

Allinger N L. Calculation of molecular structure and energy by force-field methods.
Advan. Phys. Organ. Chem. 13:1-82, 1976.
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The structure of a molecule and many of the physical and chemical properties of that molecule may be calculated from the series of forces involved in the bending, stretching, and torsion that act within the molecule. A general force field for describing molecules has been outlined and extensively tested, and this article is a review of the strengths and present weaknesses of this force field. [The *SCI*® indicates that this paper has been cited in over 460 publications.]

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It has long been known to spectroscopists that the vibrational spectrum of a molecule requires and is explained by a force field that consists of a description of the interactions within the molecule in terms of its internal coordinates, i.e., the stretching of bonds, the bending of bond angles, and the twisting of torsion angles. It was recognized in the late 1940s, especially by F.H. Westheimer,¹ that many physical and chemical properties of molecules were in principle determinable by calculation if the force fields were sufficiently general (transferable from one molecule to another) and if one could in fact carry out the lengthy mathematical operations required. This kind of computational method to study molecules is now usually referred to as the molecular mechanics method.

While the lack of computers proved to be a severe stumbling block at the time, subsequent studies by J.B. Hendrickson,² K.B. Wiberg,³ and others in the early 1960s utilized then available computers, which were sufficiently powerful for the task. Hence, by 1965 the tools for carrying out such calculations were available, although it was not yet then known just how transferable force fields would turn out to be. Several groups were active worldwide in studying

this problem in the late 1960s and early 1970s. The most successful applications of the method at this time were in the hydrocarbon field,^{2,3} but similar studies on proteins were also being carried out.⁴

In 1968 P.V.R. Schleyer and coworkers were able to review the hydrocarbon field,³ and they outlined the potential power of the method for studying chemical problems. The title paper of this note was written in early 1974 and reviewed the field generally at that time. There were four different hydrocarbon force fields that were being widely used then, and their results were being described in the current literature. These force fields differed somewhat from one another, although the similarities were certainly greater than the differences. At the time, the interest was in deciding which of the force fields would in fact do a better job of describing molecular properties of hydrocarbons, and then, of course, it was desired to be able to extend the calculations to functionalized molecules. Such extensions had proceeded, but not very far, by the time this review was written, and only about one-third of the total number of pages in the article was devoted to such studies. Delocalized electronic systems had also been studied briefly, and it was clear that for these the calculations were more complicated, but they seemed to be possible. Heats of formation and reaction rates had also been studied briefly, and it appeared they could be dealt with as well.

During the late 1970s and thereafter, molecular mechanics began to be very widely used for the solution of many different kinds of problems in chemistry, and all of the items mentioned above were studied in much greater detail. The results were certainly good on the whole and convinced most chemists that computational chemistry had indeed become a powerful tool that could give many results with an accuracy competitive with experiment, and with much less labor.

This particular article has been cited so frequently because it was not written too early and, although rather concise, it included references to a wide variety of applications. The text is 76 pages in length. In 1982, only six years after this paper was published, the update of this article required a whole book⁶ with 316 pages of text, but which, even so, made no attempt to be comprehensive.

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