

## FINAL REPORT

LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA  
DEPARTMENT OF PHYSICS, UNIVERSITY OF CHICAGO  
CHICAGO, ILLINOIS 60637

D/A Project No. 5B51-02-044  
ARO(D) Project No. 3835-P  
Contract No. DA-11-022-ORD-3119

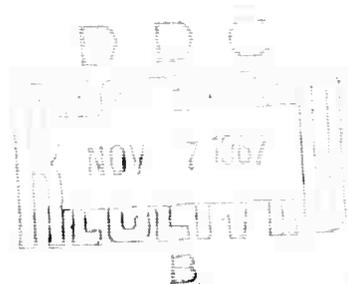
For the period 12 June 1959 thru 11 June 1966

C. C. J. Roothaan

B. J. Ransil  
(6/12/59 - 6/11/61)

Sponsored under auspices of Advanced Research  
Projects Agency, funded under ARPA Order 368

"Distribution of this document is unlimited."



AD 661065

QUANTUM MECHANICAL CALCULATION OF LIGHT METAL DIATOMIC  
HYDRIDES, OXIDES, AND HALIDES

ABSTRACT

An abbreviated discussion is given of certain quantum mechanical calculations completed, in course, or beginning for small molecules. The development of theory, computer programs, and extensive calculations on atoms is outlined. This includes polarizability studies, relativistic calculations and extensive configuration interaction for a few atomic systems.

Results for diatomic molecules in minimal LCAO-MO-SCF approximation is reviewed, and the gradual extension of this effort first to double-zeta LCAO-MO-SCF results and presently to true Hartree-Fock accuracy by the matrix method is discussed. The range of diatomic molecule-systems treated, the related molecular properties calculated, and physical or chemical interpretation efforts are outlined. A generalized Hartree-Fock method has been tried out on  $\text{Li}_2$  and  $\text{H}_2$ , and promises considerable improvement. A resume is also given of certain polyatomic calculations carried out. This latter effort includes limited (or minimal) basis set calculations for certain linear triatomic molecules, methane, and one-center expansion calculations for  $\text{AH}_n$  hydrides, all within the self-consistent-field procedure. Calculations on the hydrogen molecule using a lengthy James-Coolidge expansion, have been carried to within a few kaysers of experiment for the ground and certain few excited states.

## A. THEORETICAL DEVELOPMENTS AND CALCULATIONS ON ATOMS\*

The theoretical formulation of the matrix solution of the Hartree-Fock equations for open-shell configurations was studied extensively in this period. The generality of the allowed open-shell cases was progressively extended or simplified and machine programs (in fact a sequence of such programs) were constructed to carry out such calculations. The theory, numerical methods, and programming were unusually closely correlated as a unit. An extensive table of open-shell vector-coupling coefficients was also obtained for cases involving several open-shells of different symmetries. Using these programs, extensive calculations of wave functions and energies to Hartree-Fock accuracy were obtained for first and second row atoms (in collaboration with others). Extensive calculations were also carried out for  $1s^2 2s^m 2p^n$  states of N,  $N^+$ , O, and  $O^+$ ; ground and several excited states of Al,  $Cu^+$ , and Cu; ground states of Mo and  $Mo^+$ ; and the ground states of  $K^+$ , K, and Ca. A careful and extensive study of the K-shell and X-ray transition probabilities of some Neon-like and Argon-like ions was carried out using calculated SCF wave functions. Still in progress are calculations on transition probabilities and wave functions for certain relevant states. Complementary to this effort, and continuing, is the programme to numerically solve the Hartree-Fock equations for atoms. This latter effort has led to the development of newer and superior numerical methods for this old problem.

The fully-coupled self-consistent-field equations for a closed shell atom in an electric field have also been formulated, coded, and solved. The dipole polarizabilities of He-like, Be-like, Ne-like, and Mg-like ions have thus been calculated in good agreement with experiment (where known, except for  $H^-$ ).

A relativistic self-consistent-field theory has been developed for closed shell atoms. In this theory the many-electron Hamiltonian is taken as the sum of Dirac Hamiltonians, plus the usual Coulombic repulsion terms between electrons. This Hamiltonian is thus employed in a matrix SCF method using as basis functions Slater-Type-Orbitals with non-integer principle quantum numbers. The usual Breit interaction operator is used as the relativistic interaction term, and is treated in first-order perturbation. The program constructed using this method was employed to make relativistic calculations on He, Be, and Ne (all  $^1S_0$ ).

Several calculations considerably beyond Hartree-Fock approximation have also been carried out. Thus "correlated" orbital calculations have been carried out for He-like systems and, in a most comprehensive series of calculations, the ground-state wave functions of He, Li, and Be were approximated by a superposition of configurations with 35 terms for He and up to 55 terms for Be. Isoelectronic series were also studied for this series of atoms.

---

\*Theoretical work on atoms is also included here because of the frequent role atomic calculations have played as a preliminary to the corresponding molecular calculations, directly or indirectly.

## B. VERY ACCURATE CALCULATIONS ON THE HYDROGEN MOLECULE

A number of important results for the ground and certain excited states of  $H_2$  have been obtained. These calculations employed a James-Coolidge type expansion to represent the electronic wave function. Initial calculations for  $H_2(X \ ^1\Sigma_g^+)$  employed up to a 40-term expansion and together with a Hartree-Fock wave function gave the R variation of the "correlation" energy. These calculations were later extended to permit up to 80 terms in the expansion, and the James-Coolidge technique was generalized to permit the correct asymptotic behavior at large R. Thus calculations were made on the  $X \ ^1\Sigma_g^+$ ,  $b \ ^3\Sigma_u^+$ ,  $c \ ^1\Pi_u$ , and  $B \ ^1\Sigma_u^+$  states of  $H_2$  and the first two  $^1\Sigma^+$  states of  $HeH^+$ . The resulting wave functions were then used to obtain nuclear motion and relativistic corrections and the final energies are within a few kayers ( $cm^{-1}$ ) of experiment at  $R_e$ . These wave functions have been extensively used to calculate a number of expectation values and molecular properties; e.g. the parallel and perpendicular polarizability of hydrogen, the dipole moment of HD etc., all at several internuclear separations. In a parallel study of  $H_2(X \ ^1\Sigma_g^+)$ , the complete 4-particle problem was variationally studied, i.e. without assuming the Born-Oppenheimer separation. A number of related studies were also completed and this general program and certain ramifications continues.

### C. HARTREE-FOCK AND OTHER CALCULATIONS FOR DIATOMIC MOLECULES

Calculations on diatomic molecules have usually dominated the computational efforts and are often the results of straightforward extension to diatomic systems of theory developed for atoms. At the beginning of this period, one generation of diatomic calculations was just concluding; during this period the second generation of calculations was organized, programmed, extensively carried out, and now at the conclusion of the period, a new "Generalized" Hartree-Fock procedure is being organized and programmed, — the third generation.

The "first" generation of calculations were minimal basis set LCAO-MO-SCF calculations for a number of diatomic molecules with or without optimization of orbital exponents. Thus results were obtained for  $\text{Li}_2$ ,  $\text{Be}_2$ ,  $\text{C}_2$ ,  $\text{N}_2$ ,  $\text{F}_2$ ,  $\text{LiH}$ ,  $\text{BH}$ ,  $\text{NH}$ ,  $\text{HF}$ ,  $\text{CO}$ ,  $\text{BF}$ , and  $\text{LiF}$ , all for  ${}^1\Sigma_{(g)}^+$  states (which is not the ground state for  $\text{C}_2$  and  $\text{NH}$ ). For these molecules, certain population analyses were carried out and with a calculated potential curve, spectroscopic constants were obtained. For this same sequence of molecules, limited configuration interaction calculations were also carried out using the minimal basis set results already obtained. These results were not to Hartree-Fock accuracy and suggested more extensive calculations were needed.

Between these results and the "second" generation were several double-zeta LCAO-MO-SCF calculations; thus slightly more extended calculations were carried out for  $\text{N}_2$  and  $\text{N}_2^+$  and for  $\text{O}_2$ . Finally,

a relatively extended basis set calculation was made for HF, which was the closest yet to a molecular Hartree-Fock result (except for H<sub>2</sub>).

The "second" generation of diatomic calculations began with the completion of two completely revised and extended (e.g. to study open-shell cases) machine programs; one for homonuclear and one for heteronuclear diatomic molecules. This also coincided with a new generation of high-speed computing equipment. Two to three years of heavy computation followed and continues. These new codes and increased machine speed permitted optimization of orbital exponents and, more importantly, allowed large enough basis sets to obtain true Hartree-Fock orbitals for many diatomic molecules using the matrix method of Roothaan. Thus for a selected group of molecules, convergence studies were made to establish the necessary basis set size, composition, and extent of optimization of orbital exponents. This ground work laid, a very broad and intensive series of calculations were started. These calculations are outlined as follows:

1. Results for First Row Homonuclear Diatomic Molecules, A<sub>2</sub>. -

Calculations have been completed (or near completion) for Li<sub>2</sub>(X <sup>1</sup>Σ<sub>g</sub><sup>+</sup>), Li<sub>2</sub><sup>+</sup>(X <sup>2</sup>Σ<sub>g</sub><sup>+</sup>, A <sup>2</sup>Π<sub>u</sub>), Be<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>), B<sub>2</sub>(X <sup>3</sup>Σ<sub>g</sub><sup>-</sup>), C<sub>2</sub>(a <sup>1</sup>Σ<sub>g</sub><sup>+</sup>, A' <sup>3</sup>Σ<sub>g</sub><sup>-</sup>), N<sub>2</sub>(X <sup>1</sup>Σ<sub>g</sub><sup>+</sup>), N<sub>2</sub><sup>+</sup>(X <sup>2</sup>Σ<sub>g</sub><sup>+</sup>, A <sup>2</sup>Π<sub>u</sub>, B <sup>2</sup>Σ<sub>u</sub><sup>+</sup>), O<sub>2</sub>(X <sup>3</sup>Σ<sub>g</sub><sup>-</sup>, a <sup>1</sup>Δ<sub>g</sub>, b <sup>1</sup>Σ<sub>g</sub><sup>+</sup>), O<sub>2</sub><sup>+</sup>(X <sup>2</sup>Π<sub>g</sub>), O<sub>2</sub><sup>-</sup>(X <sup>2</sup>Π<sub>g</sub>), F<sub>2</sub>(X <sup>1</sup>Σ<sub>g</sub><sup>+</sup>) and F<sub>2</sub><sup>+</sup> ions. Most of these results include a calculation of potential curves and a detailed calculation of molecular property functions, M(R). Gradual extension of the scope of these investigations has delayed their preparation for publication. These results

are believed to be quite good approximations to the true Hartree-Fock orbitals and results. Much less accurate, minimal LCAO-MO-SCF results have been obtained for the second row homonuclear series,  $\text{Na}_2$  to  $\text{Cl}_2$ .

## 2. Results for First and Second Row Diatomic Hydrides, AH.-

Wavefunctions to Hartree-Fock accuracy have been obtained for  $\text{LiH}(X^1\Sigma^+)$ ,  $\text{BeH}(X^2\Sigma^+)$ ,  $\text{BH}(X^1\Sigma^+)$ ,  $\text{CH}(X^2\Pi_r)$ ,  $\text{NH}(X^3\Sigma^-)$ ,  $\text{OH}(X^2\Pi_1)$ ,  $\text{HF}(X^1\Sigma^+)$ ,  $\text{NaH}(X^1\Sigma^+)$ ,  $\text{MgH}(X^2\Sigma^+)$ ,  $\text{AlH}(X^1\Sigma^+)$ ,  $\text{SiH}(X^2\Pi_r)$ ,  $\text{PH}(X^3\Sigma^-)$ ,  $\text{SH}(X^2\Pi_1)$  and  $\text{HCl}(X^1\Sigma^+)$  at  $R_e$  (Exptl.), and as a function of internuclear separation. These results include a study of convergence to the Hartree-Fock limit. From the potential curves, spectroscopic constants were calculated and compare very favorably with experiment. These wavefunctions have also been extensively employed to calculate molecular properties as a function of  $R$ . The "correlation" energy of the hydrides is discussed for these sequences of hydrides in comparison with corresponding separated atoms and united atom values appropriate.

These ground state AH results have also lead to preliminary, but very good, wavefunctions for the corresponding  $\text{AH}^+$  series, a number of excited states, and a few negative ions. For example, calculations are started on the excited states of  $\text{BeH}(1\sigma^2 2\sigma^2 1\pi, A^2\Pi)$  and  $\text{MgH}(KL4\sigma^2 2\pi, A^2\Pi)$  to eventually calculate the transition probability for the  $X^2\Sigma^+ - A^2\Pi$  transition. Calculations were also started for the  $\text{OH}(A^2\Sigma^+)$  and  $\text{SH}(A^2\Sigma^+)$  excited states also. A Hartree-Fock-Roothaan wavefunction (with optimized orbital exponents) was also

obtained for  $\text{OH}^-(X^1\Sigma^+)$  for various R values which permitted an estimate of the spectroscopic constants of  $\text{OH}^-$ , which is in very good agreement with experiment.

3. Miscellaneous Results for Other Heteronuclear Diatomic Molecules.— The most extensive non-hydride heteronuclear results have been for  $\text{CO}(X^1\Sigma^+)$  and  $\text{BF}(X^1\Sigma^+)$  which are near comparable accuracy to the results for  $\text{N}_2(X^1\Sigma_g^+)$ . A large number of calculations of a preliminary nature were carried out to obtain a repository of wavefunctions for many heteronuclear diatomic molecules. These calculations made use of information already gained in choice of basis set composition and orbital exponents. Results for approximate 50 molecules and states were thus obtained, although in most cases Hartree-Fock accuracy is not claimed. These include results for the 13 electron sequence  $\text{FeF}$ ,  $\text{BF}^+$ ,  $\text{BO}$ ,  $\text{CO}^+$ , but not  $\text{CN}$ , each for the  $X^2\Sigma^+$ ,  $A^2\Pi_1$ ,  $H^2\Pi_r$  states, results for  $\text{BeO}$ ,  $\text{LiO}$ ,  $\text{LiF}$ ,  $\text{LiCl}$ ,  $\text{NO}$ , and others. Among other things, these calculations suggest a  $^2\Pi_1-^2\Sigma$  band system for  $\text{LiO}$  in the red or infrared (experimentally unknown) and an electron affinity for  $\text{BO}$  of about 1 eV.

The first beginnings of the third generation of diatomic calculations, again coinciding with a new generation of computers, is the development and demonstration of the value of the "Generalized Hartree-Fock" method. In this approach, a relatively small number of configurations are mixed with the ground configuration, and the "configuration mixing" problem is solved. However, the new orbitals which give rise to the excited configurations are also optimally

determined in concert with the ground state or "core" orbitals. Thus a doubly iterative method obtains as the configuration mixing coefficients and all orbitals are successively re-determined by the variational principle to a certain threshold for both configuration mixing coefficients and molecular orbitals. By a judicious choice of the excited configurations as those arising only from exciting "valence shell" molecular orbitals, the calculated potential curves go to the correct values at large R (in contrast to the Hartree-Fock curves) and, in the calculations carried out to date, the potential curves calculated are in very good agreement with experiment. Generalized Hartree-Fock calculations were carried out for  $H_2$ ,  $Li_2$ , and  $F_2$  with greater emphasis on  $Li_2$ . These calculations served as an important trial case for examining the feasibility and accuracy of the Generalized Hartree-Fock method and the successes have prompted major programming efforts to extend these calculations to diatomic molecules in a general way.

Certain other miscellaneous diatomic calculations have also been carried out. These include the extensive configuration interaction results for the He-He interaction potential to resolve an experimental-theoretical disagreement and a very illustrative configuration interaction calculation for  $H_2(X \ ^1\Sigma_g^+)$  to study the correlation energy as associated with specific kinds of configurations.

#### D. CALCULATIONS ON POLYATOMIC MOLECULES

The calculations on polyatomic molecules involved limited LCAO-MO-SCF calculations on certain closed shell linear molecules and the one-center expansion SCF calculations. The LCAO-MO-SCF calculations were an outgrowth of the earlier minimal basis set calculations on diatomic molecules, and were not near Hartree-Fock accuracy. These calculations were for  $\text{CO}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_3$ ,  $\text{C}_4$ ,  $\text{N}_3^-$ ,  $\text{NO}_2^+$ ,  $\text{HF}_2^-$ ,  $\text{HCN}$ , and  $(\text{CN})_2$ ; all linear molecules, each at the equilibrium configuration (if known). In several cases, double-zeta basis sets were employed ( $\text{HF}_2^-$  and  $\text{CO}_2$ ). These calculations were often accompanied by results for certain molecular properties and interpretative data, and have served as a useful starting point for further work which is in course elsewhere. In another minimal LCAO-MO-SCF calculation,  $\text{CH}_4$  was studied including all integrals.

The one-center expansion SCF calculations involve no basis functions on the peripheral atoms, always hydrogen, for molecules  $\text{AH}_n$ . The initial set of one-center calculations did not use a symmetry-specific program, which limited the basis set size, and calculations were carried out for  $\text{HF}$ ,  $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{NH}_3$ ,  $\text{NH}_4^+$ ,  $\text{PH}_3$ ,  $\text{PH}_4^+$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ , and  $\text{HCl}$ . These calculations clearly indicated for the first time the limitations and possibilities of the one-center expansion SCF method. Crude but useful wavefunctions were obtained for certain moderately large polyatomic molecules. The second phase of the one-center SCF calculations involved a symmetry-specific program for  $\text{C}_{3v}$  and  $\text{C}_{2v}$  symmetry. Using these programs, extensive

one-center SCF calculations were carried out for  $\text{NH}_3$  to study the inversion barrier. Calculations for the isoelectronic molecules  $\text{OH}_3^+$  and  $\text{CH}_2^-$  have also been completed. The eight electron sequence  $\text{BeH}_3^-$ ,  $\text{BH}_3$ ,  $\text{CH}_3^+$ ,  $\text{NH}_3^+$  and  $\text{OH}_3^+$  were also considered and all are predicted to be planar in their ground states. In all of these later calculations, very large basis sets (including d, f, g, and h STO's) have been employed and the orbital exponents were carefully optimized. A similar computer program was completed for  $\text{C}_{2v}$  symmetry, and some preliminary calculations were made for  $\text{H}_2\text{O}$ .

PERSONNEL ASSOCIATED WITH CONTRACT

STAFF

- Professor Clemens C. J. Roothaan, Principal Investigator.
- Professor Robert S. Mulliken, Consultant.
- Professor Wlodzimierz Kołos, Visiting Associate Professor, Summer, 1961. (On leave of absence from Institute of Nuclear Research, Warsaw, Poland.)
- Dr. Bernard J. Ransil, Research Associate, Co-Principal Investigator on Contract 6/12/59 thru 6/11/61. (From 6/12/61 thru 6/30/62; 4/1/63 thru 9/30/63. Presently at Harvard Medical School, Boston, Massachusetts.)

RESEARCH ASSOCIATES

- Dr. Paul E. Cade, from 9/12/61 thru 9/11/65. (Presently Physicist, from 9/12/65.)
- Dr. Enrico Clementi, from 10/1/60 thru 6/15/61. (Presently Professorial Lecturer, Department of Chemistry, University of Chicago; on leave of absence from IBM Research Laboratory, San Jose, California.)
- Dr. Stanton Ehrenson, from 10/1/62 thru 12/31/62. (Now at Brookhaven National Laboratory, Upton, Long Island, New York.)
- Dr. Serafin Fraga, from 6/12/59 thru 4/31/61. (Now Asst. Professor, University of Alberta, Edmonton, Alberta, Canada.)
- Prof. John B. Greenshields, from 9/1/62 thru 8/31/64. (Associate Professor, on leave of absence from Duquesne University, Pittsburgh, Pennsylvania.)
- Dr. Winifred Huo, from 4/1/64 thru 9/30/64. (Now at Harvard University, Cambridge, Massachusetts.)

- Dr. B. D. Joshi, from 11/1/65 thru 6/30/66. (Now at Indian Institute of Technology, Kanpur, India.)
- Dr. Roberto Moccia, from 12/1/61 thru 8/31/62. (On leave of absence from Istituto Chimico della Universita, Napoli, Italy.)
- Prof. James W. Richardson, from 8/1/59 thru 9/15/59. (Assistant Professor, on leave of absence from Purdue University, Lafayette, Indiana.)
- Dr. Keith D. Sales, from 9/26/61 thru 9/25/63. (On leave of absence from Queen Mary College, London, England.)
- Prof. Charles W. Scherr, from 6/15/60 thru 2/22/61. (Associate Professor, on leave of absence from University of Texas, Austin, Texas.)
- Dr. John J. Sinai, from 3/15/63 thru 9/31/64. (Now at the University of Louisville, Louisville, Kentucky.)
- Dr. W. Roy Wessel, from 11/1/64.

#### RESEARCH ASSISTANTS

- Mr. Paul Bagus, from 10/1/59 thru 4/13/62. Physics Ph.D. degree 3/19/65. Now at Argonne National Laboratory.
- Mr. Philip E. Bloomfield, from 10/1/59 thru 6/30/60.
- Miss Alice Chung, from 6/27/60 thru 12/31/60.
- Mr. Howard D. Cohen, Chemistry Ph.D. degree, 6/11/65. (Now at the National Bureau of Standards, Washington, D. C.)
- Mr. Gurupada Das, from 10/1/61 thru 11/30/65. Physics Ph.D. degree, 6/10/66. (Now at the University of Wisconsin, Madison, Wisc.)
- Mr. John Detrich, from 11/1/64. Physics Ph.D. Candidate.
- Miss Winifred M. Huo, from 6/15/61 thru 3/30/64. Chemistry Ph.D. degree, 3/15/64. (Now at Harvard University, Cambridge, Mass.)

- Mr. Bhairav D. Joshi, from 10/1/61 thru 12/31/64. Chemistry Ph.D. degree, December 18, 1964.
- Mr. Yong-Ki Kim, from 10/1/61 thru 4/30/66. Completed Physics Ph.D. requirements, Spring 1966. Now at Argonne National Laboratory.
- Mr. G. L. Malli, from 6/20/60 thru 3/31/64. Chemistry Ph.D. degree March 15, 1964. Now at Simon Fraser University, Burnaby, Canada.
- Mr. Douglas A. McLean, from 6/12/59 thru 12/19/59. Now at IBM Research Laboratories, San Jose, California.
- Mr. Ramesh C. Misra, from 9/19/62 thru 2/28/64. Graduate Student in Physics.
- Mr. Joseph P. Olive, from 7/1/63. Physics Ph.D. Candidate.
- Mr. Toby C. Owen, from 10/1/59 thru 6/30/60. Graduate Student in Physics.
- Mr. Hideo Sambe, from 10/1/64. Physics Ph.D. Candidate.
- Mrs. Eugenia Schwartz, from 6/17/63. Physics Ph.D. Candidate.
- Mr. Zoran Sibinic, from 4/1/62. Physics Ph.D. Candidate.
- Mr. George A. Soukup, from 4/1/62. Physics Ph.D. Candidate.
- Mr. Miroslav Synek, from 6/12/59 thru 8/31/62. Physics Ph.D. degree, March 15, 1963. Now at DePaul University, Chicago, Illinois.
- Mr. Arnold C. Wahl, from 9/19/60 thru 2/28/63. Chemistry Ph.D. degree, June 13, 1964. Now at Argonne National Laboratory.
- Mr. Andrew W. Weiss, from 7/1/59 thru 1/31/61. Physics Ph.D. degree, June 9, 1961. Now at the National Bureau of Standards, Washington, D. C.
- Mr. Irving Wladawsky, from 1/1/54 thru 5/31/66. Physics Ph.D. Candidate. Now working at University of Chicago Computation Center.

Mr. William Worley, from 10/1/60 thru 3/30/62. Graduate Student in Physics. Now employed at Illinois Institute of Technology Computation Center, Chicago, Illinois.

Mr. Megume Yoshimine, from 10/1/59 thru 6/14/60. Graduate Student in Physics. Now at IBM Research Laboratory, San Jose, California.

### TECHNICIANS

Mr. Tracy Kinyon, Mathematics Assistant, from 6/12/59.

Mr. John J. Sinai, Technical Computer Aid, from 9/1/61 thru 3/14/63.

Mr. Allen E. Peterson, Programmer, from 8/30/60 thru 4/30/63.

Mrs. Anna Predazzi, Programmer, from 9/1/65.

Mr. Thomas Sherrard, Programmer, from 11/1/64.

### Student Technicians:

Mr. Stephen Dorenzo, from 5/1/61 thru 3/10/63.

Mr. Steven A. Holland, from 5/1/61 thru 3/10/63.

Mr. Paul R. Kozinski, from 6/19/61 thru 4/20/62.

Mr. Joseph P. Olive, from 10/1/62 thru 5/31/63.

Mr. George A. Soukup, from 6/12/61 thru 9/30/61.

Mr. Ray Strecker, from 6/12/61 thru 8/31/62.

Miss Ann T. Walinski, from 6/30/61 thru 9/10/62.

PUBLICATIONS

1. A. D. McLean, "LCAO-MO-SCF Ground State Calculations on  $C_2H_2$  and  $CO_2$ ", J. Chem. Phys. 32, 1595 (1960).
2. A. D. McLean, B. J. Ransil, and R. S. Mulliken, "Charge Distribution, Hybridization, and Bonding in Acetylene and Carbon Dioxide", J. Chem. Phys. 32, 1873 (1960).
3. S. Fraga and B. J. Ransil, "Studies in Molecular Structure. III. Population Analyses for Selected First-Row Diatomic Molecules", J. Chem. Phys. 34, 727 (1961).
4. B. J. Ransil, "Studies in Molecular Structure. IV. Potential Curve for the Interaction of Two Helium Atoms in Single-Configuration LCAO-MO-SCF Approximation", J. Chem. Phys. 34, 2109 (1961).
5. S. Fraga and B. J. Ransil, "Studies in Molecular Structure. V. Computed Spectroscopic Constants for Selected Diatomic Molecules of the First Row", J. Chem. Phys. 35, 669 (1961).
6. S. Fraga and B. J. Ransil, "Studies in Molecular Structure. VI. Potential Curve for the Interaction of Two Hydrogen Atoms in the LCAO-MO-SCF Approximation", J. Chem. Phys. 35, 1967 (1961).
7. S. Fraga and B. J. Ransil, "Studies in Molecular Structure. VII. Limited Configuration Interaction for Selected First-Row Diatomics", J. Chem. Phys. 36, 1127 (1962).
8. S. Fraga and B. J. Ransil, "Studies in Molecular Structure. VIII.  $He_2^{++}$  in the Single- and Many-Configuration LCAO-MO-SCF Approximation", J. Chem. Phys. 37, 1112 (1962).
9. R. S. Mulliken, "Criteria for the Construction of Good Self-Consistent-Field Molecular Orbital Wave Functions, and the Significance of LCAO-MO Population Analysis", J. Chem. Phys. 36, 3428 (1962).

10. E. Clementi and A. D. McLean, "SCF Wavefunctions for the  $N_3^-$  and  $NO_2^+$  Molecules", J. Chem. Phys. 39, 323 (1963).
11. J. J. Sinai, "Octopole Moment of Methane", J. Chem. Phys. 40, 3596 (1964).
12. R. Moccia, "One-Center Basis Set SCF MO's. I. HF,  $CH_4$ , and  $SiH_4$ ", J. Chem. Phys. 40, 2164 (1964).
13. R. Moccia, "One-Center Basis Set SCF MO's. II.  $NH_3$ ,  $NH_4^+$ ,  $PH_3$ ,  $PH_4^+$ ", J. Chem. Phys. 40, 2176 (1964).
14. R. Moccia, "One-Center Basis Set SCF MO's. III.  $H_2O$ ,  $H_2S$ , and  $HCl$ ", J. Chem. Phys. 40, 2186 (1964).
15. A. C. Wahl, P. E. Cade and C. C. J. Roothaan, "Study of Two-Center Integrals Useful in Calculations on Molecular Structure. V. General Methods for Diatomic Integrals Applicable to Digital Computers", J. Chem. Phys. 41, 2578 (1964).
16. A. C. Wahl, "Analytic SCF Wavefunctions and Computed Properties for Homonuclear Diatomic Molecules", J. Chem. Phys. 41, 2600 (1964).
17. G. L. Malli, "Relation Between Electrons and Holes in Atomic Configurations", Phys. Rev. 135, A978 (1964).
18. G. L. Malli and J. P. Olive, "Vector Coupling Coefficients for Atomic SCF Calculations", J. Chem. Phys. 43, 861 (1965).
19. W. M. Huo, "Electronic Structure of CO and BF", J. Chem. Phys. 43, 624 (1965).
20. S. Peyerimhoff, "Hartree-Fock-Roothaan Wavefunctions, Potential Curves, and Charge-Density Contours for the  $HeH^+(X^1\Sigma^+)$  and  $NeH^+(X^1\Sigma^+)$  Molecule Ions", J. Chem. Phys. 43, 998 (1965).

21. B. D. Joshi, "SCF Wavefunctions and Computed Potential-Energy Curves for the  $\text{NH}_3$  and  $\text{NH}$  Molecules, in One-Center Approximation", J. Chem. Phys. 43, S40 (1965).
22. H. D. Cohen and C. C. J. Roothaan, "Electric Dipole Polarizability of Atoms by the Hartree-Fock Method. I. Theory for Closed-Shell Systems", J. Chem. Phys. 43, S34 (1965).
23. H. D. Cohen, "Electric Dipole Polarizability of Atoms by the Hartree-Fock Method. II. The Isoelectronic Two- and Four-Electron Series", J. Chem. Phys. 43, 3558 (1965).
24. G. Das and A. C. Wahl, "Extended Hartree-Fock Wavefunctions: Optimized Valence Configurations for  $\text{H}_2$  and  $\text{Li}_2$ , Optimized Double Configurations for  $\text{F}_2$ ", J. Chem. Phys. 44, 87 (1966).
25. P. E. Cade, K. D. Sales and A. C. Wahl, "Electronic Structure of Diatomic Molecules. III.A. Hartree-Fock Wavefunctions and Energy Quantities for  $\text{N}_2(X \ ^1\Sigma_g^+)$  and  $\text{N}_2^+(X \ ^2\Sigma_g^+, A \ ^2\Pi_u, B \ ^2\Sigma_u^+)$  Molecular Ions", J. Chem. Phys. 44, 1973 (1966).
26. B. D. Joshi, "Study of the  $\text{H}_3^+$  Molecule Using SCF One-Center Expansion Approximation", J. Chem. Phys. 44, 3627 (1966).
27. H. D. Cohen, "Electric Dipole Polarizabilities of Atoms by Hartree-Fock Method. III. The Isoelectronic Ten-Electron Series", J. Chem. Phys. 44, 10 (1966).
28. P. E. Cade and W. M. Huo, "The Electric Dipole Moment for First and Second Row Diatomic Hydride Molecules,  $\text{AH}$ ", J. Chem. Phys. 44, 1063 (1966).
29. G. L. Malli, "Accurate Analytical SCF Hartree-Fock (H-F) Wave Functions for Second Row Atoms", Can. J. Phys. 44, 3131 (1966).

30. W. Kołos and L. Wolniewicz, "Potential-Energy Curve for the B  $1\Sigma_u^+$  State of the Hydrogen Molecule", J. Chem. Phys. 45, 509 (1966).
31. W. Kołos and L. Wolniewicz, "Vibronic Energy and Dipole Moment of HD", J. Chem. Phys. 45, 944 (1966).
32. W. Kołos, "Long-Range Interaction Between 1s and 2s or 2p Hydrogen Atoms", Int'l. J. Quantum Chem. 1, 169 (1967).
33. B. D. Joshi, "A Study of  $\text{BeH}_3^-$ ,  $\text{BH}_3$ ,  $\text{CH}_3^+$ ,  $\text{NH}_3^{++}$  and  $\text{OH}_3^{+3}$  by One-Center Expansion SCF Method", J. Chem. Phys. 46, 875 (1967).
34. B. J. Ransil and J. J. Sinai, "Toward a Charge Density Analysis of the Chemical Bond", J. Chem. Phys. 46, 4050 (1967).
35. G. Das, "Extended Hartree-Fock Ground State Wave Functions for the Lithium Molecule", J. Chem. Phys. 46, 1568 (1967).
36. Y-K. Kim, "A Relativistic SCF Theory for Closed-Shell Atoms", Phys. Rev. 154, 17 (1967).

LMSS JOINT TECHNICAL REPORTS

- LMSS Technical Report 1959-60.
- LMSS Technical Report 1961.
- LMSS Technical Report 1962-3, Part I.
- LMSS Technical Report 1962-3, Part II.
- LMSS Technical Report 1964.
- LMSS Technical Report 1965.
- LMSS Technical Report 1966.

## DOCUMENT CONTROL DATA - R&amp;D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Department of Physics University of Chicago Chicago, Illinois 60637		2a. REPORT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>	
		2b. GROUP	
3. REPORT TITLE <b>QUANTUM MECHANICAL CALCULATION OF LIGHT METAL DIATOMIC HYDRIDES, OXIDES, AND HALIDES</b>			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) <b>FINAL REPORT (For the period 12 June 1959 thru 11 June 1966)</b>			
5. AUTHOR(S) (Last name, first name, initial) Roothaan, Clemens C. J. (Principal Investigator) Ransil, Bernard J. (Co-Principal Investigator, 6/12/59 - 6/11/61)			
6. REPORT DATE 12 June 1959 thru 11 June 1966	7a. TOTAL NO. OF PAGES 21	7b. NO. OF REFS	
8a. CONTRACT OR GRANT NO. DA-11-022-ORD-3119	8b. ORIGINATOR'S REPORT NUMBER(S)		
b. PROJECT NO. D/A Project 5b51-02-004			
c. ALO (D) Project No. 3835-P	8b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
d. Task Order 4			
10. AVAILABILITY/LIMITATION NOTICES  "Distribution of this document is unlimited."			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Army Research Office (Durham), Box CM Duke Station, Durham, North Carolina	
13. ABSTRACT Results for diatomic molecules in minimal LCAO-MO-SCF approximation is reviewed, and the gradual extension of this effort first to double-zeta LCAO-MO-SCF results and presently to true Hartree-Fock accuracy by the matrix method is discussed. The range of diatomic molecule-systems treated, the related molecular properties calculated, and physical or chemical interpretation efforts are outlined.  A resume is also given of certain polyatomic calculations carried out. This latter effort includes limited (or minimal) basis set calculations for certain linear triatomic molecules, methane, and one-center expansion calculations for $AH^+$ hydrides, all within the self-consistent-field procedure. Calculations on the hydrogen molecule using a lengthy James-Coolidge expansion, have been carried to within a few kaysers of experiment for the ground and certain few excited states.			

14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
Hartree-Fock Wave Functions Diatomic Molecules LCAO-MO-SCF Approximation Basis Set Calculations							

**INSTRUCTIONS**

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through \_\_\_\_\_."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through \_\_\_\_\_."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through \_\_\_\_\_."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.