

This Week's Citation Classic

Pariser R & Parr R G. A semi-empirical theory of the electronic spectra and electronic structure of complex unsaturated molecules. *J. Chem. Phys.* **21** 466 and **21**: 767; 1953.

A new semi-empirical theory is presented for the prediction and correlation of the electronic spectra and structure of complex unsaturated molecules. Application is demonstrated for ethylene, benzene and other molecules. [The *SCI*[®] indicates that this paper was cited 2450 times in the period 1961-1977.]

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February 14, 1978

"I have often been asked about the origin of our work. Specifically, how and why did I, a chemist at the Jackson Laboratory of E. I. DuPont DeNemours & Co., get together with Bob Parr, an associate professor at Carnegie Tech, to work on a semi-empirical quantum theory? My interest began in 1951, shortly after my employment at Jackson Laboratory, where a large part of the effort was devoted to the synthesis and evaluation of organic dyes.

As one of a very few physical chemists whose assignment it was to characterize the many dyes being synthesized by a host of organic chemists, I felt a strong desire to gain a better understanding of structure/property relationships —particularly with regard to the color of dyes —since I hoped that such understanding might save me and my colleagues a considerable amount of work in searching for the desired structures. Also, perhaps naively, I believed that quantum chemistry should contain the answers to many of our problems.

"My management was very supportive of my ideas and encouraged me to do what I could. Since my experience in the field was limited to the few courses at the University of Minnesota as taught (very inspiringly) by Bryce Crawford, I felt that I needed someone to consult and to help me in my new endeavor. Thus, I approached Bob Parr, who had done his thesis research under Crawford on the most advanced quantum mechanical

calculations at that time on simple organic molecules, and whom I had learned to

respect at Minnesota as a friend and teacher. I have always felt grateful to Bob that he encouraged me in my youthful enthusiasm for calculating the spectra of complex dyes when the state of the art at the time was hardly adequate to explain the spectrum of ethylene!

"We strongly believed that electronic repulsions would need to be included specifically in any theory which was going to be predictive in a quantitative way. But this was practically impossible for any molecule larger than benzene, especially with the limited computers of the early fifty's. The breakthrough came from Bob Parr, with his invention of the Zero Differential Overlap (ZDO) approximation. By applying this method, it was possible for me to calculate benzene —and even naphthalene — without too much difficulty on a mechanical desk calculator!

"But the results of such calculations were still far from agreement with experiment. In taking the next step, my training as an experimentalist came in handy. With ZDO it was simple enough to adjust quantum mechanical parameters to fit the experimental data. In particular, the important one-center 11/11 electron-repulsion integral for carbon assumed an 'experimental value' of about 11 e.v. vs the 'theoretical' 17 e.v.! Realizing that 11 e.v. was close to the ionization potential, I found it easy to rationalize why the one-center integral should indeed have an empirical value such as this and why the other integrals should also be adjusted.

"The new empirical integrals, together with the ZDO approximation and the advent of the first solid-state, high-speed computers, was all that was needed to apply our semi-empirical theory to many aromatic molecules with very gratifying results. We did not quite meet our goal at the time of predicting the color of complex organic dyes, but it is good to know that our method, with its many extensions and refinements as developed subsequently by others, may indeed be of widespread use to-day in helping to solve many complex problems involving organic molecules."