

McIver J W & Komornicki A. Rapid geometry optimization for semi-empirical molecular orbital methods. *Chem. Phys. Lett.* 10:303-6, 1971.  
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For semiempirical molecular orbital methods the gradient of the potential energy can be obtained at negligible additional cost. This allows the efficient use of powerful gradient-based optimization methods to determine molecular geometries. It is shown that the gradient transforms according to the totally symmetric representation of the point group of the molecule and that, consequently, these methods preserve the starting symmetry. [The *SCF*® indicates that this paper has been cited in over 300 publications.]

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I had been at Buffalo less than a year when we began working on this project. I was fresh from postdoctoral studies with John Pople at Carnegie-Mellon University, where I had learned how to write computer programs for molecular orbital calculations of magnetic resonance parameters. Andy Komornicki, the co-author of this our first paper, was a new graduate student. Andy was really an organic chemist with an encyclopedic memory and a voracious appetite for the organic literature; he knew almost nothing about computing then but was well aware of the importance of molecular structure in organic chemistry. Andy also had a refreshing, if somewhat naive, vision. "Let's put the experimentalists out of business," he would say. "Let's calculate organic structures better and cheaper than they can measure them in the laboratory." It was his motivation and infectious enthusiasm that led to this new (for us) research area.

It had been known for some time that both the *ab initio* and semiempirical molecular orbital theories could predict molecular geometries (the spatial arrangement of the atoms in the molecule) with remarkable accuracy. The problem was the cost. In order to get the geometry one had to move the atoms around, recalculate the energy of the molecule, and continue until the energy was as low as it was

possible to get it (i.e., a minimum with respect to displacing the atoms). The interesting organic molecules had lots of atoms to move and calculating the energy was expensive. Our discovery was that during the process of calculating the energy in the semiempirical (as opposed to *ab initio*) methods, one could calculate the energy gradient at a small fraction of the energy cost. In other words, one could determine how all the atoms should be moved collectively in order to make the energy go down the fastest. Once this energy gradient was calculated, it could be plugged into the new and powerful gradient-based optimization methods in order to quickly and automatically obtain molecular geometries.

We had originally prepared a much longer paper that included a detailed derivation of our formula for the gradient. We were horrified to then find almost our exact formula, complete with the derivation, in a paper by R. Moccia<sup>1</sup> written nearly four years earlier. Subsequently, we became embarrassingly aware of the seminal work of P. Pulay<sup>2</sup> (because we did not cite it!), who was calculating gradients for use in determining *ab initio* molecular orbital geometries and vibrational spectra. From the activity at the time it was clear that the trick of getting the semiempirical geometries quickly was about to be discovered by somebody. It was mainly a matter of luck that it happened to be us.

Computational chemistry has grown up since those days of impatiently waiting in line for a keypunch while clutching a box of ragged IBM cards. Highly developed semiempirical software packages such as MOPAC<sup>3</sup> have passed from the hands of theoreticians into those of the experimentalists themselves. Very much still in business, they use these methods as but one in their arsenal of research instruments. One of the more powerful of the *ab initio* packages is GRADSCF,<sup>4</sup> written for the CRAY supercomputer. Andy is its author.

The gradient methodology has also expanded to the more general problem of determining transition states and reaction paths for chemical rate processes. A recent review of this methodology was presented by H.B. Schlegel.<sup>5</sup> In addition, Pulay has recently reviewed the advances made in the evaluation of the gradient itself.<sup>6</sup>

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