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STEREOELECTRONIC PROPERTIES OF AGGREGATED CHLOROPHYLL SYSTEMS

MASTER

Progress Report
for Contract Period January 1, 1977 through December 31, 1977

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Progress Report Abstract

Contract No. EY-77-S-02-2837.*000

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During the first eight months of the second contract period substantial progress was made on a number of the projects proposed. For example, ab initio configuration interaction calculations on magnesium porphine, porphine, magnesium chlorin, and chlorin have been completed, and the electronic structure and properties (e.g. transition energies and oscillator strengths) of their low-lying singlet and triplet states have been analyzed. Preliminary results from similar calculations on ethyl pheophorbide a and ethyl chlorophyllide a have also been obtained, and a detailed analysis of these results is currently in progress.

In order to investigate the geometric aspects of monomeric and aggregated chlorophyll systems, extensive characterization and development of empirical potential functions was undertaken. A set of potential functions suitable for the study of chlorophyll-type systems has been obtained, and initial studies on the geometry of ethyl chlorophyllide a have been completed with excellent results. Currently, conformational analysis of chlorophyllide macrocycle substituents is being carried out to assess the presence of energetically important conformational states, which will be used in the study of dimeric chlorophyll systems.

Methodology assessment, development, and implementation was also continued during the second contract period. Of particular importance in this regard is the implementation of an N^5 algorithm for transforming atomic into molecular two-electron integrals. This procedure was crucial to the chlorophyllide studies, and will greatly extend the size of molecules that can be investigated in the future (e.g. chlorophyll dimers). Work has continued on basis set development, and double-zeta quality basis sets are now available for carbon, nitrogen, and oxygen. Development

of comparable single-zeta basis sets and inclusion of polarization functions in the double-zeta basis sets are currently being investigated. Studies aimed at developing suitable computation procedures for calculating optical activity are also being continued.

I. Introduction

During the period January 1 to September 30, 1977, many of the projects proposed for 1977 were either totally or substantially completed. The main emphasis centered on four principal areas of research: (1) characterization of low-lying singlet and triplet states of porphines, chlorins and chlorophyll analogs (e.g., ethyl chlorophyllide a), (2) characterization and development of suitable empirical potential functions for chlorophyll monomer and dimer geometric studies, (3) application of empirical potential functions for conformational analysis of macrocycle substituents and dimer structures of ethyl chlorophyllide a and related molecules, and (4) continued effort on basis set generalization, and development of other theoretical techniques (ORD/CD spectral calculations).

Several important findings have emerged from these investigations which will have long term implications in our future photosynthesis research. Of major importance in this regard is the implementation of a new N^5 algorithm for transforming atomic into molecular two-electron integrals, a procedure which will greatly extend the size of molecules and the range of CI calculations we can handle. Furthermore, extensive characterization studies of electrostatic point charge[1] and Scheraga-type[2] empirical potential functions have led us to adopt a more flexible and accurate set of empirical potential functions for our geometry studies. Initial geometry calculations on prototype systems with these potentials are very promising, and because of this we intend to extend our range of geometry studies.

II. Work Completed

A. Electronic Spectral Studies on Ethyl Chlorophyllide *a* and Related Systems.

1. Free Base and Magnesium Porphine

Extensive self-consistent field molecular orbital configuration interaction (SCF-MO-CI) calculations, using techniques described in previous progress reports, have been completed for all the low-lying singlet and triplet excited states of these molecules (manuscript submitted). These mark the first *ab initio* CI calculations on molecular systems of this size and, more importantly, these calculations provide the most complete picture of the state structure of the low energy singlet and triplet manifolds available to date. The calculated transition energies of the major singlet-singlet absorption bands and phosphorescence emission bands are found to be related linearly to their corresponding experimental transition energies. Polarizations and relative oscillator strengths are also in excellent agreement with experiment.

The linear relationship is then used to scale the state energies (relative to the ground state) of *all* calculated singlet and triplet states. The predicted state energies thus obtained have provided an excellent basis for further analysis of the photophysics of these molecules.

Analysis of the charge distributions of the lowest singlet and triplet excited states has also been carried out, and the implications of the charge distributions to the physico-chemical properties of these states have been discussed.

Finally, an analysis of the configurational parentage of the states showed strong four-orbital configuration mixing in the lower singlet states and more single configuration character in magnesium porphine triplets. In the low-lying free base triplets, however, considerable four-orbital configurational mixing was observed. The apparent divergence of this result with earlier semi-empirical calcuations and with several experimental observations is discussed in detail. A copy of the manuscript describing this work has been submitted earlier.

2. Free Base and Magnesium Chlorin.

Analogous to the porphine studies, SCF-MO-CI calculations have been completed for all the low-lying singlet and triplet states of free base and magnesium chlorin. Again, this represents the first *ab initio* CI calculation on these molecules. Since the macrocyclic rings constitute the basic structures from which the photosynthetic pigments chlorophyll and pheophytin are derived, an understanding of their detailed excited state structure is of great importance to our studies on ethyl chlorophyllide *a* and ethyl pheophorbide *a*.

Using the linear relationship derived for free base and magnesium prophine, the predicted transition energies are found to be in good agreement with available experimental data. Calculated polarizations and relative oscillator strengths are also well described.

Analyses similar to those carried out on the porphines were also carried out in this case. Of interest is the finding that, contrary to

the observation in porphine, the configurational parentage of the low-lying chlorin triplet states is essentially described by single four-orbital configurations. A copy of the manuscript describing this work is enclosed.

B. Methodology Development and Assessment

1. CI Techniques

a. N^5 algorithm for integral transformations.

One of the main problems confronting any large scale CI calculation is the two-electron integral transformation from integrals over basis functions (floating spherical Gaussian orbitals-FSGO-in our case) to integrals over MO's. Under most circumstances the integral transformation is or is close to the rate limiting step in such a calculation. Furthermore, for molecules of the size treated in the current studies (e.g., ethyl pheophorbide a), integral transformation times are greater than 10 hours, based on an N^6 algorithm and the IBM 370/195 at Argonne National Laboratory. Therefore, implementation of a feasible N^5 algorithm would have substantial benefits both in computing time and in the size and number of large molecular systems that we can investigate. Most of the usual N^5 algorithms had core and/or other mass storage requirements which rendered them unusable for our calculations. Fortunately, an N^5 algorithm developed by Shavitt[3] combines both the advantage of speed and minimum core and tape requirements. This algorithm has now been implemented, and thus we are able to carry out the necessary integral transformations for ethyl pheophorbide a and ethyl chlorophyllide a in approximately one-half hour in each case, a substantial

saving in computation time.

b. Pyrazine Characterization.

In order to evaluate the adequacy of the molecular fragment FSGO basis for CI spectral calculations, several studies on experimentally and theoretically well characterized molecules were undertaken. Of particular interest to our studies on porphyrins and chlorophylls is the study of pyrazine excited singlet and triplet states.

Comparison with experimentally derived singlet and triplet state energies (relative to the singlet ground state) shows an excellent linear correlation between the values calculated in the current study and experiment. Of particular importance in this regard is the fact that the linear relationship includes $^1(n,\pi^*)$, $^3(n,\pi^*)$, and $^1(\pi,\pi^*)$ states. Hence, even (n,π^*)-type states, which are difficult to observe spectroscopically by traditional methods and which are of different electronic character than (π,π^*) states, adhere to the same linear relationship as (π,π^*) states. Furthermore, as discussed by a number of authors,[4] the more "ionic" $^1(\pi,\pi^*)$ states are generally expected to be less well described than the more "covalent" $^3(\pi,\pi^*)$ states in a minimum basis set CI calculation. Contrary to this observation, our rather simple basis appears to produce $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ states of about comparable accuracy. Thus, scaling <u>via</u> the linear relationship of state energies of difficult to observe states <u>e.g.</u>, $^{1,3}(n,\pi^*)$ and $^3(\pi,\pi^*)$ in related molecular systems is expected to be quite useful for characterization of excited states. This finding has important implications for our photosynthesis studies, and its

general validity is being continually assessed. A copy of the manuscript describing this work has been submitted earlier.

III. Work in Progress and Probable Efforts for the Remainder of 1977.

A. Electronic Spectral Studies on Ethyl Chlorophyllide a and Ethyl Pheophorbide a.

Ab Initio SCF-MO-CI calculations on the low-lying singlet and triplet states of ethyl chlorophyllide a and ethyl pheophorbide a have been substantially completed, and preliminary analysis of the results will be presented at the Midwest Regional American Chemical Society Meeting in November. Implementation of the N^5 algorithm discussed earlier has allowed the use of a substantial MO basis set in the CI calculations (e.g., 20 occupied and 9 virtual MO's for ethyl chlorophyllide a).

Preliminary analysis on ethyl pheophorbide indicates the presence of two low-lying $^1(\pi,\pi^*)$ states in the visible region of the spectrum, as expected from our studies on chlorin. The Soret region exhibits a number of closely spaced $^1(\pi,\pi^*)$ states, with two $^1(n,\pi^*)$ states appearing to the high energy side of the Soret band. Large scale CI studies and oscillator strength calculations are now underway, to quantify further these and other preliminary observations on pheophorbide, and to complete the studies on ethyl chlorophyllide.

It is anticipated that the data analysis will be completed by the end of the year, and at that time a manuscript will be submitted for publication.

B. Potential Function Techniques

1. Point Charge Model

As described in the original proposal, purely electrostatic interactions between Chl molecules can be effectively treated using a point charge model derived from the electronic ground state wavefunction after the method of Shipman.[1] Earlier studies (Oie, Maggiora, and Christoffersen)[5] showed that the Shipman point charge model provided an adequate description of the molecular electrostatic potential of porphyrins in the region beyond the Van der Waals radii of the various atoms. Hence, it might be expected that, if two interacting molecules do not get "too close", the current point charge model should provide an adequate means for calculating the long range intermolecular interactions energy.

Using this technique, the long range electrostatic interaction energy between two ethyl chlorophyllide a molecules was investigated. Calculations were carried out for fixed values of the inter-macrocylic ring separation (measured with respect to the two Mg atoms). The remaining five rigid-body rotational degrees-of-freedom between the two molecules were "scanned" in a sequential fashion to locate the relevant local minima. After carrying out numerous calculations in this manner it became obvious that, due to the considerable spatial extension of the macrocyclic chlorin ring and its substituent groups, even for inter-ring separations of more than 10 A, close contacts (within the Van der Waals radii) between atoms are not uncommon. Since static electrostatic terms do not contain proper account of repulsive interactions (among

other things) at short range, the point charge model produced a number of chemically unreasonable stable structures.

Furthermore, due to the number of terms required in each summation of the intermolecular interaction energy, it was decided to investigate the possible use of empirical potential functions.

2. Empirical Potential Functions (EPF)

EPF have provided one suitable means for reliably studying the conformations and molecular dynamics of molecular systems for a number of years. More recently, EPF have been developed which allow similar studies to be carried out on molecular systems as large as proteins.[6] Although a number of different types of EPF are available, their ability to provide a satisfactory basis for studying chlorophyll and related systems must be carefully assessed.

With this thought in mind, several types of EPF were examined for their ability to predict the conformational energetics of macrocyclic substituent groups of Chl-like molecules, and to predict intermolecular interactions energies of aggregated Chl-like systems (initially dimeric systems).

Initially our investigations centered on the EPF developed by Scheraga and his students.[2] A variety of factors, such as barriers-to-rotation and intermolecular separations of stable noncovalent dimers and oligomers, were studied. While a number of features were satisfactorily treated, a number were poorly described (e.g., barriers-to-rotation in ethyl acetate and butadiene--models for important substituents in Chl). Furthermore,

Scheraga's potentials do not account for bond length and bond angle variations.

After attempting a number of refinements of these EPF's, we decided to test a set developed by D. Duchamp at Upjohn Laboratories.[7] These EPF's were tested extensively in a similar fashion to those developed by Scheraga, et al,[1] and the results were very encouraging. Several modifications, additions, and adjustments have been made, but in general the Duchamp potentials are superior to Scheraga's for short and medium range interactions, the regions of the molecular configuration space of greatest interest to us. Very long range interactions (e.g., beyond Van der Waals minima) which depend more heavily on electrostatic forces are less well described, due to the lack of explicit inclusion of atomic partial charges (although "formal" atomic charges are included). This deficiency, however, should not cause serious problems in our studies.

It is also of interest to note that Duchamp's EPF allow bond length and bond angle variations as well. In fact, Duchamp has applied his EPF's as an aid to x-ray structural analysis of molecular crystals with excellent results. These findings provide additional support for the efficacy of his EPF's for our work.

Use of Duchamp's EPF's required the development of a set of EPF's for magnesium. The development has recently been completed, and the EPF's are currently being used in our monomer and dimer geometry studies. Analysis of the adequacy of this potential will continue throughout the remainder of this year. Finally, it is of interest to note that the Duchamp EPF program

currently used at KU has recently been implemented at ANL. This should greatly expedite our dimer studies of ethyl chlorophyllide a and related molecules.

3. Geometry Studies of Ethyl Chlorophyllide a and Model Dimers.

A number of computational studies based on the modified Duchamp EPF's are currently being carried out in our laboratory. These studies are designed to characterize the potentials as to their adequacy for studies of ethyl chlorophyllide a and ethyl pheophorbide a dimers. For example, starting with the x-ray crystal structure of ethyl chlorophyllide a, we have carried out an extensive calculation to find the energy-optimized structure of this molecule. More than 120 degrees-of-freedom were considered in the search for minimum energy structures, including essentially all the substituent groups as well as a number of macrocylic ring atoms. The structure obtained was, as might be expected, quite close to that determined by x-ray methods.[8]

Studies currently in progress are designed to investigate the conformational energetics of various substituent groups using the "adiabatic mapping" technique developed by Warshel.[9] Results of these studies will play an important role in the dimer studies by providing "energetic guidelines" to likely (or unlikely) substituent conformations, thus expediting the search for reasonable dimer structures by restricting the regions of molecular configuration space that must be searched.

It is anticipated that the monomer geometry studies on ethyl chlorophyllide a should be substantially complete by the end of this year.

Aslo, with regard to providing energetic guidelines for dimer studies,

model studies are currently underway designed to assess regions of the molecular configuration space which are strongly affected by ring-ring interactions. These studies involve searches of the inter-ring configuration space of dimers of magnesium porphine, magnesium chlorin, and their free bases. Completion of these studies, which are in their very preliminary phase, is not expected until well into 1978.

C. Basis Set Generalization Studies

During 1976 a theoretical analysis dealing with extension of FSGO basis sets to higher accuracy and flexibility was presented.[10] During the current year, computational studies have begun which quantify the numerical aspects of the basis set generalization scheme, provide high-accuracy reference calculations for comparison with new basis sets to be developed, and begin the actual development of new basis sets. This is a particularly important effort, for systematic extension of basis sets to provide higher accuracy and error estimates is very important for systems like chlorophyll, where no other *ab initio* studies are available for comparison.

During the current year, a variety of studies have been completed. These include: 1) implementation of an "n^5" algorithm for transformation of integrals over FSGOs ("n" being the number of primitive or contracted FSGOs being transformed) to atomic component integrals, 2) analysis and examination of computer accuracy requirements and numerical differencing effects that will occur in the integral transformation mentioned in 1) above, 3) test calculations on CH_4 and the Ne atom to assess the actual amount of rotational variance that will be encountered as a function of placing FSGOs at a distance of $\delta=R/\rho$

from a nucleus,[10] and 4) completion of calculations on the C atom, CH_4, C_2H_6, C_2H_4, and C_2H_2 using large FSGO basis sets, to provide a set of reference calculations for comparison of energies and other properties when new basis sets are developed. Since only s and p-type FSGO basis sets are being developed in these initial studies, no polarization functions (e.g., d-type functions obtained from FSGO arranged at the corners of icosahedrons) have been included.

The results obtained thus far in these studies continue to indicate that the approach has considerable promise. For example, in the Ne atom, a rather wide range of δ values can be used ($0.003<\delta<0.04$) and still produce integral values (on the HISI 66/60 computer) that are accurate to 1×10^{-9}. Also, use of $\delta \simeq 0.003$-0.005 in CH_4 produces a worst case rotational variance of only $\sim$2 kcal/mole. Hence, both internal accuracy and rotational variance requirements can be satisfactorily dealt with using $\delta \cong 0.003$-0.004.

In the case of the reference calculations, the following results have been obtained.

	Energy (Hartees)
CH_4:	-40.195714
C_2H_6(Staggered):	-79.22463
C_2H_4:	-78.03181
C_2H_2:	-76.82157

In each of these cases, the basis set has been chosen as the FSGO analog (using s-functions and tetrahedrally-arranged FSGO) of the Husinaga (11s, 7p) basis for carbon and 6s basis for hydrogen.[11] The above energies and associated

molecular orbital energies and structure represent the best abailable calculations to date on these systems using a non-polarized basis, and hence make an excellent basis for comparison in the basis set development studies described below. Double-zeta quality basis sets for nitrogen and oxygen have recently been completed, and additional testing is being carried out to further assess their adequacy.

Work currently underway involves construction of the FSGO analog of a single zeta basis set. Since energetic characteristics are not sufficient by themselves to use for construction of small basis sets (e.g., inner shell descriptions would be emphasized at the expense of valence orbital descriptions), the following function is being used

$$f = \omega_1 E - \omega_2 \sum_{i,j} S_{ij}^2$$

where ω_1 and ω_2 are arbitrary weighting factors, and S_{ij} is the overlap integral between a given reference orbital (from the reference calculations described above) and the orbital being determined. By maximizing such a function, both energetic and "shape" characteristics of these functions can be determined to match the reference calculations as closely as possible. Studies are currently being carried out on the C, N, O, and H atoms using this procedure, in order to obtain analogs of the correpsonding single-zeta (STO-2G and STO-3G) basis sets of Pople and co-workers. This work will continue throughout the remainder of the current year, including testing of these basis sets on prototype molecular systems. Additional aspects of this project are described in the work proposed for 1978.

D. ORD/CD Studies

All of the initial ORD/CD studies proposed for this year have been

completed, and several additional studies have been undertaken. Specifically, all programs have been written and checked out, and a prototype calculation on twisted ethylene has been completed. The results indicate essentially complete agreement with available data.

In addition, studies have begun on 3-methylcyclobutene, to assess several additional characteristics of this system and the procedures used. First, since no ab initio CI calculations of ORD/CD spectra of any kind are available for molecular systems larger than ethylene, a series of calculations using a variety of (systematically more flexible) basis sets has been undertaken on this system. Initial SCF-MO plus CI studies using 25 basis functions (27 FSGO) have been completed, with 6 filled and 5 unfilled MOs having variable occupancy. In addition, rotational strength calculations have been completed. Substantial additional studies are needed to complete the necessary systematics, and they will be carried out during the remainder of this year and next year. Details of these studies are given in the proposed studies for next year, but include basis set extension (including the effect of diffuse basis orbital addition), assessing the effect of geometric variations on the calculated spectra, and assessing the adequacy of the molecular fragment basis for larger systems.

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IV. MANUSCRIPTS PUBLISHED, IN PRESS, OR SUBMITTED (Since January 1976)

1. "Stereleloctronic Properties of Photosynthetic and Related Systems. Ground State Characterization of Free Base Porphine, Chlorin, and Ethyl Chlorophyllide a", by D. Spangler, G. M. Maggiora, L. L. Shipman, and R. E. Christoffersen, J. Amer. Chem. Soc. (in press).

2. "Stereoelectronic Properties of Photosynthetic and Related Systems Ground State Characterization of Magnesium Porphine, Magnesium Chlorin, and Ethyl Chlorophyllide a", by D. Spangler, G. M. Maggiora, L. L. Shipman, and R. E. Christoffersen, J. Amer. Chem. Soc. (in press).

3. "Ab Initio Calculations on Large Molecules Using Molecular Fragments. Comparison of Charge Distribution and Molecular Electrostatic Potential for Ethyl Chlorophyllide a and Related Molecules". T. Oie, G. M. Maggiora, and R. E. Christoffersen, Int. J. Quantum Chem., 53, 119, (1976).

4. "Ab Initio Calculations On Large Molecules Using Molecular Fragments. Generalization and Characterization of Floating Spherical Gaussian Basis Sets", by G. M. Maggiora and R. E. Christoffersen, J. Amer. Chem. Soc., 98, 8325 (1976).

5. "Ab Initio Calculations on Large Molecules Using Molecular Fragments. SCF-MO-CI Studies on Low-Lying Singlet and Triplet States of Pyrazine." Int. J. Quantum Chem. (in press).

6. "Stereoelectronic Properties of Monomeric and Aggregated Chlorophyll Systems", by Ralph E. Christoffersen and Gerald M. Maggiora, Proceedings of 1st ERDA Solar Photochemistry Research Conference, Argonne National Lab., 1977 (in press).

7. "Stereoelectronic Properties of Photosynthetic and Related Systems. III. Ab Initio Configuration Interaction Calculations On the Ground and Lower Excited Singlet and Triplet States of Magnesium Porphine and Porphine, by J. D. Petke, G. M. Maggiora, L. L. Shipman, and R. E. Christoffersen, J. Molec. Spectr. (submitted).

8. "Stereoelectronic Properties of Photosynthetic and Related Systems. IV. Ab Initio Configuration Interaction Calculations On the Ground and Lower Excited Singlet and Triplet States of Magnesium Chlorin and Chlorin, by J. D. Petke, G. M. Maggiora, L. L. Shipman, and R. E. Christoffersen, J. Molec. Spectra. (to be submitted).

V. Principal Investigators' Efforts

During the first eight months of the 1977 contract, the effort devoted to this project by the principal investigators (R. E. Christoffersen and G. M. Maggiora) has been at least that indicated in the contract (10% for nine-month academic year for REC and GMM, and 100% for one summer month for REC and 100% for two summer months for GMM). During the remainder of the contract period for this year, the effort devoted by each of the principal investigators is expected to continue at least that indicated in the contract.

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1. "Sterelelectronic Properties of Photosynthetic and Related Systems. Ground State Characterization of Free Base Porphine, Chlorin, and Ethyl Chlorophyllide a", by D. Spangler, G. M. Maggiora, L. L. Shipman, and R. E. Christoffersen, J. Amer. Chem. Soc. (in press).

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