Pople J A & Segal G A. Approximate self-consistent molecular orbital theory. III. CNDO results for AB_2 and AB_3 systems *J. Chem. Phys.* 44 3289-96, 1966
[Carnegie Institute of Technology and Mellon Institute, Pittsburgh, PA]

This paper presents the CNDO/2 method, a semiempirical approach to the quantum mechanical calculation of the wave function and energy of the electronic states of polyatomic molecules [The *SCI®* indicates that this paper has been cited in over 2,295 publications]

CNDO/2, An Approximation to the Hartree-Fock Theory

Gerald A. Segal
Office of the Dean
College of Letters, Arts and Sciences
University of Southern California
Los Angeles, CA 90089-4012

June 26, 1989

In 1964 John A. Pople had just left England to come to the US. I was the first student he took in this country. Roald Hoffmann had recently published his *Citation Classic* on extended Huckel theory,[1] an approximate molecular orbital method for calculating the wavefunctions and energy of the electronic states of polyatomic molecules of arbitrary geometry, which includes no explicit consideration of electron repulsion. It was still quite difficult to carry out Hartree-Fock calculations on molecules of any size due to the number of repulsion integrals that had to be calculated and the difficulty in evaluating the three and four center integrals that arose, while Gaussian methods were still in their infancy. In talking about what I might do for my PhD dissertation, John suggested that we follow a line that had proven profitable in planar molecules, where the repulsion between π electrons had been successfully accounted for by the zero differential overlap approximation, and attempt to extend it to nonplanar systems.

As we began to develop the theory, it quickly became apparent that nonplanar systems differ strongly from planar ones, where the basis functions of π symmetry are all parallel to one another, in that the necessity that the theory be independent of the coordinate system led to a well-defined hierarchy of possible approximations that maintain geometric invariance. We moved to develop a semiempirical molecular orbital theory employing the simplest of these, complete neglect of differential overlap (CNDO), parametrizing the method to model existing *ab initio* calculations on diatomic molecules as closely as possible.

First trials showed that the method was extremely powerful. In December of that year, there was a Sanibel Island meeting in honor of Robert Mulliken, and we hurried to produce a body of application so that the new theory could be presented there. The result was the CNDO/1 method.[2,3]

It was clear to us, however, that a better semiempirical parametrization could be found and we returned from the meeting to take up the problem. We modified the theory with respect to how certain groups of terms on the diagonal of the Hartree-Fock matrix were represented by experimental quantities determined from atomic spectra and also with respect to the handling of penetration integrals, the net interaction of an electron with a neutral atom. The result was the CNDO/2 method, this *Citation Classic*.

In this paper we described the new method and, by surveying all AB_2 and AB_3 molecules containing only the atoms hydrogen and lithium through fluorine, showed that the theory was capable of determining molecular geometries with surprising accuracy as well as providing a good description of polarity as measured by the computation of electric dipole moments. The method quickly became a standard technique in the field. Today, it is regularly applied to calculations on particularly large molecules and serves as the basis for a wide variety of semiempirical approximations optimized for various molecular properties. It also provides the necessary first guess at the one electron density matrix in most *ab initio* computer programs for molecular electronic structure calculations.

[Editor's note: a recent publication citing this *Classic* paper is reference 4.]

1. Hoffmann R. An extended Hückel theory I Hydrocarbons *J Chem Phys* 39 1397-412, 1963 (Cited 2,960 times) [See also· Hoffmann R. Citation Classic *Current Contents/Engineering, Technology & Applied Sciences* 20(19) 20, 8 May 1989 and *Current Contents/Physical, Chemical & Earth Sciences* 29(19) 20, 8 May 1989]
2 Pople J A, Santry D P & Segal G A. Approximate self-consistent molecular orbital theory 1 Invariant procedures *J Chem Phys* 43 S129-35, 1965 (Cited 1,090 times)
3 Pople J A & Segal G A. Approximate self-consistent molecular orbital theory 2 Calculations with complete neglect of differential overlap *J Chem Phys* 43 S136-49, 1965 (Cited 935 times)
4 Baetzold R C. Electronic calculations of large copper oxide clusters *Inorg Chem* 28 640-4, 1989

14-14