up in a fully analogous way using many subroutines of PA30. PAG30 computes simultaneously for each integral the relevant derivatives and stores them on tape separately for the X, Y and Z coordinates. The files for the latter are approximately four times longer than a file for integrals, since for each electron repulsion integral we store its derivatives with respect to four nuclei on which, in the general case, the basis functions are centered.

The SCF part is a slightly modified version of PA40; the modification concerns the orbital energies and occupancies that are written on tape. To avoid confusion we call it PAG40. A program part PAG50 is added which reads in the derivatives of the integrals and the results of the SCF part from tape and sets up the gradient using Moccia's equation. The gradient is stored on tape for later use (e.g. for the geometry optimization).

The program POLYGRAD has been written in FORTRAN IV for an IBM 370/135 computer and will be available on request from the Gesellschaft für Mathematik und Datenverarbeitung in Darmstadt [10].

3. Model Calculation on Hydrogen Peroxide

To show the virtues of the program we compare here two calculations on hydrogen peroxide. Once the energy gradient is computed numerically, i.e. the components of the gradient are calculated using the formula

$$\frac{\partial E}{\partial \alpha_A} \approx [E(\alpha_A^0 + \Delta) - E(\alpha_A^0 - \Delta)]/2\Delta \tag{4}$$

We assumed Δ of 0.005 a.u. Hydrogen peroxide possessing four atoms, the computation of the gradient involves 24 standard SCF calculations. The second computation was performed analytically by means of the POLYGRAD program. The minimal uncontracted ($3s1p/1s$) basis set [8] was used. For the hydrogen functions we take the exponent 0.28294 [11]. The geometry assumed is given in Table 1. In actual calculations the symmetry of H_2O_2 was disregarded, because the

Table 1. Geometry assumed for H_2O_2

Centre	Coordinates[a]		
	x	y	z
H1	−1.478739	1.0068375	−1.5439130
H2	1.478739	1.0068375	1.5439130
O1	0	0	−1.3936900
O2	0	0	1.3936900

[a] In a.u.

variable metric method is, compared to the point-by-point geometry optimization, most effective with molecules of low symmetry. A single standard SCF calculation lasts 6 minutes on the IBM 370/135 computer, i.e. 144 minutes are needed for the full evaluation of the energy gradient. The calculation by the POLYGRAD program lasts 44 minutes. The results of the two calculations are given in Table 2. The entries permit to judge the degree of accuracy of the numerical procedure. Up to now no great effort was devoted to reducing the computation time. Actually, the calculation of the energy gradient lasts still rather long as it is about six times longer than the calculation of the wave function alone. Meyer and Pulay reported [12] that with their program [6] the factor is only 2. There are probably two reasons for this difference. First, the program of Meyer and Pulay is based [13] on lobe functions, the differentiation of which is considerably simpler. Second, our subroutines for differentiation of integrals are certainly less effective than the original POLYATOM subroutines for evaluation of integrals. We hope, however, to be able in future to improve the former and to accelerate the POLYGRAD program. In a forthcoming paper we are going to test the utility of the program in geometry optimizations.

Table 2. Energy gradient of H_2O_2 computed numerically and analytically

Atom	Gradient Components[a]					
	Numerical			Analytical		
	x	*y*	*z*	*x*	*y*	*z*
H1	0.00589	−0.00207	0.03421	0.00579	−0.00211	0.03424
H2	−0.00589	−0.00207	−0.03421	−0.00579	−0.00211	−0.03424
O1	0.02978	0.00205	−0.21351	0.02995	0.00211	−0.21354
O2	−0.02978	0.00205	0.21351	−0.02995	0.00211	0.21354

[a] In a.u.; for the geometry assumed see Table 1.

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