

Pulay P. *Ab initio* calculation of force constants and equilibrium geometries in polyatomic molecules. I. Theory. *Mol. Phys.* 17:197-204, 1969.

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The general expression for the forces (negative energy derivatives with respect to the nuclear coordinates) is applied to the Hartree-Fock molecular wave function. It is shown that this method is much superior to purely numerical calculations for the determination of molecular geometries and force constants. [The SCF® indicates that this paper has been cited in over 590 publications.]

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I came to *ab initio* calculations through studies of vibrational spectroscopy. After finishing my master's thesis at the Eötvös University in Budapest in 1963, Ferenc Török and I worked on the determination of molecular force fields from infrared frequencies. We thought that quantum chemical calculations could supply the missing information for this problem. This was supported by Mills's hybrid orbital model, which correctly reproduced the signs of coupling terms, and by maximum overlap calculations of M. Mezei and me.

In my thesis¹ I performed a one-center calculation on SiH₄, using a mechanical calculator. The geometry and the breathing vibrational frequency in this work were already determined from analytical gradients. The latter are, however, quite trivial for a one-center expansion.

With the support of B. Lengyel, head, and of Török, I had applied successfully for a graduate stipend from a Federal Republic of Germany agency, the Deutscher Akademischer Austauschdienst (DAAD). This was still quite exceptional in Hungary in 1967.

I started in the stimulating laboratory of J. Goubeau in Stuttgart. I decided, however, to spend the summer and fall of 1968 at the Max Planck Institute in Munich to learn *ab initio* methods. My proposal, specifying research on gradients, was accepted by DAAD and by the leader of the Munich group, H. Pruss. He did not get closely involved with this

project, but a fresh PhD of his, Wilfried Meyer, gave me invaluable help, stimulation, and critique. The wave function from his assembler-language self-consistent field (SCF) program was used in the first polyatomic gradient code. By mid-August 1968 I had results for hydrogen and water with this makeshift program that showed the viability of the method. My stipend ran out by this time, and I had to return to Stuttgart as a teaching assistant. In spite of the distance, Meyer and I began working a new *ab initio* program that, heavily modified, is still in use today.

In October 1968 I proudly submitted the manuscript to *Theoretica Chimica Acta*. It was like a cold shower when it was harshly rejected by the editor. In his defense, I did not include any computational results in this first paper, which was probably an error. After some futile arguments, I resubmitted the paper to *Molecular Physics*. Perhaps because it was first published in a physics journal, the method and the paper were slow to catch on. Only the publication of the first review paper² made the technique widely known.

What were the reasons for the relatively late introduction of gradients? Besides the mathematical difficulty of finding the derivative of an implicit function, the SCF energy, there were two reasons. First, at a time when integral calculation was difficult, most quantum chemists were horrified at the prospect of calculating their many derivatives. Second, gradients are most useful for large molecules, which were difficult to calculate at that time.

While ours was the first modern, polyatomic gradient program, there were important predecessors, notably the theory of S. Bratoz,³ which became generally known only later. J. Gerratt and I.M. Mills⁴ published their paper while I was reworking mine. J.W. McIver and A. Komornicki⁵ introduced gradients independently for semiempirical methods.

Gradient methods have increased the efficiency of quantum chemical methods by about an order of magnitude. Some problems, like the optimization of transition states, are virtually impossible to solve without them. Their further development has been reviewed recently.⁶ To me, the most important recent contributions are MP2 derivatives and SCF second derivatives by Pople, Raghavachari, Schlegel, and Binkley; the generalizations introduced by the Schaefer and Handy groups; and the integral computation techniques of Dupuis, Rys, and King.

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4. Gerratt J & Mills I M. Force constants and dipole moment derivatives of molecules from perturbed Hartree-Fock calculations. *J Chem. Phys.* 49:1719-30, 1968. (Cited 175 times.)
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