

NO CODE STAMP

FINAL REPORT

For the period June 12, 1966 through June 11, 1970

UNCLASSIFIED

1. PROJECT TITLE "Quantum Mechanical Calculations of Light Metal Diatomic Hydrides, Oxides and Halides"
2. ARPA ORDER NO. 368
3. PROGRAM CODE NUMBER 9E20
4. CONTRACTOR The University of Chicago
Chicago, Illinois
Tel: (312) NO7-4700
5. EFFECTIVE DATE OF CONTRACT 12 June 1966
6. CONTRACT EXPIRATION DATE 11 June 1970
7. AMOUNT OF CONTRACT \$475,000.00
8. CONTRACT NUMBER DA-31-124-ARO-D-447
9. PROJECT SCIENTIST Dr. Robert Mace (Durham)
Tel: (919) 286-2285
10. PRINCIPAL INVESTIGATORS Professor Clemens C. J. Roothaan
Department of Chemistry, Ext. 8315

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

Professor Juergen Hinze
Department of Chemistry, Ext. 8288

Sponsored by

ADVANCED RESEARCH PROJECTS AGENCY, ARPA 368

AD 713977

1. Evaluation of Analytic Electronic Wavefunctions and Properties for Atoms and Molecules: Theoretical Development

The theoretical formulation, as well as computer programs for the evaluation of Hartree-Fock wavefunctions and various properties of atomic and molecular systems, has been completed. Extensive calculations, carried to the limit of the Hartree-Fock independent particle model demonstrated the need for the explicit inclusion of electron-electron correlation into the electronic wavefunction, if various atomic and molecular properties were to be computed reliably. To this end the multi-configuration self-consistent-field (MC-SCF) model was developed. In this model the electronic wavefunction is represented by a linear combination of several Slater determinants, rather than only one, as in the Hartree-Fock model, and all the orbitals, as well as the configuration expansion coefficients, are determined simultaneously using the variational principle. The development of this model proceeded in two stages: first the method was restricted to pair replacement, i.e. the shell occupation numbers in the different Slater determinants of the wavefunction had to differ by even numbers. Later this restriction was removed and a completely general theory was developed. Considerable effort was expended towards the development of stable numerical procedures for the solution of the strongly coupled MC-SCF equations. This development was completed successfully. Computer programs for the calculation of MC-SCF wavefunctions for atoms and linear molecules were constructed and tested extensively. The theory for the calculation of excited states of same symmetry as lower lying states was developed. This has been incorporated into the MC-SCF

computer programs, thus the calculation of excited states, even if there are lower states of same symmetry, can be performed with equal ease and accuracy as the calculation of ground states.

Methods for the optimization of the nonlinear parameters, the orbital exponents, in analytical wavefunctions have been improved, thus allowing a more rapid accurate calculation of atomic and molecular wavefunctions. Also the calculation of wavefunctions for linear molecules has been made significantly more efficient through a completely new analysis of the required molecular integrals. This analysis was carried out in collaboration with Drs. McLean and Yosimine of IBM Research, and has lead to a molecular integrals program, which is significantly faster and more accurate than similar programs available heretofore.

2. Calculation of Electronic Wavefunctions and Properties of Atoms and Molecules

Using the available Hartree-Fock computer programs, the calculation of analytical wavefunctions close to the Hartree-Fock limit has been completed for first and second row diatomic hydrides. For these molecules potential curves and various properties were computed. The characteristic of the chemical binding and the electronic charge distribution has been analyzed extensively. Electron affinities for CH, NH, OH and SiH, PH and SH have been computed in the Hartree-Fock approximation, and corrected empirically for the correlation error inherent in the Hartree-Fock approximation. In the case of polyatomic systems, wavefunctions for

CH_3 and OH_3^+ were obtained using the one center expansion method and the Hartree-Fock approximation.

A careful study of the 2 and 4 electron atoms and ions has been undertaken, in order to assess the value of the MC-SCF model and its efficiency in accounting for electron-electron correlation. Preliminary calculations, using the MC-SCF model, have been performed for several low lying states of LiH and BeO. These calculations are still preliminary. However, indications are that in the case of LiH potential curves for several low lying states can be obtained with an accuracy of a few 100 cm^{-1} without excessive computational effort.

3. Calculation of Transition Moments

Computer programs for the calculation of absolute line strength of electronic and vibration-rotational spectra of diatomic molecules have been developed. These programs require as input information the molecular electronic energy and wave function at various internuclear distances. With this the rotation-vibration wave functions and line intensities, f-numbers, are calculated.

To date the vibrational transition probabilities of the $X^1\Sigma^+$ electronic ground states of BeO, MgO, CaO and SrO have been calculated using HF electronic wave functions and potential curves as well as experimental RKR potential curves. The detailed results of these calculations have been written up for publication.

In addition, the calculation of transition moments, in dipole length and momentum representation of

BeH	$(A^2_{\Pi} \longrightarrow X^2_{\Sigma^+})$
MgH	$(A^2_{\Pi} \longrightarrow X^2_{\Sigma^+})$
OH	$(A^2_{\Sigma^+} \longrightarrow X^2_{\Pi})$
N_2^+	$(A^2_{\Pi_u} \longrightarrow X^2_{\Sigma_g^+})$
	$(B^2_{\Sigma_u^+} \longrightarrow X^2_{\Sigma_g^+})$
N_2	$(B^3_{\Pi_g} \longrightarrow A^3_{\Sigma_u^+})$

is in progress. A report of the results obtained, together with a critical review of the reliability of measured and computed transition probabilities, has been completed.

4. Numerical SCF for Atoms

An extensive and thorough study was carried out re-examining the classical approach of Hartree and Fock to calculate atomic wave functions. In the course of this work, many refinements to the theory were discovered which influence numerical computations considerably, especially for heavier atoms.

The generally accepted formulas for the orbitals in the regions $r \rightarrow 0$ and $r \rightarrow \infty$ were found to be in error; the correct formulas were derived, and they

yielded some surprising results. For example, it was found that for $r \rightarrow \infty$ all orbitals ultimately decay with a decay constant appropriate to the weakest bound electron.

New formulas and techniques were derived which facilitated the adjustment of orbital energies, and also for matching the inner and outer portions of the wave functions.

Additional work is necessary before a computer program can be completed based on this analysis. This is expected to be accomplished in the near future. Calculations of much greater accuracy and reliability than carried out to date will then be possible.

5. Variational Treatment of Electron-atom Scattering and Atomic Resonance States

Two complimentary efforts were undertaken in this area. One involved the numerical determination of orbital and scattering wave functions, the other an expansion technique similar to the LCAO-SCF procedure. Both efforts are based on a wave function of great flexibility, in order to overcome the inherent limitations in close coupling and related methods commonly used. Much attention was paid to avoid the numerical difficulties encountered by singular behavior of the mathematical formalism, which have so often been encountered in calculations of this type. Papers describing these efforts will be forthcoming in the near future.

6. Relativistic Calculation on Atoms

The commonly used approaches to calculate relativistic wave functions for atoms were carefully examined. It was found that up to order $(v/c)^2$ the relativistic corrections are best calculated by the straightforward generalization of the Pauli approximation to the many-electron case. Hence all relativistic corrections--to this order of accuracy--can be determined as expectation values using non-relativistic Schrödinger wave functions and appropriate operators. It is also shown that this formalism can be applied to wave functions of great generality; in particular, MC-SCF wave function can be used with ease in order to calculate relativistic corrections with great accuracy.

Calculations of level splittings for several atoms with low Z have been carried out, and are continuing. A paper describing the theory and the corresponding calculations is nearing completion.

7. Atomic and Molecular Polarizabilities

Polarizabilities of atoms had been calculated successfully in this laboratory using the coupled Hartree-Fock formalism. Present investigations concentrate on using wave functions of much greater generality. Very accurate polarizabilities have been calculated for a few light atoms, and work on other atoms and the N_2 molecule is in progress.

In connection with this work, several interesting theoretical results have been derived, using Hellman-Feynman —, hypervirial —, and other well-known theorems.

8. Accurate Wave Functions for the H_2 Molecule

Further work on the H_2 molecule, in particular for excited states of interest, was carried out by Drs. Kolos and Wolniewicz. All this work has now been published, and need not be summarized separately.

PERSONNEL ASSOCIATED WITH CONTRACT**STAFF**

Professor Clemens C. J. Roothaan, Principal Investigator, June 12, 1966 to June 11, 1970.

Professor Ugo Fano, Principal Investigator, June 12, 1967 to June 11, 1969.

Professor Juergen Hinze, Research Associate, June 12, 1966 to June 11, 1967; Principal Investigator, June 11, 1967 to June 11, 1970.

Professor Robert S. Mulliken, Consultant, from June 12, 1966 to June 11, 1968.

Professor Wlodzimierz Kolos, Visiting Associate Professor of Physics, Summer 1966 and from June 1, 1967 to January 31, 1968.

Dr. Paul Cade, Physicist, from June, 1966 to August 25, 1969.

Dr. Nora Sabelli, Chemist, from January 15, 1967 to June 11, 1969.

RESEARCH ASSOCIATE

Reinhart Ahlrich, from 9/15/69 to 6/11/70.

Paul E. Bagus, from 9/27/67 to 6/30/68.

William H. Henneker, from 1/15/68 to 12/31/69.

Herbert E. Popkie, from 11/1/67 to 6/11/70.

Roy Wessel, from 6/66 to 9/1/66.

Lutoslaw Wolniewicz, from 7/17/67 to 2/29/68.

RESEARCH ASSISTANTS

James Bass, from 4/1/67 to 6/11/70. Physics Ph.D. Candidate.

Brad Cox, from 6/67 to 3/31/69.

John Detrich, from 6/12/66 to 6/11/70. Physics Ph.D. Candidate.

Kate K. Docken, from 6/69 to 6/11/70. Chemistry Ph.D. Candidate.

Warren Kosman, from 6/69 to 6/11/70. Chemistry Ph.D. Candidate.

Shiaw S. Lin, from 10/67 to 6/11/70. Physics Ph.D. Candidate.

Bowen Liu, from 6/67 to 4/30/70. Chemistry Ph.D. Candidate.

Joseph Olive, from 6/66 to 5/1/69. Physics Ph.D. Degree.

Hideo Sambe, from 6/66 to 6/11/70. Physics Ph.D. Candidate.

Eugenia Schwartz, from 6/66 to 6/11/70. Physics Ph.D. Candidate.

Kenneth J. Schwartz, from 6/69 to 6/11/70. Chemistry Ph.D. Candidate.

Zoran Sibincic, from 6/66 to 6/11/70. Physics Ph.D. Candidate.

George Soukup, from 6/66 to 6/11/70. Physics Ph.D. Candidate.

Edward Weiss, from 6/67 to 6/11/70. Physics Ph.D. Candidate.

Irving Wladawsky, from 3/1/67 to 4/30/70. Physics Ph.D. Candidate.

TECHNICIANS

Tracey Kinyon, Mathematics Assistant, from June, 1966 to June 30, 1967.

Thomas Sherrard, Programmer, from June, 1966 to December 31, 1966.

PUBLICATIONS

1. B. D. Joshi, "A Study of BeH_3^- , BH_3 , CH_3^+ , NH_3^{++} by OH_3^{3+} by One-Center Expansion Self-Consistent-Field Method", J. Chem. Phys. 46, 875 (1967).
2. Y.-K. Kim, "A Relativistic Self-Consistent-Field Theory for Closed Shell Atoms", Phys. Rev. 154, 17 (1967).
3. W. Kolos and L. Wolniewicz, "Potential-Energy Curve for the B_u^{1+} State of the Hydrogen Molecule", J. Chem. Phys. 45, 509 (1966).
4. W. Kolos and L. Wolniewicz, "Vibronic Energy and Dipole Moment of HD", J. Chem. Phys. 45, 944 (1966).
5. W. Kolos and L. Wolniewicz, "Polarizability of the Hydrogen Molecule", J. Chem. Phys. 46, 1426 (1967).
6. G. L. Malli, "Accurate Analytical Self-Consistent-Field (SCF) Hartree-Fock (H-F) Wave functions for Second-Row Atoms", Can. J. Phys. 44, 3131 (1966).
7. G. Das, "Extended Hartree-Fock Ground State Wavefunctions for the Lithium Molecule", J. Chem. 46, 1568 (1967).
8. W. Kolos, "Long-Range Interactions Between 1s and 2s and 2p Hydrogen Atoms", Int'l. J. Quantum Chem. Vol. 1, 169 (1967).
9. W. Kolos, "Relative Location of the Triplet and Singlet States in H_2 ", Chem. Phys. Letters, Vol. 1, 19 (1967).
10. P. E. Cade (with R. F. W. Bader and W. H. Henneker), "Molecular Charge Distributions and Chemical Binding. I. Homonuclear Diatomic Molecules", J. Chem. Phys. 46, 3341 (1968).
11. B. J. Ransil and J. J. Sinai, "Toward a Charge Density Analysis of the Chemical Bond: The Charge Density Bond Model", J. Chem. Phys. 46, 4050 (1967).

12. P. E. Cade and W. M. Huo, "The Electronic Structure of Diatomic Molecules. VI. A. Hartree-Fock Wave Functions and Energy Quantities for the Ground States of the First Row Hydrides, AH", J. Chem. Phys. 47, 614 (1967).
13. P. E. Cade and W. M. Huo, "The Electronic Structure of Diatomic Molecules. VII. A. Hartree-Fock Wave Functions and Energy Quantities for the Ground States of the Second Row Hydrides, AH", J. Chem. Phys. 47, 649 (1967).
14. P. E. Cade, "The Electron Affinity of the Diatomic Hydrides, CH, NH, SiH and PH", Proc. Phys. Soc. (London) 91, 842 (1967).
15. J. Hinze and C. C. J. Roothaan, "Multi-Configuration Self Consistent-Field Theory", Prog. Theoret. Phys. (Kyoto) 40, 37 (1967).
16. R. A. Sack, C. C. J. Roothaan and W. Kolos, "Recursive Evaluation of Some Atomic Integrals", J. Math. Phys. 8, 1093 (1967).
17. P. E. Cade, "Hartree-Fock Wavefunctions, Potential Curves, and Molecular Properties for $\text{OH}^- (^1\Sigma^+)$ and $\text{SH}^- (^1\Sigma^+)$ ", J. Chem. Phys. 47, 2390 (1967).
18. B. D. Joshi, "Study of CH_3^- and OH_3^+ by One-Center Expansion Self-Consistent-Field Method", J. Chem. Phys. 47, 2793 (1967).
19. W. R. Wessel, "An Iterative Quadratically Convergent Algorithm for Solving the General Hartree-Fock-Roothaan Equations", J. Chem. Phys. 47, 3253 (1967).
20. P. E. Cade (with R. F. W. Bader and I. Keaveny), "Molecular Charge Distributions and Chemical Binding. II. First-Row Diatomic Hydrides, AH", J. Chem. Phys. 47, 3381 (1967).
21. W. Kolos, "S-Wave Cross Section for $\text{D}(p, \gamma)\text{He}^3$ ", Phys. Rev. 165, 165 (1968).
22. W. Kolos and L. Wolniewicz, "Confirmation of the Discrepancy Between the Theoretical and Experimental Ground State Energies of H_2 ", Phys. Rev. Letters 20, 243 (1968).

23. W. Kolos and L. Wolniewicz, "Vibrational and Rotational Energies for the $B^1\Sigma_u^+$, $C^1\Pi_u$ and $a^3\Sigma_g^+$ States of the Hydrogen Molecule", J. Chem. Phys. 48, 3672 (1968).
24. W. Kolos, "Recent Developments in the Theory of One- and Two-Center Electron Molecules", Int'l. J. Quantum Chem. 11, 471 (1968).
25. P. E. Cade, "Theoretical Prediction of the Singlet-Triplet Inter-combination Separations for NH , OH^+ , PH , and SH^+ ", Can. J. Phys. 46, 1989 (1968).
26. W. Kolos and L. Wolniewicz, "Exchange and Coulomb Energy of H_2 Determined by Various Perturbation Methods", J. Chem. Phys. 49, 24 (1968) (with P. R. Certain and J. O. Hirschfelder).
27. W. Kolos and L. Wolniewicz, "Improved Theoretical Ground-State Energy of the Hydrogen Molecule", J. Chem. Phys. 49, 404 (1968).
28. N. Sabelli and J. Hinze, "Atomic Multiconfiguration Self-Consistent-Field Wavefunctions", J. Chem. Phys. 50, 684 (1969).
29. W. Kolos and L. Wolniewicz, "Theoretical Investigation of the Lowest Double-Minimum State $E, F^1\Sigma_g^+$ of the Hydrogen Molecule", J. Chem. Phys. 50, 3228 (1969).
30. Paul E. Cade, R. F. W. Bader, W. H. Henneker and I. Keaveny, "Molecular Charge Distributions and Chemical Binding. IV. The Second Row Diatomic Hydrides AH ", J. Chem. Phys. 50, 5313 (1969).
31. J. Hinze, "On the Optimization of Exponents for Slater Type Basis Functions", J. Chem. Phys. 51, 4168 (1969).
32. J. Olive, "Analytic Optimization in Atomic SCF Calculations", J. Chem. Phys. 51, 4340 (1969).

LMSS JOINT TECHNICAL REPORTS

LMSS Technical Report 1966

LMSS Technical Report 1967

LMSS Technical Report 1968