NASA CONTRACTOR REPORT

IN-34-CR

2901

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THEORETICAL INVESTIGATION OF GAS-SURFACE INTERACTIONS

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Prepared for

NASA

National Aeronautics and
Space Administration

Ames Research Center
Moffett Field, California 94035

(NASA-CR-195755) THEORETICAL
INVESTIGATION OF GAS-SURFACE
INTERACTIONS Final Technical
Report, 1 Sep. 1988 - 31 Jan. 1994
(Eloret Corp.) 9 p

N94-29378

Unclas

G3/34 0002901

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1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Theoretical Investigation of Gas-Surface Interactions		**5. Report Date** 14 April 1994
		6. Performing Organization Code
7. Author(s) Kenneth G. Dyall		**8. Performing Organization Report No.**
		10. Work Unit No.
9. Performing Organization Name and Address Eloret Institute 3788 Fabian Way Palo Alto, CA 94303		**11. Contract or Grant No.** NCC2-552
		13. Type of Report and Period Covered 9/1/88 - 1/31/94
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20456		**14. Sponsoring Agency Code**

15. Supplementary Notes

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16. Abstract

The goal of this project was to develop computational tools for the calculation of electronic structure of molecules containing heavy atoms, and to use these tools in the study of catalytic processes, with the overall objective of gaining an understanding of the catalytic process which could be used to design more efficient catalysts. The main catalytic system of interest was the combustion of hydrogen on platinum surfaces. Under this project, a flexible Dirac-Hartree-Fock (DHF) program has been developed, a code to calculate DHF correlation energies at the second-order Møller-Plesset perturbation (MP2) level is almost complete,]and code to include correlation at the MCSCF and MCSCF/MP2 level is planned. The tools so far developed have been validated and used to calibrate some more approximate methods, and applied to investigate the importance of relativistic effects in the bonding of hydrogen to platinum.

STAR Category H 72

17. Key Words (Suggested by Author(s)) electronic structure catalysis hydrogen combustion relativistic effects		**18. Distribution Statement** unclassified, unlimited		
19. Security Classif. (of this report) unclassified		**20. Security Classif. (of this page)** unclassified	**21. No. of Pages**	**22. Price**

THEORETICAL INVESTIGATION OF GAS - SURFACE INTERACTIONS

Final Technical Report

for
Cooperative Agreement NCC2-552

for the period
September 1, 1988 - January 31, 1994

Submitted to

National Aeronautics and Space Administration
Ames Research Center
Moffett Field, California 94035

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14 April, 1994

ABSTRACT

The goal of this project was to develop computational tools for the calculation of electronic structure of molecules containing heavy atoms, and to use these tools in the study of catalytic processes, with the overall objective of gaining an understanding of the catalytic process which could be used to design more efficient catalysts. The main catalytic system of interest was the combustion of hydrogen on platinum surfaces. Under this project, a flexible Dirac-Hartree-Fock (DHF) program has been developed, a code to calculate DHF correlation energies at the second-order Møller-Plesset perturbation (MP2) level is almost complete,]and code to include correlation at the MCSCF and MCSCF/MP2 level is planned. The tools so far developed have been validated and used to calibrate some more approximate methods, and applied to investigate the importance of relativistic effects in the bonding of hydrogen to platinum.

The chemistry of the heavy elements is strongly affected by relativity, and any approach to computing properties must therefore be based on a relativistic theory. Because of the increased difficulty of relativistic molecular structure calculations over nonrelativistic calculations – one to two orders of magnitude in storage, for example – it has been usual in the past to make approximations. Two common approximations are relativistic effective core potentials (RECPs), in which all the relativistic effects are incorporated into a potential which also replaces the core electrons, so that only the valence electrons are treated explicitly by the theory, and first-order perturbation theory (PT) using only the mass-velocity and Darwin terms (MVD) of the one-electron first-order Hamiltonian, which retains all the electrons, but truncates an expansion of the full relativistic Hamiltonian so that the approximate perturbed Hamiltonian can no longer be used variationally. However, neither of these methods is fully satisfactory, and it is necessary to ensure that they are accurately reproducing the relativistic effects. Thus efforts have been made in this project to develop methods based on the Dirac equation which will enable accurate relativistic molecular calculations to be made and calibrate the more approximate methods.

The first stage was to develop a Dirac-Hartree-Fock (DHF) code for polyatomic molecules. Because the field is a new one, there were many issues to be considered and explored in the implementation. These issues are discussed at length in two publications [1,2]. Several criteria were used to shape the code development. As a first generation code, it was desirable to get a code running as far as possible by adaption of existing codes or techniques. Thus, the integrals were taken from an adaption of MOLECULE [3]. Second, it was assumed that disk space limitations would preclude the sorting or transformation of integrals. Consequently, the program was designed to construct Fock matrices from the unordered scalar integrals which are directly output from MOLECULE. The use of MOLECULE also dictated the implementation of symmetry via symmetry-adapted basis functions rather than the petite list approach [4]. One important feature of the code is that, despite the use of scalar basis functions, the internal representation of the basis is a 2-spinor basis. This averts many of the problems of linear dependence of the basis in the only other code in existence at the time of development, namely MOLFDIR [5].

After the initial development of a closed-shell DHF code, other features were added to the program to increase its flexibility. These included convergence acceleration using the DIIS algorithm [6], the evaluation of molecular dipole and quadrupole moments, the application of a finite (constant) electric field, and various spinor population analyses. Subsequently, the code has been extended to allow calculations on molecules with up to two electrons in open-shells, including a reference function consisting of two closed-shell configurations.

Some of the issues surrounding the use of the DHF method were investigated, such as the question of whether restricted or unrestricted kinetic balance was to be preferred [7], and the appearance of intruder states which appeared in some of the calculations [8]. The second of these was prompted by the investigation of the neglect of some integrals whose contribution was argued to be small, done in an effort to reduce the space demands of DHF calculations.

Having developed a molecular code it was necessary to have some means of generating basis sets. An adaption was made to the program GRASP [9] to enable generally contracted atomic basis sets to be developed and printed in a format suitable for input to MOLECULE. The adaption has been extended to permit exponent optimization [10] using gradient techniques, a feature which may be important for heavy elements.

Several sets of calculations have been done with the DHF program. In a series on the group IV elements, the properties of the tetrahydrides, dihydrides and monoxides have been calculated, and comparisons made with RECP and PT calculations [11-13]. These calculations revealed deficiencies in some of the published RECPs, and suggest that a broader calibration study would be profitable. Two other studies have produced estimates of relativistic effects in alkali metal compounds [14,15].

In a first step towards catalytic studies, the DHF method has been applied to the mono- and dihydrides of platinum [16]. Comparisons were made with PT and the use of the second-order Douglas-Kroll transformed Hamiltonian developed by Hess [17]. The last of these should give a fairly accurate picture of the spin-free relativistic effects in the valence shell, and enable an estimate of the importance of spin-orbit effects. (It is primarily because of the spin-orbit interaction that relativistic calculations are much more expensive than nonrelativistic calculations.) The calculations showed that even for a closed shell molecule the spin-orbit effect could have a significant effect on molecular properties.

The second-order Douglas-Kroll transformed Hamiltonian is an approximation to the Dirac Hamiltonian which attempts to decouple the large and small components of the wave function, and then separate the spin-orbit and spin-free terms. It is in the first part of the process that the approximations are made. If the small component is retained, it is still possible to separate the spin-orbit and spin-free terms, in a rigorous manner. This has been achieved and exploratory calculations on atoms performed which demonstrate the potential of the use of the spin-free terms of the Dirac equation [18]. The implications of this separation are far-reaching. The cost of a correlated calculation with the spin-free Dirac Hamiltonian is little more than that of a nonrelativistic calculation. It would thus be possible to use this method in conjunction with the DHF method at a lower level of calculation to determine whether spin-orbit effects were important, and if not, the higher level calculations may be done much more cheaply with the spin-

free Hamiltonian.

Another major area of program development which is in progress is the transformation of integrals from the scalar basis in which they are generated to the 2-spinor basis employed in parts of the DHF program, and thence to supermatrix form. The reason for these developments is that the DHF program, while written efficiently for the circumstances under which it was expected to be used, is not the most efficient implementation possible, and with the rapid increase in available computer resources over the years, it is now possible to consider transforming the integrals. The use of ordered integrals, either in the scalar basis or in the 2-spinor basis, would considerably speed up the construction of the Fock matrix, and even more so if supermatrices were constructed. Furthermore, in order to proceed beyond the SCF level and include electron correlation it is necessary to transform the integrals to the molecular 4-spinor basis. Therefore, a considerable amount of effort has been spent on analyzing the integral ordering and transformation for the DHF problem. Much of this work was used in preparation for the NATO Advanced Summer Institute in Vancouver, BC, in August 1992 [1].

The transformation of the integrals is part of the second stage of the code development, which is to include methods for electron correlation, a necessity for accurate description – and in many cases even for qualitative description – of metal compounds. The first step in the inclusion of electron correlation has been made at the simplest level, namely second-order Møller-Plesset (MP2) perturbation theory, which has been developed for systems involving up to two open shells [19], following recent open-shell nonrelativistic theories [20]. The method has been applied to the coinage metal hydrides [21]. The coding of the sections for two open shells is nearing completion.

Møller-Plesset (MP2) perturbation theory is useful where the wave function is dominated by a single configuration. This is much less frequently the case in the (relativistic) double-group representation. Therefore it is essential to develop multi-reference correlation methods. To this end, a collaboration has been initiated to develop a MCSCF code based on the SIRIUS code [22]. At this point, most of the theoretical groundwork has been completed [23]. The use of MP2 theory based on a MCSCF reference has been shown to be useful [24]; thus the development of an MP2 code was a preliminary to the development of an MCSCF MP2 code.

In summary, a flexible DHF program has been developed, a code to calculate DHF correlation energies at the MP2 level is almost complete, and code to include correlation at the MCSCF and MCSCF/MP2 level is planned. The tools so far developed have been validated and used to calibrate some more approximate methods, and applied to investigate the importance of relativistic effects in the bonding of hydrogen to platinum.

REFERENCES

[1] K. G. Dyall, K. Fægri, Jr. and P. R. Taylor, *"Polyatomic molecular Dirac-Hartree-Fock calculations with Gaussian basis sets,"* in " The effects of relativity in atoms, molecules and the solid state," ed. S. Wilson, I. P. Grant, and B. L. Gyorffy (Plenum Press: New York, 1991), pp. 167–184.

[2] K. G. Dyall, *" Polyatomic molecular Dirac-Hartree-Fock calculations with Gaussian basis sets: theory, implementation and applications,"* in " Relativistic and correlation effects in molecules and solids," ed. G. L. Malli (Plenum Press: New York, 1994), in press.

[3] MOLECULE, a vectorized integral program written by J. Almlöf and P. R. Taylor.

[4] P. D. Dacre, *"On the use of symmetry in SCF calculations,"* Chem. Phys. Lett. **7**, 47, 1970; M. Elder, *"Use of molecular symmetry in SCF calculations,"* Int. J. Quantum Chem. **7**, 75, 1973.

[5] P. J. C. Aerts, *"Towards Relativistic Quantum Chemistry,"* Thesis, Groningen, 1986; O. Visser, P. J. C. Aerts and L. Visscher, *"Open-shell relativistic molecular Dirac-Hartree-Fock program,"* in " The effects of relativity in atoms, molecules and the solid state," ed. S. Wilson, I. P. Grant, and B. L. Gyorffy (Plenum Press: New York, 1991), pp. 185–195.

[6] P. Pulay, *"Convergence acceleration of iterative sequences. The case of SCF iteration,"* Chem. Phys. Lett. **73**, 393, 1980.

[7] K. G. Dyall and K. Fægri, Jr., *"Kinetic balance and variational bounds failure in the solution of the Dirac equation in a finite Gaussian basis set,"* Chem. Phys. Lett. **174**, 25, 1990.

[8] K. G. Dyall, *"Negative-energy states in the Dirac-Hartree-Fock problem: the effect of the omission of small-component two-electron integrals,"* Chem. Phys. Lett. **196** 178, 1992.

[9] K. G. Dyall, I. P. Grant, C. T. Johnson, F. A. Parpia and E. P. Plummer, *"GRASP – a General-purpose Relativistic Atomic Structure Program,"* Computer Phys. Commun. **55**, 425, 1989.

[10] K. G. Dyall and K. Fægri, Jr., *"Optimization of Gaussian basis sets for Dirac-Hartree-Fock calculations,"* in preparation.

[11] K. G. Dyall, P. R. Taylor, K. Fægri, Jr. and H. Partridge, *"All-electron molecular Dirac-Hartree-Fock calculations: the group IV tetrahydrides CH_4, SiH_4, GeH_4, SnH_4 and PbH_4,"* J. Chem. Phys. **95** 2583, 1991.

[12] K. G. Dyall, *"All-electron molecular Dirac-Hartree-Fock calculations: properties of the XH_4 and XH_2 molecules and the reaction energy $XH_4 \rightarrow XH_2 + H_2$, $X = Si$, Ge, Sn, Pb,"* J. Chem. Phys. **96** 1210, 1992.

[13] K. G. Dyall, *"All-electron molecular Dirac-Hartree-Fock calculations: properties of the group IV monoxides GeO, SnO and PbO"*. J. Chem. Phys. **98** 2191, 1993.

[14] C. W. Bauschlicher, H. Partridge and K. G. Dyall, *"The $^2\Sigma^+ - \,^2\Pi$ separation in KO,"* Chem. Phys. Lett. **199** 225, 1992.

[15] K. G. Dyall and H. Partridge, *"Relativistic corrections to the properties of the alkali fluorides,"* Chem. Phys. Lett. **206** 565, 1993.

[16] K. G. Dyall, *"Relativistic effects on the bonding and properties of the hydrides of platinum,"* J. Chem. Phys. **98** 9678, 1993.

[17] B. A. Hess, *"Relativistic electronic structure calculations employing a two-component no-pair formalism with external-field projection operators,"* Phys. Rev. A **33**, 3742, 1986.

[18] K. G. Dyall, *"An exact separation of the spin-free and spin-dependent terms of the Dirac-Coulomb-Breit Hamiltonian,"* J. Chem. Phys., in press.

[19] K. G. Dyall, *"Second-order Møller–Plesset perturbation theory for molecular Dirac-Hartree-Fock wave functions,"* in preparation.

[20] C. Murray and E. R. Davidson, *"Perturbation theory for open-shell systems,"*, Chem. Phys. Lett. **187**, 451, 1991.

[21] C. L. Collins, K. G. Dyall and H. F. Schaefer III, *"Relativistic and correlation effects in CuH, AgH and AuH: comparison of various relativistic methods,"* in preparation.

[22] H. J. Aa. Jensen, H Ågren and J. Olsen, *"SIRIUS: a general purpose direct second-order MCSCF program,"* in "Modern Techniques in Computational Chemistry: MOTECC-90," ed. E. Clementi (ESCOM: Leiden, 1990), p. 435.

[23] K. G. Dyall, H. J. Aa. Jensen, Knut Fægri, Jr. and T. Saue, *"Relativistic 4-component multi-configurational self-consistent field theory for molecules: formalism,"* in preparation.

[24] K. Andersson, P.-Å. Malmqvist, B. O. Roos, A. J. Sadlej and K. Wolinski, *"Second-order perturbation theory with a CASSCF reference function,"* J. Phys. Chem. **94**, 5483, 1990.