

Ransil B J. Studies in molecular structure. II. LCAO-MO-SCF wave functions for selected first-row diatomic molecules. *Rev. Mod. Phys.* 32:245-54, 1960.
[Lab. Molecular Structure and Spectra, Dept. Physics, Univ. Chicago, IL]

This paper presents tabulations of single configuration SCF wave functions in LCAO-MO approximation for the ground states of a series of first-row diatomic molecules, employing three different minimum AO basis sets. Derived properties include total molecular energies, ionization potentials, and internuclear distances. [The *SCI*[®] indicates that this paper has been cited in over 380 publications since 1960.]

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"This paper presented the first *ab initio* electronic wave functions generated by a computer for a homologous series of molecules. With its companion paper,¹ it transmitted the initial results of the 'diatomic molecule project' that was carried out at the Laboratory of Molecular Structure and Spectra, University of Chicago, from 1956 to 1969, under the sponsorship of R.S. Mulliken and C.C.J. Roothaan. Initially under my direction (1956-1960), and then P.E. Cade's (1960-1969), the diatomic molecule project was an unprecedented computer experiment designed to evaluate how well the molecular orbital (MO) theory, at two levels of approximation (minimal orbital and close-to-Hartree-Fock), could predict selected chemical and physical observables for a homologous series of diatomic molecules. In this and six subsequent papers,²⁻⁷ the project documented the descriptive and predictive capabilities of the MO theory in minimal orbital LCAO-MO-SCF approximation, demonstrated the indispensable role of

the computer in molecular calculations, and set both a standard and a design prototype for subsequent studies.

"The minimal orbital results were subsequently followed by publication of the close-to-Hartree-Fock results,^{8,9} and in 1980, by a demonstration,¹⁰ using standard statistical methodologies, of how well these functions, and functions of equivalent or better accuracy,¹¹ predicted four spectroscopic constants, the only observables at the time for which most experimental values were available for first- and second-row diatomic hydrides.

"The project was built upon Roothaan's landmark paper¹² which introduced a rigorous methodology for analytical solutions to the Schrödinger wave equation, paving the way for computer generation of accurate *ab initio* atomic and molecular wave functions. Other vitally contributory circumstances were: the decade or more of work by Roothaan, Ruedenberg, and others on atomic and molecular integrals; an Air Force grant for computer time on the UNIVACs at Wright Field; the exemplary mathematical and computer science skills of Andrew Weiss (now at the National Bureau of Standards), Douglas McLean, and Megumu Yoshimine (IBM, San Jose); and the painstakingly accurate hand checks by Tracy Kinyon on a mechanical desktop calculator.

"Publication of the study came about fortuitously. As it happened, the journal editor attended the Boulder Conference on Molecular Quantum Mechanics (June 21-27, 1959) at which this paper was given, and decided to dedicate one issue to the conference proceedings.

"Possible reasons for the paper's frequent citation are: it is the prototype for systematic computer studies of molecular electronic structures; it contains both the wave functions and an authoritative glossary of terminology compiled in collaboration with Mulliken; it provides a reliable check for homologous computer programs; and Mulliken received the Nobel prize for the MO theory in 1966."

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2. Fraga S & Ransil B J. Studies in molecular structure. III. Populations analyses for selected first-row diatomic molecules. *J. Chem. Phys.* 34:727-42, 1961.
3. Ransil B J. Studies in molecular structure. IV. Potential curve for interaction of two helium atoms in single-configuration LCAO MO SCF approximation. *J. Chem. Phys.* 34:2109-18, 1961.
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5. Studies in molecular structure. VI. Potential curve for interaction of two hydrogen atoms in the LCAO MO SCF approximation. *J. Chem. Phys.* 35:1967-77, 1961. (Cited 80 times.)
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7. Studies in molecular structure. VIII. He₂⁺⁺ in single- and many-configuration LCAO MO SCF approximation. *J. Chem. Phys.* 37:1112-19, 1962.
8. Cade P E, Wahl A C, Sales K, Greenhields J B & Malli G. Hartree-Fock-Roothaan wavefunctions for diatomic molecules. I. *At. Data Nucl. Data Tables* 12:415-66, 1973.
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10. Ransil B J. How good is good agreement? Evaluating the reliability of quantum mechanically calculated observables. *Int. J. Quantum Chem.* 17:467-78, 1980.
11. Meyer W & Rosmus P. PNO-CI and CEPA studies of electron correlation effects. III. Spectroscopic constants and dipole moment functions for the ground states of the first-row and second-row diatomic hydrides. *J. Chem. Phys.* 63:2356-75, 1975. (Cited 170 times.)
12. Roothaan C C J. New developments in molecular orbital theory. *Rev. Mod. Phys.* 23:69-89, 1951. (Cited 2,120 times since 1955.)