SUMMARY

The scope of the thesis is to find rational explanations for some of the observed physicochemical data on metallo-porphyrins and related systems, using semi empirical molecular orbital calculations. The thesis consists of four chapters and an appendix.

In the first chapter a brief review is presented on the status of molecular orbital calculations on porphyrins. Emphasis is laid on the literature that has appeared during the past eight years. A comparative evaluation is made on the various methods used for theoretical calculations, based on how well the results of these calculations explain the experimental data. Extended Hückel approach (EHT) and Pariser-Parr-Pople \( Z \)-electron approach (PPP) have serious limitations. In many situations, the correct ground state is not obtained with these methods. Semi empirical all valence electron methods like CMDO/2, CMDO/3S, INDO are more promising, but the multiplicity of the approach is discouraging the theoretical chemists and it is difficult to choose among the plethora of various modifications of CMDO/2 and INDO formalisms. SCF-X-\( \alpha \) approach and ab initio calculations have yielded good results. There are still many problems regarding the physicochemical aspects of porphyrins which deserve, the attention of theoretical chemists. Some of these are mentioned at the end of Chapter I.
One of the intriguing problems in porphyrins is that the redox potentials of metalloporphyrins are very sensitive to the nature of the metal ion but the optical spectra are relatively independent of the metal ion. This aspect has been dealt with in Chapter II. The influence of the effective nuclear charge of the metal ion on the energy levels of porphyrins is estimated using SCF perturbation theory. CNDO/2 and PPP wave functions of porphine dianion are used as zeroth order functions. The first order changes in the orbital energies of porphine dianion have been estimated as a function of the perturbing positive charge. The energy levels obtained by this coulombic perturbation are corrected with the observed ionisation potential and redox potential data. The calculations have indicated that the effective nuclear charges of the metal ions in the metalloporphyrins varying from Mg(II) porphyrin to Sn(IV) porphyrin are in the range 1-1.6. The variation in the charges in this range is enough to change the oxidation potentials considerably; but the excitation energies in this range are not affected much.

Many of the tetrapyrrole systems which have biological relevance and are related to porphyrins have not been investigated by semi empirical all valence electron methods or ab initio methods. Some of these systems have been investigated in this thesis using CNDO/2 approach. Comparison of the chemical reactivities of these systems is made with
that of porphyrin. In Chapter III, CNDO/2 calculations on phlorin trianion is presented. The CNDO/2 energy levels are compared with those of porphine dianion. Good agreement is obtained with observed trends in the redox potentials. The reactivity parameters, namely frontier electron densities and superdelocalisabilities have been estimated for various positions in the molecule. The reactivity parameters show good agreement with the observed experimental data.

In Chapter IV CNDO/2 calculations are presented for corrole and tetradehydrocorrin. These systems are related to vitamin B\textsubscript{12}. The energy levels are checked with the trends in the redox potential data. The observed electrophilic and nucleophilic reactions of these molecules are rationalised in terms of the reactivity parameters.

The listings of two computer programmes are presented in the Appendix. These programmes are used to perform SCF perturbation calculations using CNDO/2 or PPP data for the zeroth order level. The computer programmes are written in Fortran IV language.
Appendix

Computer programs used for performing SCF-perturbation Calculations.

The listing of two computer programmes written in Fortran IV language are presented here, which are used for performing SCF perturbations calculations. One of the programmes uses PPI wave functions as the zeroeth order functions while the other uses the CNDO/2 data as the starting point. The programmes can be used to calculate first order changes in orbital energies, total energy and bond order. A brief account of the method of SCF perturbation calculations is presented in chapter 11. The relevant expressions are presented here for the sake of understanding the computer programmes.

A.1.1. SCF perturbation calculations using PPI data as the starting point:

The perturbing Hamiltonian $H^{(1)}$ matrix is given by

$$H_{\mu\mu}^{(1)} = -\frac{ze^2}{r_{\mu}}$$

(A.1.)

where $\mu$ is the atomic centre, $r$ is the distance of centre $\mu$ from the perturbing positive ion with charge $+z$.

and

$$H_{\mu\nu} = 0 \text{ if } \mu \neq \nu$$

(A.2.)

In the HP method the elements of the first order Fock matrix element $F^{(1)}$ are:

$$F_{\mu\mu}^{(1)} = H_{\mu\mu}^{(1)} + \frac{1}{2} \sum_{\nu\neq\mu} F_{\mu\nu}^{(1)} F_{\nu\mu}^{(1)} + \sum_{\nu} \sum_{\mu \neq \nu} F_{\mu\nu}^{(1)} F_{\nu\mu}^{(1)}$$

(A.3.)
and
\[ F^{(1)}_{\mu \nu} = - \frac{1}{2} \left( F^{(1)}_{\mu \nu} + F^{(1)}_{\nu \mu} \right) \]  
(A.4.)

To start with \( F^{(1)}_{\mu \nu} \) is set equal to \( H^{(1)}_{\mu \nu} \).

Then \( F^{(1)}_{ij} \) is calculated by the expression
\[ F^{(1)}_{ij} = \sum_{\mu} \sum_{\nu} C^{(0)}_{\nu \mu} F^{(1)}_{\nu \mu} C^{(0)}_{ij} \]  
(A.5.)

where the indices \( \mu \) and \( \nu \) refer to the atomic orbitals and \( i \) and \( j \) refer to the energy levels.

Thus the \( F^{(1)}_{ij} \) matrix is denoted by \( FMJ(K,I) \) in the program.

The elements of the matrix \( A \) are given by
\[ A_{ik} = F^{(1)}_{ik} \left/ \left( E^{(0)}_{k} - E^{(0)}_{i} \right) \right. \]  
(A.6.)

The first order change in the charge density matrix \( r^{(1)} \) is now expressed in terms of \( 'A' \) matrix.
\[ r^{(1)} = 2 \sum_{\mu} \sum_{\nu} \sum_{\omega} A_{k \nu i} \left( C^{(0)}_{\nu \mu} C^{(0)}_{\omega \mu} + C^{(0)}_{\mu \nu} C^{(0)}_{\nu \omega} \right) \]  
(A.7.)

Now, the first order correction to the total energy is given by
\[ W^{(1)} = \left( \frac{1}{2} \right) \sum_{\mu} \sum_{\nu} \left\{ C^{(0)}_{\mu \nu} \left( H^{(0)}_{\mu \nu} + F^{(1)}_{\mu \nu} \right) + F^{(1)}_{\mu \nu} H^{(0)}_{\mu \nu} \right\} \]  
(A.8.)
Also, the first order change in the orbital energies are given by the diagonal elements of the $F^{(1)}$ matrix:

$$F_{ii}^{(1)} = E_i^{(1)} = \sum_{\mu} \sum_{\nu} C_{\mu i}^{(0)} F_{\mu \nu}^{(1)} C_{\nu i}^{(0)} \quad (A.9)$$

The $F_{\mu \nu}^{(1)}$ elements are now substituted in equation $(A.1)$ for reevaluation of $W^{(1)}$ and $E_i^{(1)}$ and the cycle is repeated till the self-consistency in the first order correction to the total energy $W^{(1)}$ is reached.

A. 1. 2. Operation of the Program

SCFPERTurbation1 program is written for calculation of first order changes in bond order, total energy and orbital energies in PPP formalism. The input data for the calculation is given below:

Initially some files are read from the magnetic tape, these files were created while performing PPP calculations for a molecule under consideration. These files are:

File No. 25 Title 'MATRIXV': It contains LCAC coefficients of the zeroth order wave functions.

File No. 26 Title 'MATRIXE': It contains zeroth order orbital energies.

File No. 27 Title 'MATRIXR': It contains repulsion integrals.

File No. 29 Title 'MATRIXP3': It contains zeroth order bond order.

File No. 29 Title 'MATRIXH': It contains core Hamiltonian matrix in the PPP formalism; the expression is given below. ($A.10$ and $A.11$.)
The data to be read are:

\[ H_{\mu \nu}^{\text{core}} = \sum_{\nu} \frac{Z_{\nu} \beta_{\mu \nu}}{\beta_{\mu \nu}} \quad (\alpha.10.) \]

\[ H_{\mu \nu}^{\text{core}} = \beta_{\mu \nu} \quad (\alpha.11.) \]

First Card: A title card in A format containing any identification for the molecule.

Second Card: A series of control variables in I format.

Na: The total number of pi-atomic orbitals.

NCCC: The total number of occupied pi-electron level.

NUM: The number of perturbation calculation to be done.

NCENT: The number of centres for which perturbation calculation is to be done.

Third Card: Two variables, TGL and MIXT in F and I format respectively.

TGL: Self-consistency limit i.e. the difference in the total energies obtained from successive cycles.

MIXT: The maximum number of iterations to be performed.

Fourth Card: Co-ordinate of all the atoms read in F format.

Fifth Card: Co-ordinate of perturbing centre to be read in F format.

Sixth Card: The location of the perturbing centre is given by NFGS in I format.

Seventh Card: The charge of the perturbing centre is read in F format.
A. 2.1. SCF perturbation calculation using CNDO/2 data:

In this method the perturbing Hamiltonian $H^{(1)}$ is same as used in A.1.1.

In the CNDO/2 method the elements of the first order Fock matrix $F^{(1)}$ is given by

\[ F^{(1)} = H^{(1)} + \left( \frac{1}{2} \right) \sum_{AB} \gamma_{AB} \]

(A. 12.)

\[ F^{(1)}_{\mu \nu} = - \left( \frac{1}{2} \right) \sum_{AB} \gamma_{AB} \]  

(A. 13.)

Expressions for first order changes in the bond order ($P^{(1)}_{\mu \nu}$), total energy change ($\omega^{(1)}$) and orbital energies ($E^{(1)}_i$) are same as used in A.1.1.

A. 2.2. Operation of the program.

SCFPERTURBATION2 program is written for calculation of first order changes in bond order, total energy change and orbital energies in CNDO/2 formalism. The input data for the calculation is given below:

Initially some files are read from the magnetic tape, these files were created while performing CNDO/2 calculation for a molecule under consideration. These files are:

File No. 75 Title 'LCCATOM': It contains the atomic number of all the atoms.
File No. 80 Title 'HIJ' : It contains the off diagonal elements of core Hamiltonian matrix in CNDO/2 formalism; the expression is given below (Eqn. A. 14)

File No. 81 Title 'HII' : It contains the off diagonal elements of core Hamiltonian matrix in CNDO/2 formalism; the expression is given below (Eqn. A. 15)

File No. 83 Title 'GAMMA' : It contains the repulsion integrals.

File No. 86 Title 'LCAO' : It contains the LCAO coefficients of the zeroth order wave function.

File No. 87 Title 'ENERGY' : It contains the zeroth order orbital energies.

File No. 89 Title 'BONDORDER' : It contains the zeroth order bond order.

\[
H = \frac{-1}{2} (I + A) + \frac{1}{2} \sum_{A} \sum_{\mu} |A^A_{\mu}\rangle \langle A^A_{\mu}| + \sum_{A} \sum_{\mu} \sum_{B} \sum_{\nu} |A^B_{\nu}\rangle \langle A^B_{\nu}| AB \langle \mu | \mu \rangle \quad (A. 14)
\]

\[
H = \beta_{AB} S_{\mu\nu} \quad (A. 15)
\]

The data to be read are as follows:

First Card : A title card in A format containing any identification for the molecule.

Second Card : A series of control variables in I format, these are NA, NATOMS, NOCC, NCUT, INDEX, NBOND. The description of which are given in the program by comment cards.

Third Card : Two variables, TOL and MIXT in CF and I format respectively.

TOL : Self-consistency limit i.e. the difference in the total energies obtained from successive cycles.

MIXT : The maximum number of iterations to be performed.
Fourth Card : Co-ordinates of all the atoms are read in F format.

Fifth Card : Co-ordinates of the perturbing centre are read in F format.

Sixth Card : The charge of the perturbing centre is read in F format.