Quarterly Management Report

for the Period

18 March 1972 - 17 June 1972

CALCULATION OF PHYSICAL PROPERTIES OF DIATOMIC MOLECULES

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5

I. RESEARCH PROGRAM

Major accomplishments for the report period are described in Section II below. Reports detailing these accomplishments will be included in the final report for this contract.

II. MAJOR ACCOMPLISHMENTS

A. Electronic f-numbers

Programs for the calculation of electronic f-numbers have been written in two general parts. M. Yoshimine has completed and debugged a program for the calculation of matrix elements of $\underset{\sim}{r}$ between CI wave functions for different electronic states. The program permits the MO's used for the construction of the final state wave function to be different from those used for the initial state wave function. The CI expansions involved may be quite long; for example, for the $X^2\Pi$ and $A^2\Sigma^+$ states of LiO approximately 1500 symmetrized configurations and ~ 4500 determinants were used for each state. Because of these long expansions, the calculation of $\langle\Psi_I|\Sigma_i \underset{\sim}{r}|\Psi_F\rangle$ may become reasonably time consuming. To reduce the computational time, thresholds for the selection of only a part of the total number of configurations and a part of the total number of matrix elements between configurations have been included as an essential part of the program. For the second general part of this work, B. Liu has extended his vibration-rotational analysis program to calculate electronic band f-numbers and Frank-Condon factors. This program uses as input the electronic transition matrix elements of $\underset{\sim}{r}$ generated by the first program.

M. Yoshimine has, using the programs described above, obtained electronic band f-numbers for the $X^2\Pi \leftrightarrow A^2\Sigma^+$ transition of LiO and the $X^2\Sigma^+ \leftrightarrow A^2\Pi$ transition of AlO.

B. Sigma States of AlO

B. Liu and P. S. Bagus attempted to use the multi-configuration SCF (MCSCF) method to study the $X^2\Sigma^+$ state of AlO. This state has an anomolous behavior in the one-configuration SCF approximation which caused considerable difficulties in the selection of a reference state for subsequent CI calculations. It was hoped that the MCSCF method would provide an unambiguous reference state avoiding these difficulties. Unfortunately, the self-consistent field iterations for the MCSCF orbitals failed to converge.

In order to gain insight into the $B^2\Sigma^+$ state of AlO, M. Yoshimine performed limited CI calculations on $^2\Sigma$ states. These calculations involved, beyond the orbitals occupied in the $X^2\Sigma^+$ SCF calculations, two additional sigma and one additional pi orbital. The total number of configurations was 140 and both the lowest ($X^2\Sigma^+$) and second lowest ($B^2\Sigma^+$) roots were obtained. The energy separation of the two states is 10 percent larger than that observed experimentally. Electronic f-numbers will be calculated with these wave functions and compared to those obtained by Michels [J.C.P., <u>56</u>, 665 (1972)].

C. Electronic States of FeO

P. S. Bagus has completed atomic correlation energy calculations on Fe and O using the same set of excitations as used for the $^5\Sigma^+$ state of FeO. These calculations give a dissociation energy of 1.2eV for the $^5\Sigma^+$ state. However, because of the limited number of molecular orbitals used in $^5\Sigma^+$ CI calculation, the treatment of the separated atoms is expected to be far better than for the molecule. To avoid this problem, pair correlation energy calculations on the $^5\Sigma^+$ state using essentially a full basis set of MO's were performed at three points around the computed minimum of the potential curve. These calculations indicate that the dissociation energy is below 2eV. This is much lower than the previous estimate but still short of the ~4eV observed for the ground state.

Earlier calculations on the singly ionic $^7\Sigma^+$ state have been extended. SCF calculations have been performed for $^7\Sigma^+$ states on models of neutral and of doubly ionic systems. In addition, limited CI calculations have been performed which mix all of these types of configurations. The doubly ionic configuration, in particular, was found to have an important effect on the behavior of this state. In addition SCF calculations on a singly ionic model for the $^5\Sigma^-$ state were attempted.

For most states, SCF convergence problems were encountered and for several states convergence could not be obtained. The use of adjusting equivalent, in principle, forms of Fock operators to obtain convergence was investigated with limited success.

D. Polyatomic Matrix Elements

A. D. McLean has worked on the analysis of the evaluation of matrix elements between Slater type basis functions for molecules of general geometry. A report on methods for evaluation is near completion.

E. ALCHEMY Documentation: Program Use and Large Scale CI Methodology

P. S. Bagus has completed an article describing the theory of open shell energy expressions and their use in SCF calculations. A. D. McLean continues work on an ALCHEMY "User Manual" including detailed reports on the methods currently available for use with this program system.

A. D. McLean and B. Liu have developed a scheme for the classification of configuration state functions forming the n-particle basis of CI calculations. The classification includes the order of perturbation theory in which a configuration state function makes a correction to a given zeroth order function. They have shown how to minimize the number of configuration state functions having a non-zero matrix element with members of the zeroth order function. This work is of importance in reducing the size of CI calculations designed to yield some prescribed accuracy, at the same time it makes available a language for interpreting a wave function and is of assistance in preparing CI calculations. A report on this work is in preparation.

F. Methods for Large Scale CI Calculations

B. Liu has worked on methods for applying Rayleigh-Schrödinger perturbation theory as a guide for selecting configurations in large CI calculations. He has also used perturbation theory as a method to obtain approximate natural orbitals. The method was studied and applied in calculations on the low-lying states of CH. Effective methods for selection of configurations and approximate natural orbitals are essential to make accurate CI calculations tractable.

III. Problems Encountered

None

IV. Fiscal Status

Research Labor and Research Burden expenditures under this contract for the period June 18, 1971, to May 19, 1972, were $68,178; computer time and support time charges for the same period were $13,112.

V. Action Required by the Government

None.

P. S. Bagus
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