

Hoffmann R. An extended Hückel theory. I. Hydrocarbons. *J. Chem. Phys.* 39:1397-412, 1963.

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The Hückel theory, with an extended basis set consisting of 2s and 2p carbon and 1s hydrogen orbitals, with inclusion of overlap and all interactions, yields a good qualitative solution of most hydrocarbon conformational problems. Calculations have been performed within the same parametrization for nearly all simple saturated and unsaturated compounds, testing a variety of geometries for each. Barriers to internal rotation, ring conformations, and geometrical isomerism are among the topics treated. It is stressed that the geometry of a molecule appears to be its most predictable quality. [The SCF® indicates that this paper has been cited in over 2,960 publications.]

A Simple Quantum Chemical Method

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The extended Hückel method was the first molecular orbital method that included all valence electrons and so could be applied to any organic or inorganic molecule. It was developed in the Lipscomb research group at Harvard, with essential contributions by L.L. Lohr, Jr., W.N. Lipscomb, and me.

In the spring of 1960, in my second year in graduate school, I was working with Martin Gouterman, trying to do a molecular orbital calculation on C_8H_8 , cubane. Since people were attempting to make the molecule, I thought it would be nice to know its electronic structure. The paradigmatic model of the time, the Hückel method, wasn't directly applicable because cubane obviously didn't have a $\sigma-\pi$ separation. Undaunted, I set up a 40x40 matrix for all the valence electrons in cubane, and, using my newly

learned group theory, I reduced the matrix as much as possible. I was still left with many distinct interactions, which I labeled with a mass of Greek letters— $\beta, \gamma, \delta, \epsilon$, and so on.

These matters lay while I went off for a year to the Soviet Union. When I came back, I switched to working with Lipscomb on bonding in boranes. These marvelous molecules are nonplanar, so the simple Hückel model wouldn't work. Still within the framework of a one-electron theory, Lipscomb advised setting the off-diagonal matrix elements of the Hamiltonian proportional to the overlap. The idea goes back to the R.S. Mulliken group at Chicago and was used in borane calculations by H.C. Longuet-Higgins and M.D. Roberts.^{1,2} Earlier work by W.H. Eberhardt, B.L. Crawford, and Lipscomb on the boron hydrides was an important guide to us.³ At just the same time the Lipscomb research group, including Bill Kern, Dick Stevens, Lohr, Russ Pitzer, and me, was learning computing on the IBM 604. So I programmed the vector decompositions of the overlap integrals and adapted from others in the group the actual integral evaluation and matrix diagonalization routines. A paper by E.B. Moore, Lohr, and Lipscomb⁴ shows that pieces of the procedure were in place in 1961. Lohr suggested the use of valence state ionization potentials and the Wolfsberg-Helmholtz formula, and there was the first extended Hückel program—except we didn't call it that, yet.

Lipscomb and I used the method with some success for a theoretical analysis of boron hydrides and carboranes,^{5,7} and Lohr did so for XeF_4 and inorganics. In general we looked at orbital energies, charge distributions, but never thought of comparing total energies. One day, as I was finishing my PhD and getting ready to begin a Junior Fellowship at Harvard, I got to talking to Pitzer. He was also in the group, in the throes of doing the first Hartree-Fock SCF calculation of the barrier to internal rotation of ethane. I thought I could do the same, using the energies that our semiempirical programs were giving, but to which heretofore we had not paid much attention. Remarkably, I also got a reasonable value for the ethane barrier.

The idea was planted in my mind to use the method to study all organic molecules; the beginnings of that project are shown in this paper. I named the methodology developed in the Lipscomb group "extended Hückel theory," so as to draw a connection with the successes and limitations of the Hückel method—and also not to overadvertise it.

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2. ———. The electronic structure of an icosahedron of boron atoms. *Proc. Roy. Soc. London Ser. A* 230:110-9, 1955. (Cited 125 times.)
3. Eberhardt W H, Crawford B L & Lipscomb W N. The valence structure of the boron hydrides. *J. Chem. Phys.* 22:989-1001, 1954. (Cited 145 times.)
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5. Hoffmann R & Lipscomb W N. Theory of polyhedral molecules. I. Physical factorization of the secular equation. *J. Chem. Phys.* 36:2179-89, 1962. (Cited 660 times.)
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