

This Week's Citation Classic

Del Bene J & Jaffé H H. Use of the CNDO method in spectroscopy. I. Benzene, pyridine, and the diazines. *J. Chem. Phys.* **48**:1807-13, 1968. [Dept. Chemistry, Univ. Cincinnati, Cincinnati, OH]

In this paper, the CNDO/S method was introduced as an SCF-CI method for computing the electronic spectra of polyatomic molecules. The method was applied to the isoelectronic compounds benzene, pyridine, pyridazine, pyrimidine, and pyrazine, and quite satisfactory agreement between computed and experimental singlet $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition energies was obtained. [The *SCI*[®] indicates that this paper has been cited over 530 times since 1968.]

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"In 1966, the most sophisticated quantum chemical method for calculating the energies of excited electronic states of organic molecules was the Pariser-Parr-Pople SCF-CI method (PPP). Although this method was widely used, it is restricted to $p \rightarrow \pi^*$ states in planar molecules which have separable n -electron systems. Because such molecules often exhibit $n \rightarrow \pi^*$ transitions as well, there had been attempts made to modify PPP to include $n \rightarrow \pi^*$ states, but these modifications were somewhat arbitrary, and computed results were not consistent. Since $n \rightarrow \pi^*$ states are chemically important lowenergy excited molecular states, there existed a need for a reliable method for their investigation.

"Hans H. Jaffé suggested the $n \rightarrow \pi^*$ problem to me as a thesis problem. Although I had been warned by the senior members of his research group to avoid this problem, 'The Boss' was convincing, and the $n \rightarrow \pi^*$ problem became mine. Not long after I began working on this problem, John A. Pople presented a seminar at the University of Cincinnati on his new ground-state CNDO-SCF method, which treats explicitly all valence electrons. Jaffé and I were intrigued. 'Why couldn't a CI calculation be added to CNDO?', we asked. 'Then, the

entire lowenergy electronic spectrum, including $n \rightarrow \pi^*$ as well as $n \rightarrow \pi^*$ transitions, could be computed.'

"After writing and debugging a CNDO-CI computer program, we ran our first calculation. We chose benzene for the test case, since its electronic spectrum had been well-characterized experimentally. Our disappointment was great, for the calculations predicted more than 20 $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ states which were of lower energy than the $p \rightarrow \pi^*$ state observed at 179m μ . These various states were tangled as badly as a Gordian knot. We eventually resolved the problem of the intermingling of states by introducing the parameter κ to distinguish in a diatomic sense, p - σ from p - n overlap. This necessitated a reparameterization of CNDO, which we did during the summer of 1967 when our research group had the unprecedented opportunity of spending six nights a week on the midnight shift with the computer. By the end of the summer, the modified CNDO method (subsequently designated CNDO/S) came to be.

"The popularity of CNDO/S may be attributed to several factors. First, the method has proven to be reliable for predicting transition energies in a wide variety of chemical systems, including charged as well as uncharged, and nonplanar as well as planar, species. Second, the computed transition energies have been found to correlate well with various molecular properties which depend upon the energies of excited electronic states. Third, the method produces reasonable excited-state wave-functions, from which other excited state properties have been computed successfully. Fourth, the method can be applied to very large molecules without incurring prohibitive computational expense. Finally, the basic methodology has been extended to other important problems, including triplet-triplet transitions, and two-photon excitations.'

"In retrospect, I'm glad 'The Boss' was convincing, and the $n \rightarrow \pi^*$ problem became mine."

1. Marchese F T, Seliskar C I & Jaffé H H. The use of CNDO in spectroscopy. XV. Two photon absorption. *J. Chem.* **72**:4194-203, 1980.