MOLECULAR ORBITAL CALCULATIONS
ON
SOME METALLOPORPHYRINS AND RELATED SYSTEMS

Bhattacharya

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DOCTOR OF PHILOSOPHY

To

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FEBRUARY, 1985

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Pre- Ph.D Course Work evaluation Report

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2.	Chem-443	Physical Chemistry II	A	4.90
3.	Chem-541	Chemical Binding	B	4.40
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3.
4.

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Shillong (Kaushik Kumar Bhattacharjee)

PREFACE

The scope of this thesis is to present the results of semi empirical molecular orbital calculation on porphyrins and related systems. Emphasis is laid on the chemical reactivities of the systems that have been studied. CNDO/2 method has been used in all the cases and where necessary, the results are compared with those obtained from Pariser Parr Pople - π electron approach.

In the first chapter a brief review is presented on the present status of molecular orbital calculations on porphyrins. Since earlier reviews are available up to 1977, the papers that have appeared after this period have been dealt with in detail. Some of the shortcomings of the calculations that have appeared so far have been mentioned. Some problems which deserve the attention of theoretical chemists are also mentioned.

It has been observed that the redox potentials of metalloporphyrins are very sensitive to the nature of the metal ion whereas the visible absorption spectrum is relatively unsensitive to the metal ion. This problem is handled in the framework of SCF perturbation approach. The metal ion is considered to perturb the porphyrins through a Coulombic effect and the influence of the perturbation on the m.o energy levels, ionisation and redox potentials is estimated. The results are presented in Chapter II.

Many of the reduced porphyrins have not drawn the attention of theoretical chemists and some of these systems have been investigated by CNDO/2 method. In Chapter III, CNDO/2 calculations are presented for phlorin trianion which serves as a model for bilatriene type of bile pigments. The chemical reactivity parameters (Frontier electron densities and superdelocalisabilities) have also been calculated. The results of CNDO/2 calculations on corrole and tetradehydrocorrin are discussed in Chapter IV. The overall reactivity patterns of porphyrin, phlorins corrole and tetradehydrocorrin are compared.

Listings of the computer programs developed for the purpose of doing SCF perturbation calculations are presented in the Appendix.

CONTENTS

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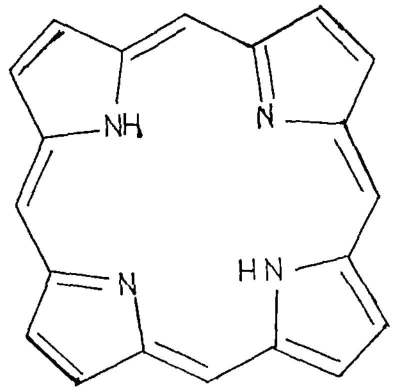
CHAPTER I

A BRIEF REVIEW OF THE THEORETICAL CALCULATIONS ON PORPHYRINS AND METALLOPORPHYRINS

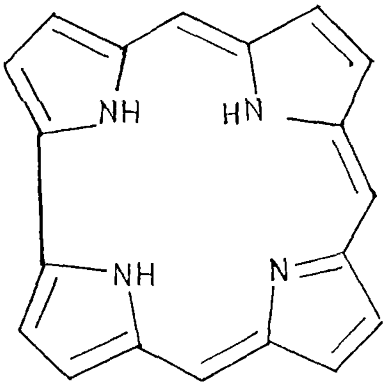
I. 1. Introduction

Porphyrins and related tetrapyrrole systems have attracted considerable attention of chemists, physicists and biologists in recent years.[1,2] In view of the biological importance of these systems, a large volume of spectroscopic and chemical data have accumulated in the past twenty years or so. Quantum mechanical calculations on these systems have also been quite substantial, and have helped to rationalise the experimental results. In the present chapter, some important aspects of the theoretical calculations on porphyrins will be reviewed. Out of the reviews[3,4,5] that have appeared in the past, two are quite extensive. Chantrell et al[3] have reviewed the status of molecular orbital calculations on porphyrins and their metal complexes. The emphasis in this review is on the various methods of calculations. It covers the different aspects of calculations performed using free electron model, Hückel, Pariser-Parr-Pople (PPP) and the extended Hückel (EHT) methods. A few calculations that had been done using the semi empirical all valence electron SCF methods (CNDO/2) have also been mentioned in this work. The later review by Gouterman[5] deals mostly with spectroscopic properties and includes the semi empirical π- electron and all valence electron methods of calculations. During the last seven years, a large number of calculations have appeared using the semi empirical all valence electron approach as well as ab initio methods. The aim of the review here will be to cover the theoretical calculations that have appeared after 1977. Only a brief mention will be made of the work that has appeared earlier, for the sake of continuity. The material in this chapter is classified broadly under three categories, namely, π -electron calculations, semi empirical all valence electron calculations and ab initio calculations.

The basic skeletons for porphyrins and related compounds are shown in figure 1.1. The term porphyrin is used where there are substituents on the pyrrole rings or on the methine bridges. The unsubstituted macrocyclic system is termed as porphine. The free base porphine has D_{2h} symmetry and its metal complexes possess D_{4h} or C_{4v} symmetry. In a metalloporphyrin with four fold symmetry, the two highest occupied π-molecular orbitals (HOMO) are nearly degenerate and belong to the A_{1u} and A_{2u} representations.[3] The lowest unoccupied molecular orbitals (LUMO) are degenerate and belong to the E_g representation under D_{4h} symmetry. When the symmetry is reduced to D_{2h} or C_{2v}, the energy gap between the HOMO levels increases and the degeneracy of the LUMO levels is lifted. Porphyrins, reduced porphyrins and their metal derivatives give characteristic electronic absorption spectra which are used as finger prints to identify the nature of the macrocycle.[4]



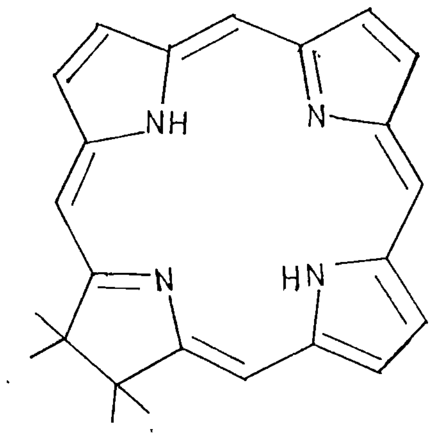
PORPHINE



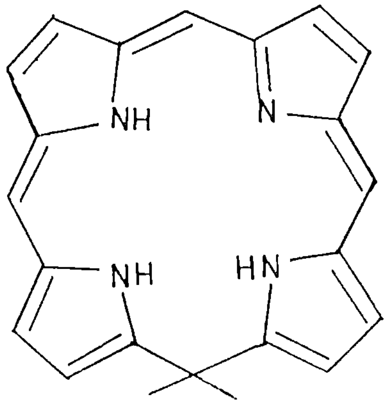
CORROLE

Fig. 1.1

SKELETONS FOR PORPHINE AND RELATED COMPOUNDS

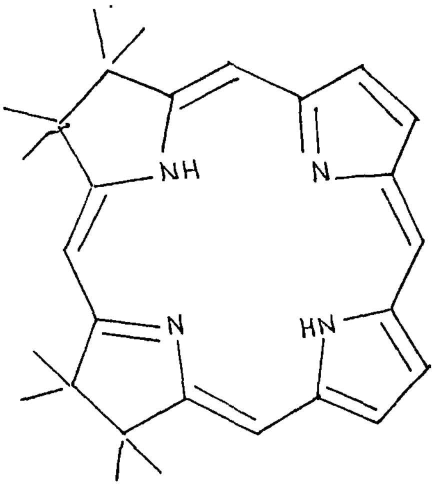


CHLORIN

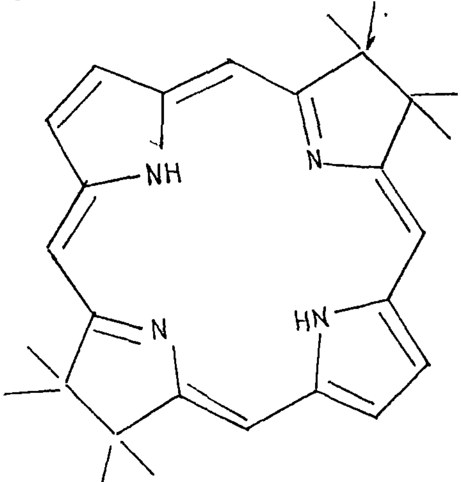


PHLORIN

Fig. 1.1 CONTINUED



TETRAHYDROPORPHYRIN - a



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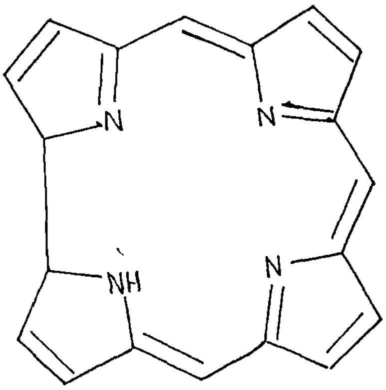
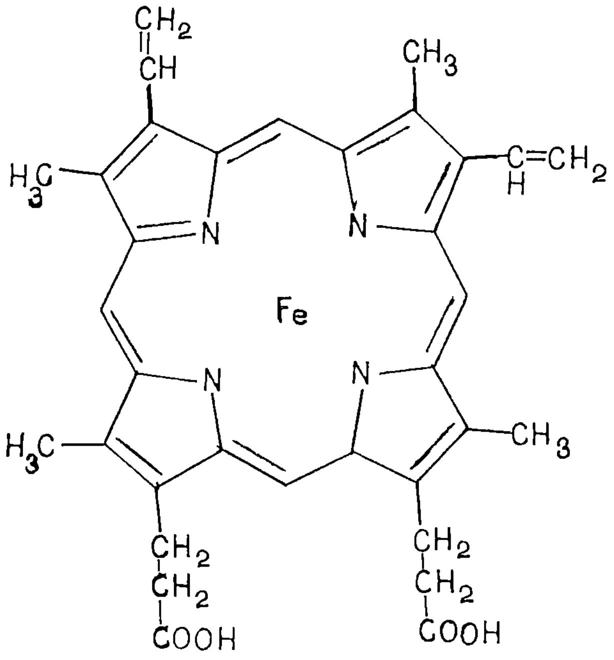


TETRADEHYDROCORRIN

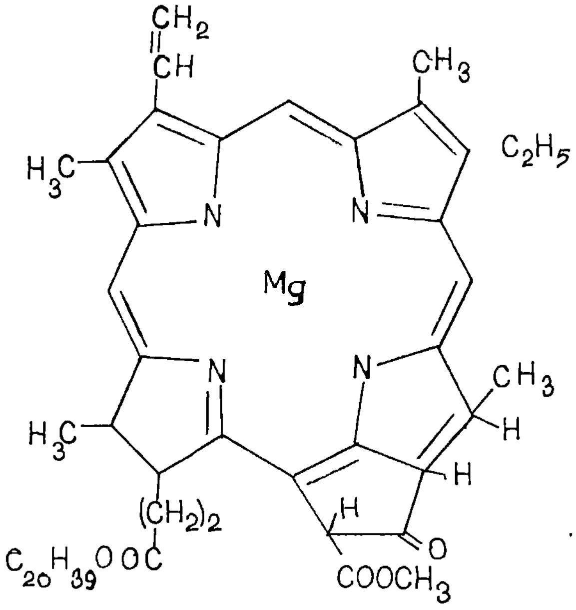
Fig. 1.1 CONTINUED

SKELETONS FOR TETRAHYDROPORPHYRINS a AND b ;

TETRADEHYDROCORRIN



HEME



CHLOROPHYLL

Fig. 1.1

The reactivity of a porphyrin can be extensively varied by either changing the central metal ion or by reducing the macrocycle. Thus the Fe(III) & Fe(II) porphyrins which form the chromophores of heme proteins, are involved in the activation of oxygen, oxidation and hydroxylation of substrates, electron transfer reactions, decomposition of hydrogen peroxide, etc. In these reactions, the iron undergoes changes in its oxidation state with the porphyrin playing a secondary role. On the other hand, reduced porphyrins like chlorins and tetrahydroporphyrins, in the form of their magnesium complexes are involved in the primary electron transfer processes in photosynthesis. In this case, the main reacting center is the porphyrin π -system which forms the radical cation. The metal ion (i.e., Mg) plays only a secondary role by lowering the oxidation potential of the π -system. The large number of theoretical calculations that have been attempted so far have been aimed at understanding the electronic structure of porphyrins, their electronic spectra, nature of excited states, chemical reactivity and the nature of bonding of metal ions to the porphyrins ligand. Two of the earlier reviews[4,5] deal exclusively with the optical spectra of porphyrins. Hence, emphasis in this review will be laid on those theoretical calculations which deal with the ground state properties and the chemical reactivity of metalloporphyrins.

I.2 Summary of the previous reviews:

From the results of the theoretical calculations that have appeared so far, a fairly clear picture of the electronic structure of porphyrins and their spectroscopic properties has emerged. The earliest theories that provided a simple and convincing model of the electronic states of porphyrins were proposed by Simpson[6], Kuhn[7] and Platt[8]. The porphyrins with D_{4h} symmetry is treated as a 16 membered cyclic polyene (4n membered) with 18 π-electrons. In the simple Hückel framework, the orbital energies are obtained.

$$E_M = \alpha + 2\beta \cos\left(\frac{2m\pi}{16}\right)$$

where α and β are Huckel parameters. The orbitals with $m = 0, \pm 1, \pm 2, \pm 3$ and ± 4 are filled with electrons in the ground state. The lowest energy transitions are from the $m = \pm 4$ to $m = \pm 5$ orbitals. The transitions with the change in angular momentum $\Delta L_z = \pm 1$ are allowed and those with $\Delta L_z = \pm 9$ are forbidden. By including configuration interaction, one obtains a lower energy transition with $\Delta L_z = \pm 9$ around 580 nm and higher energy transition with $\Delta L_z = \pm 1$ around 390 nm (Soret band). A free base porphyrin with D_{2h} symmetry can be considered as a 18 membered (4n + 2 membered) cyclic polyene with 16 π- electrons. It has been shown by Moffit that while going from a 4n membered ring system to a 4n + 2 membered ring system, the degeneracy of the lower-energy singlet transition ($\Delta L_z = \pm 9$) is lifted while the higher-energy transition (Soret band) is unaffected[9]. These predictions based on this simple model explain the observed optical spectra of metalloporphyrins (D_{4h}) and free base porphyrins (D_{2h}). Though this model is very crude, it gives a fairly reasonable physical insight of the energy levels and optical transitions of the porphyrin system. Very extensive and pioneering calculations have been made by Martin Gouterman and his group[5] on the ground and excited states of porphyrin using PPP and extended Hückel methods. On the basis of these calculations, Gouterman has proposed a four-orbital model[10,11] for metalloporphyrins. He obtained that the two highest occupied molecular orbitals with the a_{1u} and a_{2u} symmetries are nearly degenerate and the two lowest vacant molecular orbitals are truly degenerate having e_g symmetry. All the other levels are well-separated from these four orbitals. Most of the electronic spectral data can be interpreted on the basis of the four-orbital model though certain finer aspects like relative intensities do require inclusion of extensive configuration interaction(CI). The properties of porphyrins studied in detail by Gouterman's group include[5] singlet-singlet transitions by including extensive CI, triplet-triplet transitions, magnetic circular dichroism, angular momenta in the ground and excited states and metal-porphyrin binding. Very extensive calculations have been done in the EHT framework[5] (iterative

EHT-method) for metalloporphyrins with alkali and alkaline earth metals, first and second row transition metals as well as some non-metals like P, As etc. These calculations provide reasonable insight into the nature of the Metal-porphyrin binding but the EHT method is inadequate in rationalising the observed physicochemical properties of metalloporphyrins. In the light of the above comments, we shall discuss the results of the theoretical calculations that have appeared in recent years.

I.3 Pi electron calculations[12-20]

In recent years efforts are being directed towards calculating the wavefunctions for porphyrins using CNDO/2 and INDO methods or ab initio approach. Only a few meaningful calculations have appeared using PPP-pi electron approach. The interaction energy of two porphyrins molecules in a dimer in the ground state has been calculated using standard perturbation approach.[21] The PPP wave function have been used for the monomer in the ground state. The calculations indicate that a tilted dimer is more stable than a face-to-face dimer. A similar type of calculation has been reported for the excited states of the dimer with reference to the mixing of exciton resonance and charge transfer states.[22] The calculations predict the appearance of a charge transfer transition on the long wavelength side of the Soret band. The reported calculations on the dimers, so far have partly been in agreement with the experimental data. Detailed calculations have been done on the ground and excited states of the Fe(II) porphins-with imidazole as the fifth ligand in the framework of extended PPP formalism (Peel method).[18] All the π -orbitals of the porphine and the imidazole, one Sp^2 hybridised sigma orbital pointing to the Fe atom from each of the four nitrogen atoms of the porphine and from the nitrogen atom of the imidazole were included in the calculation along with the five d-orbitals of the Fe atom. Some molecular integrals were adjusted using spectroscopic data. Overall reasonable agreement was obtained with the magnetic properties, optical spectra and MCD spectra. The main drawback of this method, apart from the adjustment of some important integrals, is the non-inclusion of the 3s and 3p orbitals of the Fe atom.

The spin densities and zero field splitting (ZFS) energies of the lowest triplet state of a light metal porphyrin have been determined by PPP method using the ope-shell SCF approach with configuration interaction.[16] The metal ion has not been included in the calculation. Satisfactory agreement has been obtained with the experimentally observed ZFS parameters and hyperfine couplings obtained for the zinc and magnesium porphins. The chemical shifts of protons, ^{13}C and ^{15}N were calculated for porphyrins in the PPP framework including the contributions from pi electron ring currents.[17] The results are in good agreement with the experimental nmr data. On the basis of the strength of pi electron ring currents an aromaticity scale has been proposed for porphyrins and related systems.

Considering the overall impact of the π -electron calculations in the understanding of the physical and chemical aspects of porphyrins the following comments may be made.

1. The pi electron calculations lead to a reasonable understanding of the spectroscopic properties of metalloporphyrins, where the metal ion does not seriously influence the spectral behaviour. These calculations are less useful for the reduced porphyrins like chlorin, tetrahydroporphin corrins, corroles etc.

2. Inclusion of the effect of metal in the π -electron calculations has a limited scope. It also involves extensive parametrisation schemes for each metal ion and thus limiting the usefulness of this approach.

I.4. All valence electron methods:

I.4.1. Extended Hückel approach (EHT):

Very extensive calculations have been done on metalloporphyrins involving light and heavy metals, in the framework of iterative extended Hückel approach.[5] These calculations have been reviewed in detail earlier.[5] These calculations have thrown some light on the nature of metal-ligand bonding, but suffer from the inherent defects of the EHT method. The relative ordering of the π -electron energy levels and the d-electron energy levels in transition metal porphyrins has not been correctly predicted by this method in many situations. Some recent calculations reported using this method include the electronic states of Co, Ni, Rh and Pd porphyrins[23], iron(II) porphin-pyridine complex[24], nitric oxide and carbon monoxide adducts of iron porphyrins[25], phosphorous complexes of porphin[26], an isostructural macrocycle B_8S_{16}[27] and porphyrins containing heteroatoms other than nitrogen.[28]

I.4.2. CNDO/2 and related methods:

The first calculations using CNDO/2 method on porphyrins were done by Maggiora,[29] on free base porphine, porphine dianion, Mg(II) Porphine and aquo Mg(II) Porphine. The orbital energies were in good agreement with the ionisation potential data. For the first time the HOMO level was correctly predicted for Mg(II) Porphine as a_{1u}. This is supported by the esr hyperfine couplings for the radical cation of the Mg(II) Porphyrins. The electronic spectra of the porphine dianion, free base porphine and reduced porphines have been studied by the modified CNDO/S method.[30,31] An improved version called as CNDO/3S method[32,33] leads to very good agreement of theoretical results with the optical absorption spectra of porphyrins as well as with the UV photo-emission spectra. The tautomerism in free base porphine has also been investigated by a CNDO/2 method as well as by the INDO formalism.[34,35] The calculations done in the CNDO/INDO framework have yielded better results in terms of the correct ordering of energy levels and spectroscopic transition energies than those obtained from the extended Hückel method. But a systematic set of calculations over a large number of metalloporphyrins is lacking in the literature. This is perhaps due to two main reasons (i) The large amount of computer time involved for the CNDO calculation compared to the EHT approach and (ii) existence of at least half-a-dozen modifications in the formalisms, like CNDO/2, INDO, MINDO/3, CNDO/3S etc. Each of these methods applied to limited number of systems has been claimed to give better results than others.[36-38] The calculations reported using the CNDO, INDO and related methods include those on the Li and Na porphyrins[39], Cu porphyrin (esr parameters)[40], Fe(II) porphine[41,42] Fe(II) porphine adducts of dioxygen and carbon monoxide[41], ferryl porphine[41], nuclear spin couplings in porphine dianion and free base porphine[43], chlorins, bacteriochlorins[31], sirohydrochlorin[35] and azaporphyrins[44,45].

I.5. Slater's SCF X -α method[46]

Two types of calculations have been made in the framework of the SCF X -α model. One involves all the electrons in the molecule using muffin-tin approximation. The other approach involves only the valence electrons, without employing muffin-tin or overlapping spheres approximation. Sambe and Felton[47] used the latter approach to calculate the energy levels and wave functions for free base porphine, All the other reported calculations have been done using the former approach, i.e. all the electrons are included using the muffin-tin approximation. Case and Karplus[48] have reported detailed calculations on Cu(II) porphyrin on the basis of spin-restricted and spin-unrestricted models. The correct ordering of energy levels has been obtained in this approach. The ligand pi levels lie above the level of the unpaired d-electron. This is the correct order obtained on the basis of redox potentials and esr spectra. The earlier calculations based on the EHT and extended PPP- π electron approaches predict that the unpaired d-electron is in the highest occupied level, which is contrary to the experimental findings. The SCF $X-\alpha$ calculations also lead an excellent agreement with the esr data (g-values, anisotropic hyperfine coupling constants etc.) for the Cu(II) porphine. Similar calculations have been reported for the Mg(II) and Fe(II) porphines[49]. In general the formal atomic charges obtained by the SCF - $X-\alpha$ method are at variance with those obtained from other semi empirical models as well as from ab initio calculations. No systematic calculations have been reported for a large number of metalloporphyrins and hence it is difficult to assess the relative superiority of this approach over the other semi-empirical models so far as porphyrins are concerned. Particular mention has to be made on the SCF-$X-\alpha$ calculations made on the Fe(II)

Porphine[50] and Fe(II) porphine-dioxygen adduct with imidazole as the axial ligand, by Case et al[51]. The results of these calculations will be discussed along with similar calculations done in the ab initio formalism. Other SCF X-α calculations include those on Cu, Ag and Fe porphine using the discrete variational X-α technique.[52,53]

I.6. Ab Initio calculations

I.6.1. Free base porphyrins

The first ab initio m.o calculation on porphine has been reported by Almlöf using the linear combination of Gaussian orbitals.[54] Symmetry-adapted basis functions were used to simplify the computations. Ionisation potentials were obtained by ΔSCF method. The energy level pattern is similar to that obtained by the CNDO/3S method.[33] In another set of calculations, Christofferson and coworkers have employed the ab initio molecular fragment technique using floating spherical Gaussian orbitals (FSGO).[55-60]

In the case of free base porphine,[54] the ordering of the two highest occupied m.o's is reverse compared to that reported by Almlöf.[54] The energy values obtained using the molecular fragment technique cannot be directly compared with those computed by using the extended basis. A linear fit has been made between these two values for a small molecule like pyrrole. The same linear relationship has been used for porphyrins. In this way certain amount of arbitrariness is introduced in the m.o energy values obtained from molecular fragment technique. This method has been used to calculate the ground states of free base porphine,[56] chlorin,[56] ethyl pheophorbide[56] and the corresponding Mg(II) complexes.[57] The m.o energies, charge densities, bond orders and the electrostatic isopotential maps have been computed for these systems.[58] The calculations indicate that there is no pi-interaction between Mg-orbitals and the ligand pi orbitals and the role of Mg is essentially to provide a coulombic effect on the π-levels. The same authors have used limited configuration interaction to calculate the excitation energies of the free-base porphine, and chlorin as well as their Mg-complexes.[59,60] Since the ground state orbital energies were obtained by the molecular fragment method, the excitation energies calculated for these systems cannot be directly compared with the experimental data. A linear fit is used to obtain the estimated transition energies from the calculated energies. The estimated transition energies together with the calculated oscillator strengths yield good agreement with the spectroscopic data on these systems.[58]

Ab initio calculations have been reported by two groups[61,62] using contracted Gaussian type orbitals (CGTO) for transition metals containing porphyrins. Different basis sets have been employed: minimal, minimal + diffuse, partial double zeta and double zeta. The calculations on free base porphine[61,62] are similar to those reported by

Almlöf. The interesting aspect is that calculations of Almlöf and Ohno et al predict the same ordering of the HOMO levels for free base porphin ($b_{1u} > a_u$) while that of Christofferson et al[56] (molecular fragment technique) predicts a reverse ordering of these levels. In the ensuing discussion, a brief account of the results of ab initio calculations on some transition metal-porphyrins is presented.

I.6.2. Copper and Cobalt porphines[64,65]

For Cu porphine, a minimal basis of CGTO's were used with augmented diffuse function. Ionisation potentials were computed by Δ SCF procedure and excitation energies by limited π-CI calculations. The calculations clearly indicate that the π levels are above the level of the unpaired d electron. The ground state is correctly predicted to be $^2B_{1g}$. The first and second ionisations are expected to lead to the formation of the π cations and dications respectively. This is indeed observed experimentally, supported by oxidation potentials and visible electron spectrum. It may be pointed out here that the only other calculation which reproduces the ab initio results is that reported by Case and Karplus using SCF - $X\text{-}\alpha$ model.[48] The excitation energies calculated by the ab initio π - CI method are highly overestimated. The authors attribute this discrepancy to the $\sigma - \pi$ correlation which may be important in the lower excited states of metal porphines.

In the case of Co(II) porphine,[65] a basis set of single zeta for core and double zeta for valence orbitals for the Co and N atoms was used. For carbon and hydrogen, minimal basis was used. Calculations had been done for the low-spin, high-spin and π ionised states of the Co porphine. The ground state is obtained as $^4B_{2g}$ while the esr data on the Co(II)-TPP indicates $^2A_{1g}$, $(d_{\pi}{}^4 d_{xy}{}^2 d_{z^2}{}^1)$ as the ground state. Four quartet states ($^4B_{2g}$, $^4A_{2g}$, ^4E_g) lie below the expected $^2A_{1g}$ state. The improvement of electron correlation by inclusion of CI also leads to the situation where a quartet state has a lower energy (0.8 eV) than the doublet state, $^2A_{1g}$. In the opinion of the reviewer, this need not be taken as being at variance with the experimental data. It is very difficult to obtain pure Co(II) porphyrin without any axial ligand. Even a weakly coordinated axial ligand may raise the energy of the d_{z^2} level and consequently change the spin state of the Co(II).

A very careful sample preparation is required for obtaining the esr spectrum of a purely four coordinated Co(II) porphyrin. The ab initio calculations indicate that (i) The bonding between Co and porphine is essentially ionic. (ii) The net charge distribution in the four quartet states and doublet state is almost independent of the state of the system. (iii) The highest occupied orbitals are the π orbitals. This result is again in contradiction to the experimental findings. One-electron oxidation of Co(II) Porphyrin leads to the formation of Co(III)P$^+$; Subsequent oxidation leads to a π-dication radical, $[Co(III)P]^{++}$. Again, axial ligands might influence this behaviour. In fact, the photoelectron spectroscopic studies of Co(II) and Fe(II) octaethylporphyrins indicate that the ring oxidation takes place before the metal oxidation. Since PES studies are done in the vapour phase, influence of the medium is not present. The molecular species is truly a four coordinated one. It has been observed in the ab initio calculations on the transition metal, porphyrins that Koopmans' theorem can be applied only when the ionisation involves a π -electron. The reorganisation energy is quite small. When an electron is removed from the d-orbital of the metal atom, it is noticed from the Δ SCF calculations, that the reorganisation energy is quite large. Hence Koopmans' theorem is not applicable in this situation.

I.6.3. Iron and Manganese porphyrins-deoxy systems

In normal deoxyhemoglobin A, the iron(II) atom of the heme is 5-coordinated, high spin (S = 2), and is axially bound to the imidazole ring of the proximal histidine residue. The Fe-atom is displaced out of the plane of the porphyrin ring by an extent of about 0.6 Å.[66-68] This out-of-plane displacement plays a key role in the theoretical models developed to explain the cooperativity in the binding of oxygen in hemoglobin.[69-72] When oxygen binds to deoxyhemoglobin, the iron moves into the plane of the porphyrin ring and becomes low spin. The proximal histidine residue moves with the iron. Thus a knowledge of the intrinsic equilibrium position of the iron in a high-spin five coordinated ferro-porphyrin is essential for the understanding of cooperativity of hemoglobin in oxygen binding. A large body of experimental data has become accessible to theoretical studies, obtained from various physical techniques like X-ray crystallography, EXAFS study,[73] NMR,[74-76] Mössbauer spectra[77], and Resonance Raman spectroscopy.[78] A number of ab initio calculations have been reported on iron porphyrins and related systems to rationalise the observed experimental data and a brief account of the results of these calculations is presented here.

I.6.3.1 Four coordinated Fe(II) and Mn(II) porphyrins:

A number of ab initio calculations have been reported for the four coordinated Fe(II) porphine, using minimal basis set, partial double-zeta and double zeta basis sets.[62,79,80] All the calculations lead to similar results. The ground state is predicted to be either the $^3A_{2g}$ ($d_{xy}^2 d_\pi^2 d_{z^2}^2$) or the ^3E_g ($d_{xy}^2 d_\pi^3 d^1_{z^2}$). Even the inclusion of configuration mixing does not lead to a clear choice between the $^3A_{2g}$ and ^3E_g since these two levels lie very close to each other. Theoretical analysis of Mössbauer data using the ab initio wavefunctions lead to the conclusion that the ground state is

^3E_g. Magnetic susceptibility measurements, NMR contact shifts and Resonance Raman data point to the triplet ground state for this system. Energy levels and wave functions have been obtained for the Mn(II) Porphine[62] using minimal as well as partial double zeta (minimal for inner shells and double zeta for valence shells) basis sets for the $^6A_{1g}$ ground state.

I.6.3.2. Five-coordinated Fe(II) porphine, (Fe P).

In the five coordinated system, the metal orbital, d_{z^2} is destabilised through the interaction with the axial ligand. The iron atom in the deoxyheme is high-spin (S=2), with the iron atom being out-of-plane of the porphyrin ring. Calculations on the Fe P(NH_3)[62] and Fe P(Pyridine)[80] lead to the configuration, d^1_{xy} $(d_{xz}d_{yz})^3 d_{z^2}^1$ $d^1_{x^2-y^2}$. A detailed theoretical analysis of the observed Mössbauer parameters, namely the isomer shift, the quadrupole splitting and the asymmetry parameter also confirmed the above configuration for the ground state.[80]

I.6.4 The oxy systems of Ti, Mn, Co and Fe

The detailed nature of the metal-oxygen bond in the oxyhemoglobin and other dioxygen complexes of metalloporphyrins has been the subject of discussion for a long time. Whether the correct formulation is M(II)O_2 (neutral dioxygen) or M(III)O_2^- (Superoxide) has been the point of controversy. The experimental data on this problem may be summarised as follows:

(i) In the $TiPO_2$ system, the bond length O-O is 1.445 Å and the compound is diamagnetic (peroxo type of bond is indicated)[81,82]

(ii) For the CrO_2 TPP (Pyridine)[83] (TPP : tetraphenyl porphyrin), a magnetic moment of 2.7 Bohr magneton and the IR band at 1142 cm^{-1} (ν_{O-O}) have been observed. A superoxo formulation has been proposed.

(iii) $MnPO_2$: A spin state S = 3/2 has been assigned on the basis of epr data. The system has been formulated as Mn(IV) (O_2^{2-}) on the basis of epr data.[84-86]

(iv) $FePO_2$ system: O-O bond length is between 1.16 - 1.23 Å and the IR band at 1159 cm^{-1} corresponding to the ν_{O-O} has been reported.[68] The system is diamagnetic.[87] The superoxide formulation is proposed mainly on the basis of IR data. (ν_{O-O} for the free superoxide ion is at 1145 cm^{-1}).

(v) Co(III)PO_2 : A spin state S = 1/2 has been assigned on the basis of esr data.[88-90] On the basis of esr and IR data the superoxide formulation, Co(III) O_2^- is proposed.

I.6.4.1. $TiPO_2$ system (P = Porphine)

Ab initio calculations have been reported for $TiPO_2$,[91] $MnPO_2$,[92] $FePO_2(NH_3)$[92], $FePO_2Im$,[92] and $CoPO_2(NH_3)$[92]. For $TiPO_2$, the perpendicular structure was found to be more stable than a bent structure by 83 kcal/mole. This is in agreement with the X-ray crystal structure data. This structure corresponds to the peroxo formulation, Ti(IV)PO_2^{2-}.

I.6.4.2. MnPO$_2$ system

Regarding MnPO$_2$ system, the experimental assignment[84-86] (esr data) is $d^3\pi_g^4$ (π_g- antibonding π m.o of O_2 molecule) with the Mn(IV)O_2^{2-} configuration. But the theoretical calculations, involving perpendicular orientation of O_2 moiety,[92] predict that this structure is about 1 eV higher than the $d^4\pi_g^3$ configuration with Mn(III) intermediate spin (d^4, S = 1) state. Perhaps more extensive CI or a change in the orientation of the O_2 moiety or both are required to obtain the correct ground state, for this system.

I.6.4.3. Fe PO$_2$ system

Ab initio calculations have been done for the Fe PO$_2$(NH$_3$) and Fe PO$_2$ (Imidazole) systems with NH$_3$ as the axial ligands.[92,93] A singlet state with $d^6\pi^2$ configuration has been predicted for the ground state with the bent structure of O_2 moiety (Pauling structure). A low lying triplet state in the vicinity of ground state has also been predicted. The totally spin-paired ground state provides a satisfactory explanation for the observed transition energies and the electronic absorption spectra of oxymyoglobin and oxyhemoglobin. The SCF X-α calculations by Case and Karplus[51] for the FePO$_2$ (imidazole) and INDO-SCF-CI calculations of Herman and Loew[41] also lead to the conclusion that the ground state is diamagnetic. The SCF-X-α calculations indicate that the ground state contains equal contributions from the $d^6\pi_g{}^2$ (d^6, S = 0, $\pi_g{}^2$, S = 0) and $d^6\pi_g{}^2$ (d^6, S = 1, $\pi_g{}^2$, S = 1), configurations. The charge distributions as obtained from the ab initio calculations indicate that the moiety FeO_2 is neutral. The charge transfer from Fe to O_2 through sigma bond is compensated by pi-back-donation. Thus the system is clearly Fe(II) $PO_2(NH_3)$, as proposed by Pauling. This model is at variance with the superoxo formalism, Fe(III) $O_2{}^-$ based on the interpretation of the O-O stretching frequency in the IR spectrum. In recent years it has been shown that this frequency is insensitive to ligand and metal variation and hence insensitive to the amount of electron transfer. The experimental shift ($\simeq$400 cm^{-1}) of the O-O frequency in O_2 to the dioxygen complex of picket-fence porphyrin is well-reproduced in the ab initio calculations.

I.6.4.4. The Co PO_2 (NH_3) system:

From the ab initio calculations of Dedieu *et al*.[62] the ground state configuration for the bent structure (which is more stable) has been found to be $d^6\pi^3$, which corresponds to Co(III) $O_2{}^-$ superoxo-type configuration. This is in agreement with the known experimental data.

The results of the calculations and experimental data for Ti, Mn, Fe and Co porphyrin-dioxo complexes can be rationalised, following the arguments of Dedieu *et al*.[62] The electron population on the O_2 unit is 16.66 and decreases as we go to $MnPO_2$ and $FePO_2$, systems. In TiP, the metal d orbital is at a much higher energy level than the $^1\pi_g$ level of O_2 and hence the peroxo-type $Ti(V)O_2^{2-}$ configuration. In Fe, the energy gap between the metal d-orbital and the $^1\pi_g$ level is very small. Hence there is no net charge transfer from Fe to O_2 (electron population: 15.98). In the case of $CoPO_2$ systems, the additional electron has the choice between one of the e_g orbitals of Co or the π_g orbital of O_2. Since the e_g orbital is at a much higher energy level, the electron goes to π_g, leading to the superoxo formalism, $Co(III)PO_2^-$. Regarding the choice between a bent structure (Pauling) and a parallel structure (Griffith) one must consider the interaction between the metal d_π orbital and the π_g orbital of O_2. The interaction leads to a bonding and antibonding level (See figure 1.2). This interaction is stronger for the perpendicular structure than for the bent structure. In $TiPO_2$, only the lower bonding level is filled and hence a perpendicular structure leads to high stability. In Fe, and Co, the bonding and antibonding orbitals are both filled completely leading to some destabilisations. Hence the bent structure is favoured to minimise the $d_\pi - \pi_g$ interaction. The situation in the case of $MnPO_2$ is not clear-cut. More detailed calculations involving variations in the geometry and also extensive CI may be necessary to understand its properties.

Ab initio calculations have also been reported for the carbon monoxide adduct of iron porphine.[93] Recent studies include the calculations on oxo iron porphyrins[94] which are

Fig. 1.2 (a) GEOMETRICAL STRUCTURES OF OXY SYSTEMS

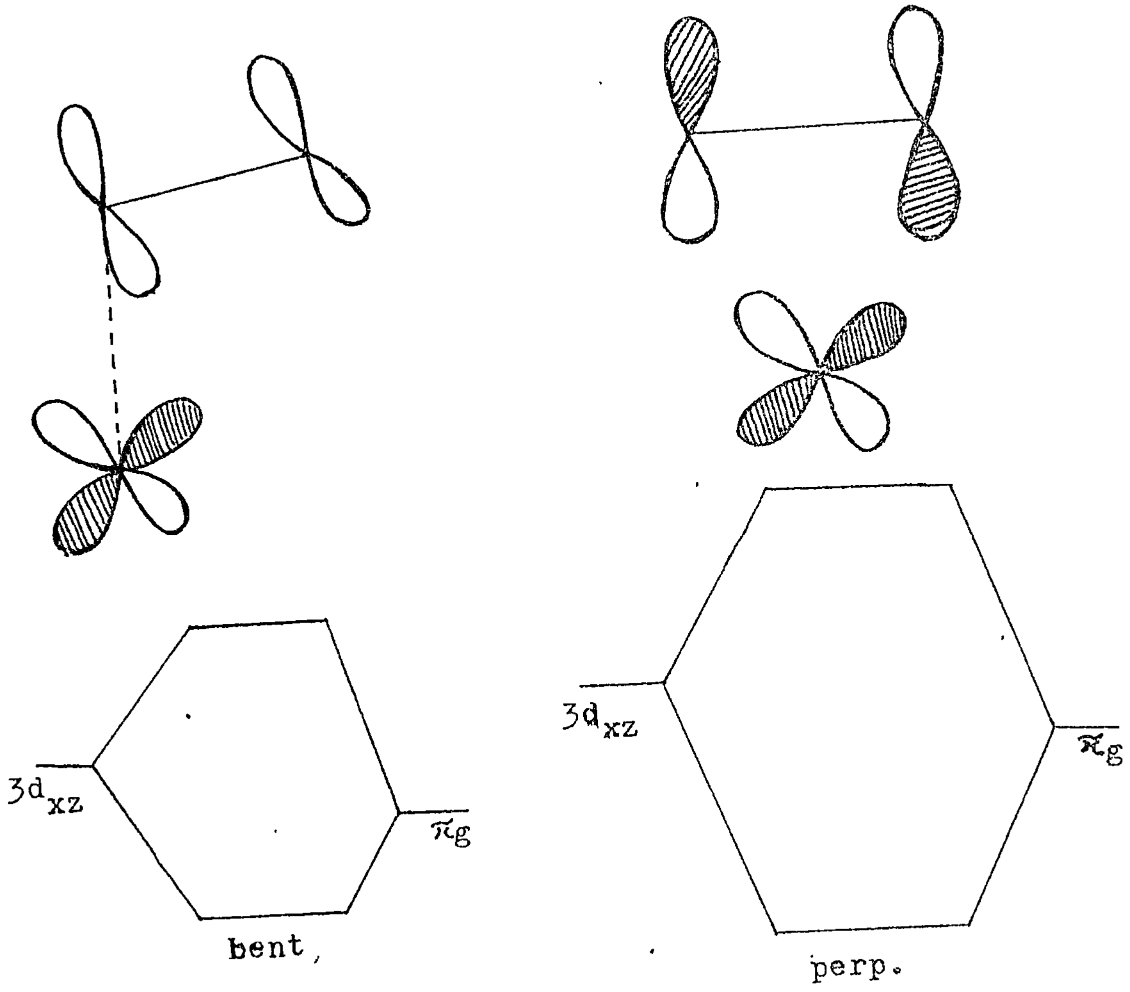


Fig.1.2 (b) THE $3d_{xz}$ - π_g INTERACTION FOR THE TWO STRUCTURES

proposed as models for the active sites of peroxidase and catalase enzymes. On the basis of experimental data (optical spectroscopy, esr, magnetic susceptibility) the active site has been proposed as (Fe = O)P with Fe in the oxidation state IV (S = 1). The ab initio calculations indicate that the ferryl structure (Fe = O) is less stable than a structure in which an oxygen atom is inserted between Fe atom and one of the pyrrole nitrogens. The oxygen is bonded to the Fe atom and the nitrogen of the pyrrole, keeping the Fe in the oxidation state of +2 with S = 1. Thus more experimental data are required to understand the active species responsible for the reactions of peroxidase and catalase.

In this review an attempt has been made to consider the various aspects of the theoretical calculations that have been reported on porphyrins in recent years. In spite of extensive calculations that have appeared, there is no systematic calculations on a large number of metalloporphins using the more sophisticated semi empirical methods like INDO, CNDO/3S or SCF - X-α. The only systematic calculations that are still available have been done in the EHT framework and for many situations, this method has not predicted the correct ground state. A second problem that crops up is that, the various semi empirical methods (INDO, SCF - X-αetc) as well as the ab initio calculations predict a wide range of charges on a metal in a metalloporphyrin. This aspect again requires a systematic study of a number of metalloporphyrins.

A related problem is the relative insensitivity of the electronic spectrum of a metalloporphyrin to the metal as well as a strong dependence of the redox potentials on the metal. Theoretical calculations on the above aspects are needed to rationalise the experimental data. Also, calculations in the all-valence electron semi empirical frame work or at the ab initio level are not available for many of the reduced porphyrins like phlorins, open-chain tetrapyrrole systems like bilatrienes and for the modified macrocyclic systems like corroles and tetradehydrocorrins related to Vitamin B_{12}.

In the present work some of the above-mentioned problems are handled in the framework of CNDO/2 approach. We have investigated using the SCF - perturbation approach (i) the insensitivity of the electronic spectrum of metalloporphyrins on the nature of the metal ion (ii) the strong dependence of the porphyrin ligand redox potentials on the metal. Both PPP and CNDO/2 wavefunctions are used as the zero-order functions. This aspect is discussed in in Chapter II.

In Chapter III CNDO/2 calculations are presented for phlorin trianion. The reactivity parameters for this system are compared with those of porphyrins.

CNDO/2 calculations are presented for corrole and tetradehydrocorrin in Chapter IV. The emphasis here again is given on the reactivity parameters and a rationalisation of the experimentally observed reactivity patterns in these systems.

A summary of the work presented in the thesis appears at the end highlighting the results of the various calculations.

Computer programs written for the purpose of SCF perturbation calculations in the PPP and CNDO/2 framework are presented in the appendix.

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CHAPTER II

SCF PERTURBATION CALCULATION ON METALLOPORPHYRINS

II. 1. Introduction

The past twenty years have witnessed accumulation of extensive data on the physicochemical properties on porphyrins and related systems.[1,2] Progress on parellel lines has also taken place in the theoretical calculations at varying levels of sophistication on the ground and excited states of porphyrins.[3-10] A considerable volume of experimental observations have been rationalised by these calculations; yet a few basic problems remaining close to the heart of porphyrin chemists have eluded the theoretical models. It has been noticed that in the metalloporphyrins, the redox potentials are very sensitive to the nature of metal ion, but the visible electronic spectrum is relatively independent of the metal ion, barring a few exceptions.[11-13] This behaviour has been qualitatively interpreted as arising due to the Coulombic perturbation of the pi-electron levels of the porphyrin ligand by the metal ion.[12,13] Recent results on the photoelectron spectroscopic studies on porphyrins have also been interpreted on this basis.[14] An attempt has been made in this work to investigate this problem quantitatively. The metal ion is assumed to perturb the energy levels of the porphyrin ligand. A simple perturbation of the type, $H' = (-Ze^2/r)$ is used where Ze is the effective charge on the metal ion. We have used the SCF perturbation theory to obtain the first order changes in the energy levels arising out of the Coulombic perturbation.[15,16] The wave functions for the unperturbed system have been calculated by PPP-pi electron method as well as by CNDO/2 method.[17] The results are encouraging and we have obtained good correlations between the oxidation potential of the pi ligand and the charge on the metal ion.

II.2. Methods of Calculation:

The SCF perturbation theory is an elegant way of calculating the first and higher order changes in the energy of a system under the influence of a perturbation irrespective of the formalism used to calculate the wave function for the unperturbed state. This method has been successfully used for a wide range of problems.[15,16] Though this method is well documented,[15,16] for the sake of completeness, a brief account of this approach relevent to the present work is outlined here. The method aims at calculating the first order changes in the energy and the charge density matrices of a molecule arising from a perturbation, $H^{(1)}$. The Fock, overlap and coefficient matrices are given by

$$\begin{aligned} F &= F^{(0)} + F^{(1)} \\ S &= S^{(0)} + S^{(1)} \\ C &= C^{(0)} + C^{(1)} \end{aligned} \qquad \text{(II.1.)}$$

The superscript (0) refers to the operators in the unperturbed system. Starting with Roothaan's equation,

$$FC = SCE \qquad \text{(II. 2)}$$

it is expanded in a perturbation series to first order. Since our zeroeth order wave functions have been obtained using zero differential overlap approximation, (PPP and CNDO/2 methods), we can ignore $S^{(1)}$. Expanding II.2 to first order and collecting terms by the order, we get

$$F^{(0)}\ C^{(0)} = S^{(0)}\ C^{(0)}\ E^{(0)} \qquad \text{(II. 3)}$$

$$F^{(1)}\ C^{(0)} + F^{(0)}\ C^{(1)} = S^{(0)}\ C^{(0)}\ E^{(1)} + S^{(0)}\ C^{(1)}\ E^{(0)} \qquad \text{(II. 4)}$$

If the equation II.3 and II. 4 are solved subject to the constraint $\tilde{C}\ SC = 1$, E can be considered diagonal to all orders. $C^{(1)}$ is expanded in terms of $C^{(0)}$ as

$$C^{(1)} = C^{(0)}\ \Lambda \qquad \text{(II.5)}$$

where Λ is the matrix of mixing coefficients. Substituting II.5 in II.4 and premultiplying by $\tilde{C}^{(0)}$, we get,

$$F'^{\,(1)} + E^{(0)}\Lambda = E^{(1)} + \Lambda\ E^{(0)} \qquad \text{(II.6)}$$

where

$$F'^{\,(1)} = \tilde{C}^{(0)}\ F^{(1)}\ C^{(0)} \qquad \text{(II.7)}$$

The elements of $F'^{(1)}$ matrix are given by,

$$F'^{(1)}_{ij} = \sum_{\mu} \sum_{\nu} C^{(0)}_{\mu i} \; F^{(1)}_{\mu\nu} \; C^{(0)}_{\nu j} \qquad (II.8.)$$

where the indices μ and ν refer to the atomic orbitals and i and j refer to the energy levels.

The first order change in the orbital energies are given by the diagonal elements of the $F'^{(1)}$ matrix.

$$F'^{(1)}_{ii} = E^{(1)}_{i} = \sum_{\mu} \sum_{\nu} C^{(0)}_{\mu i} \; F^{(1)}_{\mu\nu} \; C^{(0)}_{\nu i} \qquad (II.9.)$$

The elements of the A matrix are:

$$A_{ik} = F'^{(1)}_{ik} \, / \, (E_k^{(0)} - E^{(0)}_{i}) \qquad (II.10)$$

The first order change in the charge density matrix, $P^{(1)}$ is now expressed in terms of the elements of 'A' matrix:

$$P^{(1)}_{\mu\nu} = 2 \sum_{i}^{occ} \sum_{k}^{vac} A_{ki} \; (C^{(0)}_{\mu i} \; C^{(0)}_{\nu k} + C^{(0)}_{\mu k} \; C^{(0)}_{\nu i}) \qquad (II.11)$$

A nice feature of this expression is that only those A_{ki} terms are involved for which i is occupied and k is vacant. Any problems arising out of the degeneracy of the occupied levels (or vacant levels) is avoided. The first-order correction to the total energy is given by,

$$W^{(1)} = (1/2)\sum_{\mu}\sum_{\nu} P^{(0)}_{\mu\nu}\left(H^{(0)}_{\mu\nu} + F^{(1)}_{\mu\nu}\right) + P^{(1)}_{\mu\nu}\, H^{(0)}_{\mu\nu} \qquad \text{(II.12.)}$$

$W^{(1)}$ is calculated by an iterative procedure using the dependence of $F^{(1)}$ on $P^{(1)}$. The $H^{(1)}$ matrix is given by

$$H^{(1)}_{\mu\mu} = (-Z/R_{\mu})$$

in a.u.

and

$$H^{(1)}_{\mu\nu} = 0 \ (\text{for } \mu \neq \nu) \qquad \text{(II.13)}$$

where R_{μ} is the distance of the atomic orbital, μ, from the central metal ion. In the PPP method, the elements of $F^{(1)}$ are given by

$$F^{(1)}_{\mu\mu} = H^{(1)}_{\mu\mu} + (1/2)\, P^{(1)}_{\mu\mu}\, \gamma_{\mu\mu} + \sum_{\mu\neq\nu} P^{(1)}_{\nu\nu}\, \gamma_{\mu\nu} \qquad \text{(II.14).}$$

$$F^{(1)}_{\mu\nu} = -(1/2)\, P^{(1)}_{\mu\nu}\, \gamma_{\mu\nu} \qquad \text{(II.15).}$$

In the CNDO/2 formalism, these elements are:-

$$F^{(1)}_{\mu\mu} = H^{(1)}_{\mu\mu} + (1/2)\, P^{(1)}_{\mu\mu}\, \gamma_{AA} + \sum_{B} Q^{(1)}_{B}\, \gamma_{AB} \qquad \text{(II.16).}$$

$$F^{(1)}_{\mu\nu} = (-1/2)\, P^{(1)}_{\mu\nu}\, \gamma_{AB} \qquad \text{(II.17)}$$

The zeroeth order functions have been obtained for porphyrin dianion with D_{4h} symmetry, using the coordinates given by Zerner and Gouterman.[18] (fig 2.1). In the first cycle of SCF perturbation calculations, $F^{(1)}$ is set equal to $H^{(1)}$ and $P^{(1)}$ matrix is computed. $F^{(1)}$ is then reevaluated using equations (II.14) and (II.15) or (II.16) and (II.17). The cycles are repeated to the desired accuracy (10^{-4}eV). Computer programs written for doing the SCF perturbation calculations using the PPP and CNDO/2 wave functions are presented in appendix.

II.3. Results and Discussion

The aim of the SCF perturbation calculations presented here is to understand the effect of a residual positive charge on the pi electron energy levels of a porphyrin. The residual charge on the metal arises out of the ionic character of the sigma bonds formed by the metal ion and the nitrogen atoms. Thus, in a crude model, the metalloporphyrin pi levels are considered to arise out of the perturbation of the pi levels of the dianion by the residual charge on the metal. This approach requires a reliable set of energy levels and wave functions for the pi electrons in porphin dianion. We have taken the result of CNDO/2 calculation on porphin dianion as the starting point.[4] The changes in the pi m.o energies (eqn. II.9) and the total energy of the system (eqn. II.12) as functions of perturbing charge were calculated. The total orbital energies, $E_i^{(0)} + E_i^{(1)}$

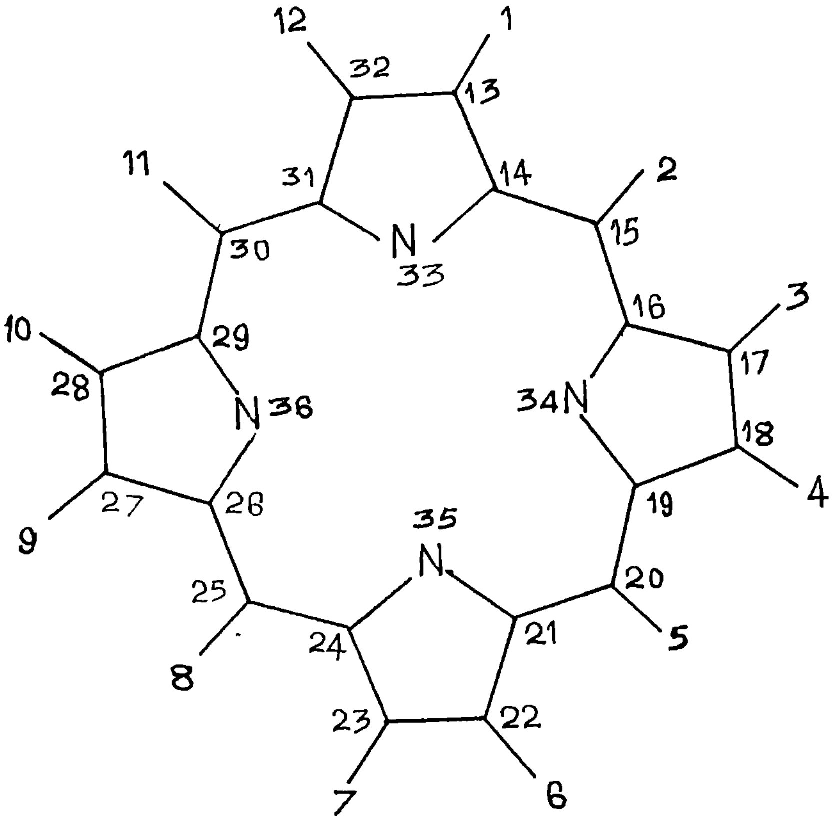

Fig. 2.1

SKELETON FOR PORPHYRIN DIANION

as functions of perturbing charges are presented in figure **2.2** for the HOMO and LUMO levels. Similar calculations were done using the PPP wave functions. In the PPP formalism, it is not possible to distinguish between a porphyrin dianion and a metalloporphyrin explicitly. In choosing the "standard parameters" for PPP-calculations on a metalloporphyrin, Weiss et al adjusted the nitrogen parameters to obtain the best fit with the electronic spectrum of zinc porphyrin.[19] Taking the CNDO/2 energy levels of porphin dianion as the criteria, we have adjusted the z value for nitrogen, to give the PPP energy values which match closely with the corresponding CNDO/2 results. Perturbation calculations were performed using these PPP energy levels. A graph of the orbital energy, $E_i^{(0)} + E_i^{(1)}$ vs the perturbing charge using the PPP-data is presented in figure 2.3. The results of the perturbation calculations indicate (i) that the outermost energy levels, $a_{iu}(\pi)$ $a_{2u}(\pi)$ and e_g (π) are affected to different extents by the point charge perturbation, (ii) a_{1u} and a_{2u} levels cross in the neighbourhood of a perturbing charge equal to +1 unit. The crossing of a_{1u} and a_{2u} levels has an experimental basis. It has been noticed that the visible electronic spectra of perchlorate and bromide salts of Co(III) tetraphenyl porphyrin cation are quite different from each other and this difference has been interpreted on the basis that the perchlorate anion and Bromide anion lead to different ground states

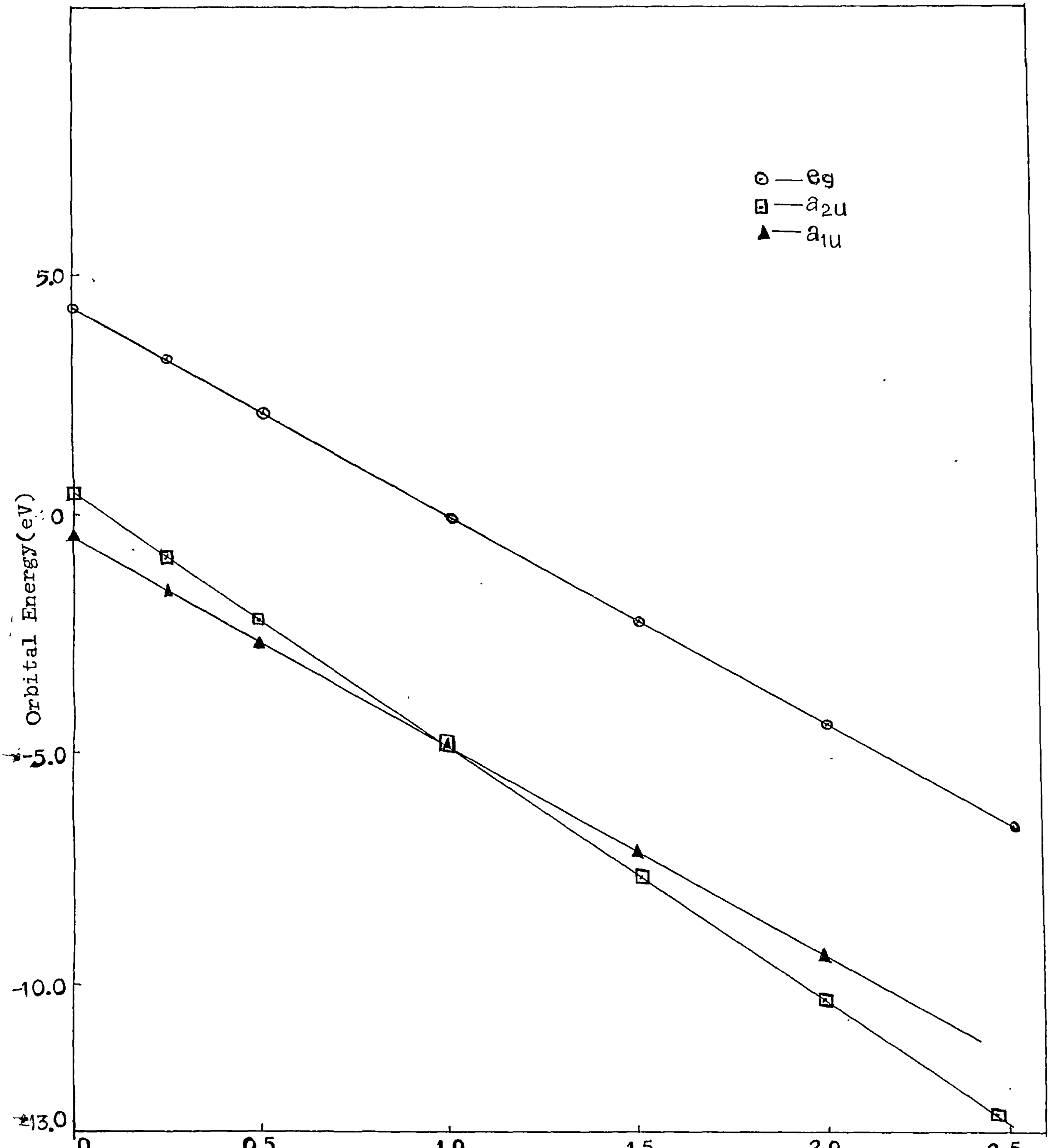

Fig.2.2 Energies of HOMO and LUMO levels of Porphin dianion obtained by SCF perturbation method using PPPwavefunctions

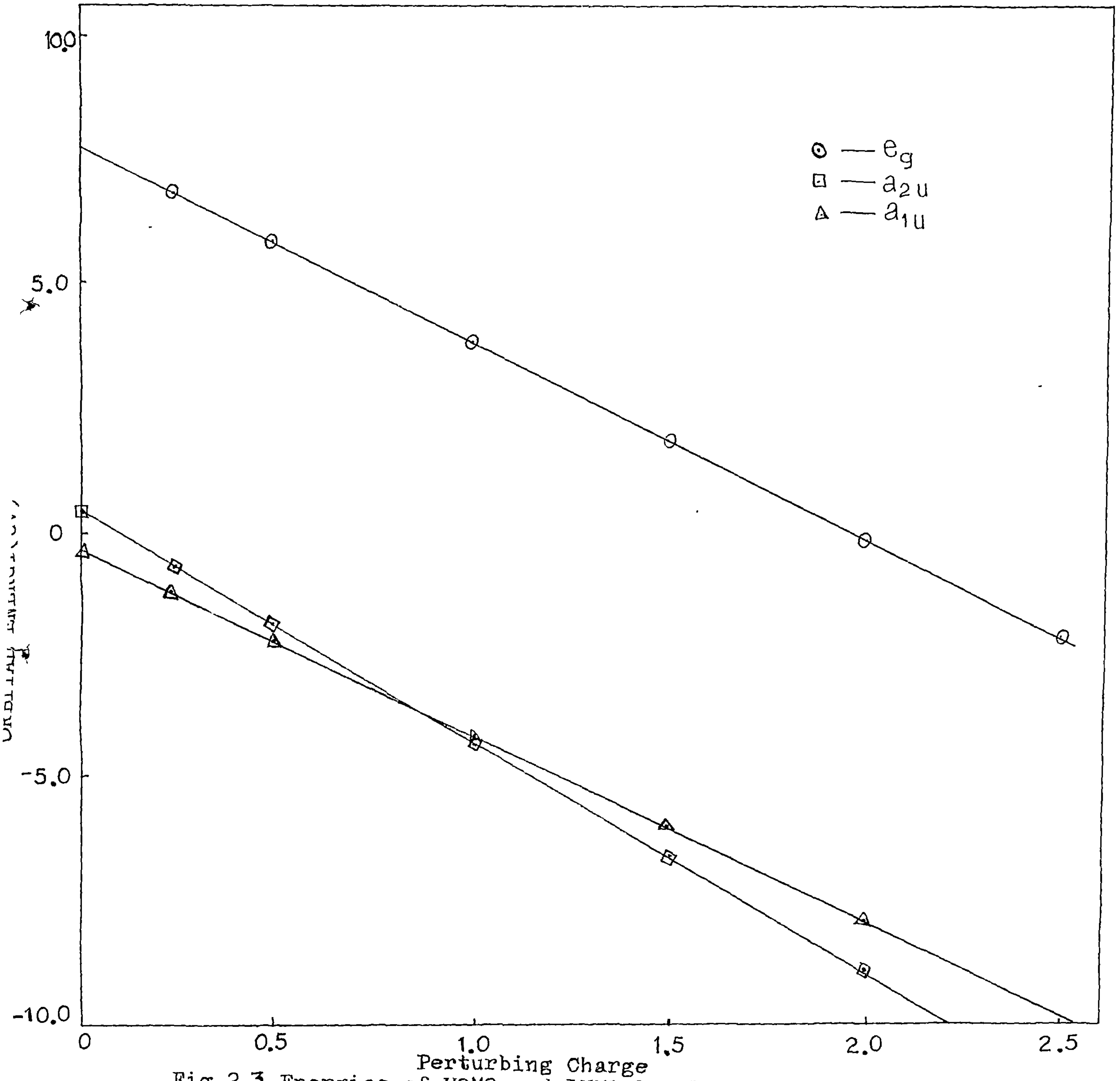

Fig.2.3 Energies of HOMO and LUMO levels of Porphin dianion obtained by SCF perturbation method using CNDO/2 wavefunctions

(a_{1u} and a_{2u}).[20,21] The presence of the counterion changes the residual charge on the metal ion and the electrostatic effect explains the situation.

The energy levels obtained from above perturbation calculations may be correlated with ionisation potentials and redox potentials. Kitagawa et al[14] have observed a linear correlation of the experimental ionisation potentials and oxidation potentials of metallooctaethyl porphyrins. Hence we have fitted the available ionisation potential values of metallooctaethyl porphyrins with their corresponding $E_{1/2}^{(OX)}$ values as follows:

$$IP\ (eV) = 5.896 + 0.5766\ E_{1/2}^{(CX)} \quad .. \quad (II.18).$$

with a standard deviation of 0.036 eV and linear correlation coefficient of 0.922.

From the ionisation potential values (experimental or estimated according to eqn. II.18, using Koopmans' theorem we have obtained the charges/ Table II.1. on the metal ions in various metalloporphyrins, using figures2.1and 2.2As pointed out earlier these charges may be considered as residual charges on the metal ion. A value of 1.34 (PPP) and 1.5 (CNDO/2) for Mg leads to an ionic character of 65% to 75% in the Mg-N σ-bond. On the basis of electronegativity difference between Mg and N we expect an ionic character of 55%. Hence these numbers are not unreasonable. We do not ascribe much importance to the absolute values of these residual charges since they depend on the accuracy of the zeroeth order energy levels as well as the experimental ionisation potential data. The interesting point that emerges out in these calculations is that from Mg(II) to Sn(IV) porphyrins the range of the residual charges is only 0.13 to 0.16 eV. This small range will lead only to marginal differences in the energy gaps between the occupied and the unoccupied π -m.o levels. Hence one does not expect much of a dependence of the electronic spectral transition energies on the metal in the metalloporphyrins. On the other hand, this small range of residual charge leads to an amplified range of oxidation potentials (0.54 V - 1.40 v vs SCE).

The conclusions of the SCF perturbation calculations depend very much on the reasonableness of the fitting of the ionisation potentials and oxidation potentials. To check this, we have fitted the oxidation potentials of a large number of aromatic hydrocarbons with the corresponding $E_{1/2}^{(OX)}$ values. The following expression is obtained with standard deviation and linear correlation coefficient being 0.154 and 0.978 respectively.

$$\mathrm{IP}\ (\mathrm{eV}) = 1.4453\ E_{1/2}^{(OX)} + 6.1880 \qquad (\mathrm{II}.19)$$

where $E_{1/2}^{(OX)}$ is expressed in volts. Accurate ionisation potential data is available from photoelectron spectroscopic data for a large number of hydrocarbons. But similar data is lacking for a large number of metalloporphyrins, since most of these systems are non-volatile. Of the limited number of papers reporting PES data on porphyrins[22-25], only the results of Kitagawa et al[14] appear to be consistent and give good fit with the oxidation potentials. Hence we believe that extrapolating the ionisation potentials of metalloporphyrins from the corresponding oxidation potentials data is reasonable. Thus the electrostatic model to a limited extent does explain the observed trends in the electronic spectra and oxidation potentials of metalloporphyrins.

The computer programme for CNDO/2 calculations was kindly supplied by Prof. D.P. Santry, McMasters University, Ontario, Canada. The programme was modified so as to be used for large molecules upto 150 atomic orbitals. The PPP programme used here is a modified version of QCP 71.2 (Bloor and Gilson, 1974) obtained from Quantum Chemistry Programme exchange.
All the computations were done at the Regional Computer Centre, Jadavpur, Calcutta, using the computer Burroughs 6700.

Table II. 1.

Correlation of oxidation potential[a] ($E_{1/2}$ values), ionisation potentials and the charges obtained from the SCF perturbation calculations. (The experimental data are for metal octaethylporphyrins, OEP).

System	Charge (PPP)	Charge (CNDO/2)	$E^{OX}_{1/2}$ (volts) (vs SCE)	IP
Mg(II)OEP	1.30	1.52	0.54	6.21
Zn(II)OEP	1.31	1.56	0.63	6.26
Ni(II)OEP	1.32	1.58	0.73	6.32
H_2OEP	1.34	1.59	0.81	6.36
Ag(II)OEP	1.38	1.63	1.10	6.53
Al(III)OEP(OH)	1.36	1.61	0.95	6.44[b]
Sn(IV)OEP$(OH)_2$	1.43	1.68	1.40	6.70[b]

[a] $E_{1/2}$ values are taken from reference(11)

[b] IP values are estimated using equation (II.18) in the text. Other values are experimental data from reference (14).

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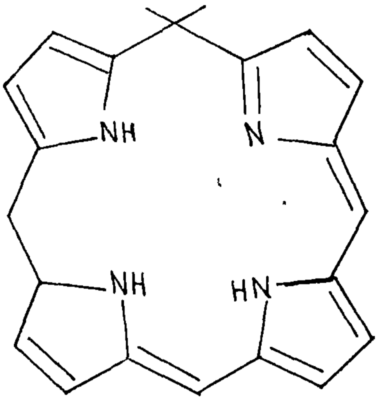
CHAPTER - III

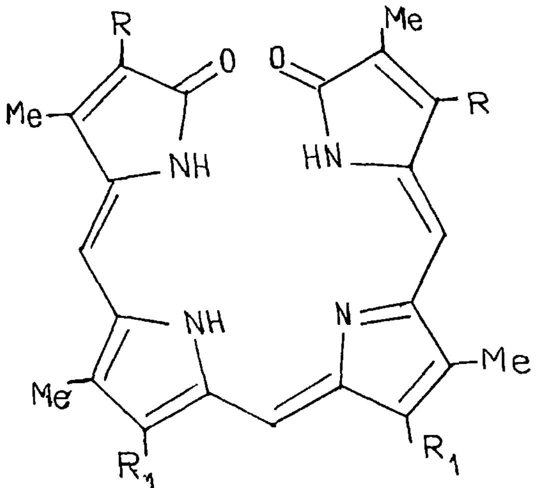
CNDO/2 CALCULATIONS ON PHLORIN TRIANION : CHARGE DISTRIBUTIONS AND REACTIVITY PARAMETERS.

III 1. Introduction

Phlorins are obtained by reversible hydrogenation of methine bridge in a porphyrin periphery. (figure 3.1) They were characterised independently by Woodward and Mauzerall.[1,2] Phlorins are reduced to porphomethanes and dimethanes and are easily oxidised to porphyrins.[2-4] On the basis of kinetic and spectral evidence, phlorins have been postulated as the first intermediates formed during photoreductions of porphyrins.[2] Pulse radiolytic studies of reduction of hematoporphyrin and its zinc complex by anion radicals had revealed that the primary reduction product is of a phlorin type.[5] Phlorins are highly reactive intermediates and can be stabilised by the presence of bulky groups.[6] The electronic spectra of phlorins and their metal complexes generally consist of two bands of nearly equal oscillator strengths occuring around 440 and 880 nm. The visible absorption spectrum is nearly identical to that of ring-opened bilatrine. (figure 3.1) Hence phlorin serves as a model system for a bilatriene in a cis-cis configuration. Closs and Closs generated zinc tetraphenyl phlorin anion which was converted fast into the corresponding chlorin.[7] Whitcock has converted chlorins into a phlorin by heating in tetrahydrofuran-potassium tertiary butoxide-tertiary butanol medium. All the chemical data indicate that phlorin is highly reactive compared to a porphyrin. We have performed CNDO/2 calculation on phlorin



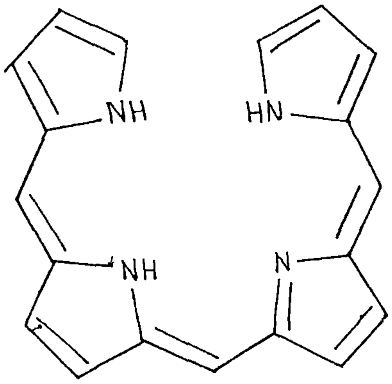
PHLORIN



BILIVERDIN

R = VINYL

R_1 = PHENYL



BILATRIENE

Fig 3.1 SKELETON FOR PHLORIN, BILIVERDIN AND BILATRINE trianion in order to understand its electronic structure in comparison with a porphyrin dianion.(Fig 3.2)

PPP calculations do not distinguish between a phlorin and bilatriene. CNDO/2 calculations point to the participation of the CH_2 group in the pi system. The phlorin trianion is chosen here because of its highly symmetric nature. It is easy to compare the behaviour of phlorin trianion and porphin dianion.

III. 2. Methods of Calculations

SCF calculations on phlorins in the PPP - π framework have already been reported.[9] The saturated methylene group was not included in the PPP calculations. In the present calculations, CNDO/2 formalism is used. The phlorin trianion has C_{2v} symmetry. Since no crystal structure data is available for this system, the coordinates are taken to be the same as those for porphin dianion.[10] The saturated methylene group is taken to lie in the σ_v plane. The CNDO/2 energy levels and wavefunctions are listed in Table III.1.

III.3. Results and Discussion

1. The energy levels obtained from CNDO/2 method for porphyrin dianion and phlorin trianion are compared in Table III.2. The disruption of conjugation in the porphyrin macrocycle leads to the lifting of the near-degeneracy of

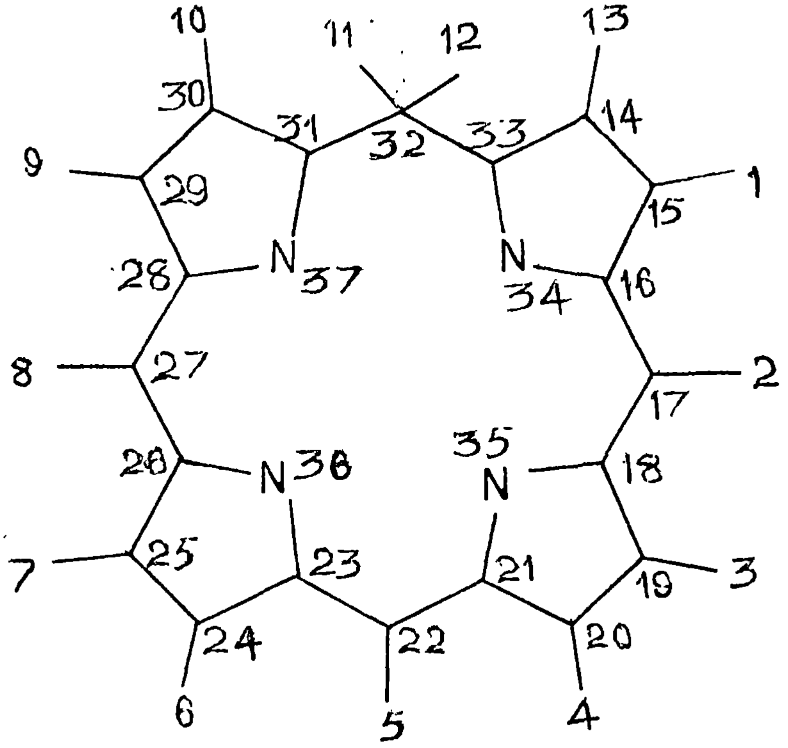


Fig.3.2

SKELETON FOR PHLORIN TRIANION

the HOMO and the true degenaracy of the LUMO levels. In comparison with a porphyrin dianion, the HOMO and LUMO of phlorin trianion are raised. Hence a phlorin trianion is expected to have a lower oxidation potential and a higher reduction potential than the corresponding values of a porphyrin. This pattern of energy levels for phlorin trianion is different from what has been obtained from PPP calculations.

In the PPP calculations for phlorins, the nitrogen parameters are taken as the average of those for three pyrrolic and one pyridine type nitrogen atoms. In a porphyrin the nitrogen parameters are the average of those for two pyrrolic and two pyridine nitrogen atoms. Other parameters are identical for phlorin and porphyrin. Under this condition, if one compares the energy levels of porphyrin (D_{4h}) and phlorin (C_{2v}), the homo level for phlorin is higher and the lumo level is lower than those of the corresponding values of porphyrin. Support for this pattern is indirect from the experimental data on biliverdins.[11] The oxidation and reduction potentials for metallobiliverdins are respectively lower than those of metalloporphyrins. But the biliverdins have a terminal carbonyl groups and they do not truely represent a phlorin or a typical bilatriene. The arbitariness in the choice of nitrogen parameters in PPP calculations should not be overlooked. The results of CNDO/2 calculations on phlorin trianion and porphin dianion are free from the arbitrariness of PPP calculations. Regarding the oxidation potentials, both these methods predict that a phlorin system is more easily oxidised than a porphyrin. This prediction is supported by experimental data. The first oxidation potential for Zn TPP (tetraphenyl porphyrin) is 0.80 V vs SCE whereas the corresponding phlorin anion is oxidised to a porphyrin at a potential of -0.45 V SCE.[12] Regarding the case of reductions the results of these calculations predict opposite trends. PPP calculations indicate that a phlorin has a lower reduction potential than that of a porphyrin, while according to CNDO/2 results phlorin trianion should have a higher reduction potential than that of a porphyrin.

There are two experimental evidences in support of the results of CNDO/2 calculations. A detailed electrochemical and spectroscopic study by Lanese and Wilson has shown that Zn TPP (Zn tetraphenyl porphyrin) is reversibly reduced to its mono anion at -1.35 V vs SCE while the corresponding phlorin anion, $ZnTPPH^-$ is reduced to its radical dianion, $ZnTPPH^{2-}$ at a potential -1.85 V vs SCE.[12] Additional support comes from photoreduction studies on metalloporphyrins. The photoreduction of porphyrins leading to phlorins and further hydrogenated products occurs only in acidic medium and not in alkaline medium. Further reduction of phlorin is very slow compared to porphyrin ⟶ phlorin step.[13,14] These observations strongly support our calculations indicating that phlorins are more difficult to reduce than porphyrins.

More experimental data on bilatrienes and stable phlorins are required to understand the relative reactivities of porphyrins and phlorins. Regarding the charge distributions, there is very little difference between the results of PPP and CNDO/2 calculations. The saturated methylene group is at the nodal plane of the LUMO-wave function. In the wave function corresponding to the HOMO level, the 2p - π charge density of the methylene carbon is very small. Thus the methylene group has very little interaction with the π framework of the phlorin molecule and essentially disrupts the conjugation in the macrocyclic system.

We have compiled the reactivity parameters for phlorin trianion. The frontier orbital charge densities and superdelocalisabilities[15] obtained from PPP and CNDO/2 wavefunctions are listed in Tables III.3 and III.4. The superdelocalisabilities are normalised with respect to the centre having the highest reactivity value. There are only slight differences between the charge densities obtained by PPP and CNDO/2 methods. Based on the charge densities in the HOMO level obtained by both the methods, the first three centers of high electrophilic reactivity in the decreasing order, are $22 > 35 > 17$ (PPP) and $22 > 17 > 33$ (CNDO/2). Based on superdelocalisabilities, the order of electrophilic reactivities are: $35 > 22 > 14$ (PPP) and $22 > 35 > 33$ (CNDO/2).

Summing up, the overall prediction of the order of electrophilic reactivity can be written as $22 > 17 > 33$. Regarding the nucleophilic reactivities, there is a good agreement between the CNDO/2 and PPP - charge densities for the LUMO level. The superdelocalisabilities also predict the same trends as the frontier electron densities. The predicted order of nucleophilic reactivity is $17 > 19 > 21$. The limited experimental data on the reactivity of bile pigments support the above predcitions.

In the porphin dianion, the charge density is uniformly distributed over all the four methine bridge positions; while in a phlorin trianion there is a larger concentration of charge at position 22 in the HOMO and at position 17 in the LUMO. Hence the electrophilic and nucleophilic reactivities are higher for phlorin than what is observed for a porphin.

In summary, we have noticed that the PPP method predicts a phlorin to have lower oxidation and reduction potentials than those of a porphin; while the CNDO/2 calculations indicate that a phlorin should have a lower oxidation potential and a higher reduction potential than the corresponding values of a porphin. The CNDO/2 results are supported by experimental data. Both the methods predict the same pattern of charge density distribution and reactivity parameters.

Table III.1

LCAO coefficients in the CNDO/2 wave functions for Phlorin trianion (only the π orbital functions are included)[a]

Atomic Center	Energy levels (energy values in a.u. in Paranthesis)		
	21(-0.5383)	22(-0.4941)	23(-0.4676)
14	-0.2174	0.1046	-0.1687
15	-0.1872	0.0606	-0.1987
16	-0.2104	0.0190	-0.2583
17	-0.1468	-0.0957	-0.2476
18	-0.1468	-0.2300	-0.2862
19	-0.1142	-0.2357	-0.2368
20	-0.1123	-0.2644	-0.2096
21	-0.1332	-0.3228	-0.1716
22	-0.1161	-0.2999	0.0000
23	-0.1332	-0.3228	0.1716
24	-0.1123	-0.2644	0.2096
25	-0.1142	-0.2357	0.2368
26	-0.1468	-0.2300	0.2862
27	-0.1468	-0.0957	0.2476
28	-0.2104	0.0190	0.2583
29	-0.1872	0.0606	0.1987
30	-0.2174	0.1046	0.1687
31	-0.3032	0.1650	0.1495
32	-0.3931	0.2563	-0.0000
33	-0.3032	0.1650	-0.1495
34	-0.2039	0.0761	-0.1729
35	-0.1147	-0.2379	-0.2011
36	-0.1147	-0.2379	0.2011
37	-0.2039	0.0761	0.1729

Table III.1 continued

Atomic Center	Enefgy levels (energy values in a.u. in paranthesis) 29(-0.3883)	32(-0.3229)	38(-0.1826)
14	0.2592	-0.1314	0.1994
15	0.2589	-0.2474	0.1663
16	0.2273	-0.3980	-0.0014
17	0.0168	-0.2236	-0.2380
18	-0.1799	-0.0934	-0.3000
19	-0.2347	0.0113	-0.2247
20	-0.2437	0.0877	-0.0212
21	-0.1924	0.1475	0.2682
22	0.0000	0.1860	0.4742
23	0.1924	0.1475	0.2682
24	0.2437	0.0877	0.0212
25	0.2447	0.0113	-0.2247
26	0.1799	-0.0934	-0.3000
27	-0.0168	-0.2236	-0.2380
28	-0.2273	-0.3080	-0.0014
29	-0.2589	-0.2474	0.1663
30	-0.2592	-0.1314	0.1994
31	-0.2248	0.0290	0.0901
32	0.0000	0.4281	-0.1643
33	0.2248	0.0290	0.0901
34	0.2415	-0.1450	0.0649
35	-0.1852	0.0337	-0.0125
36	0.1852	0.0337	-0.0125
37	-0.2125	-0.1450	0.0649

Table III.1 continued.

Atomic Center	Energy levels (energy values in a.u. in paranthesis 43(-0.1190)	47(-0.0758)	50 (-0.0107)
14	-0.2717	0.2080	-0.1328
15	-0.1012	0.1114	-0.0553
16	0.2043	-0.1318	0.1188
17	0.3801	-0.2135	0.0875
18	0.2311	-0.1071	-0.0677
19	-0.1348	0.3550	0.3236
20	-0.3002	0.3671	0.2441
21	-0.1649	-0.1065	-0.2455
22	0.0000	-0.2283	0.0000
23	0.1649	-0.1065	0.2455
24	0.3003	0.3671	-0.2441
25	0.1348	0.3550	-0.3236
26	-0.2311	-0.1071	0.0677
27	-0.3801	-0.2135	-0.0875
28	-0.2043	-0.1318	-0.1188
29	0.1013	0.1114	0.0553
30	0.2717	0.2080	0.1328
31	0.1994	0.0836	0.0386
32	0.0000	-0.0729	-0.0000
33	-0.1994	0.0836	-0.0386
34	-0.0023	-0.0470	0.0857
35	0.0313	-0.2283	-0.4686
36	-0.0313	-0.2283	0.4686
37	0.0023	-0.0470	0.0857

Table III.1 continued.

Atomic Center	Energy levels (energy values in a.u. in paranthesis		
	51(0.0058)	53(0.0136)	56(0.0519)
14	0.3053	0.2371	-0.1192
15	0.2995	0.3626	0.1899
16	-0.1580	-0.0386	0.2472
17	-0.0022	0.0772	0.1672
18	0.1366	0.0652	-0.1508
19	-0.0607	0.0666	-0.0295
20	-0.1317	-0.0130	0.1122
21	-0.0116	-0.0972	0.0227
22	-0.0988	-0.0000	0.2736
23	-0.0116	0.0972	0.0227
24	-0.1317	0.0130	0.1122
25	-0.0607	-0.0666	0.0295
26	0.1366	-0.0652	-0.1508
27	-0.0022	-0.0772	0.1672
28	-0.1580	0.0386	0.2472
29	0.2995	-0.3626	0.1899
30	0.3053	-0.2371	-0.1192
31	-0.1482	0.2771	-0.3109
32	0.0439	-0.0000	0.0998
33	-0.1482	-0.2771	-0.3109
34	-0.4232	-0.4502	-0.1661
35	0.1949	-0.0842	-0.3397
36	0.1949	0.0842	-0.3397
37	-0.4232	0.4502	-0.1661

Table III.1 continued.

Atomic center	Energy levels (energy values in a.u. in paranthesis 57(0.1102)	 58(0.2082)	 59(0.4412)
14	-0.2122	-0.1644	0.1463
15	0.1803	0.1647	-0.2053
16	0.3299	0.2118	-0.0734
17	-0.0514	-0.2546	0.4013
18	-0.3065	-0.1847	-0.1057
19	-0.1578	-0.0578	-0.2723
20	0.1771	0.1505	0.1894
21	0.2674	0.0649	0.2317
22	0.0000	-0.4380	-0.0000
23	-0.2674	0.0649	-0.2317
24	-0.1771	0.1505	-0.1894
25	0.1578	-0.0578	0.2723
26	0.3065	-0.1847	0.1057
27	0.0514	-0.2546	-0.4013
28	-0.3299	0.2118	0.0730
29	-0.1803	0.1646	0.2053
30	0.2122	-0.1644	-0.1463
31	0.2942	-0.1990	-0.1501
32	0.0000	0.0112	0.0000
33	-0.2942	-0.1990	0.1501
34	0.0409	+0.1173	-0.1790
35	0.0320	0.3300	-0.2015
36	-0.0320	0.3300	0.2015
37	-0.0409	0.1173	0.1790

Table III.1 continued.

Atomic center	Energy levels (energy values in a.u. in paranthesis) 60(0.4824)	61(0.6404)	62(0.6697)
14	-0.0972	0.3482	0.0192
15	0.1640	-0.2061	-0.0294
16	0.0070	-0.0799	0.0260
17	-0.3245	0.0244	0.0096
18	0.1684	0.0554	-0.0612
19	0.3242	-0.0750	0.3057
20	-0.3242	0.0528	-0.4181
21	-0.1376	0.0032	0.4229
22	0.3213	-0.0087	-0.0000
23	-0.1376	0.0032	-0.4229
24	-0.3242	0.0528	0.4181
25	0.3242	-0.0750	-0.3057
26	0.1684	0.0554	0.0612
27	-0.3245	0.0244	-0.0096
28	0.0070	-0.0799	-0.0260
29	0.1640	-0.2061	0.0294
30	-0.0972	0.3482	-0.0192
31	-0.1132	0.2823	-0.0021
32	-0.0377	-0.3541	-0.0000
33	-0.1139	-0.2823	-0.0021
34	0.1724	0.2744	-0.0179
35	-0.0021	-0.0391	-0.2165
36	-0.0021	-0.0391	0.2165
37	0.1724	0.2744	0.0179

Table III.1 continued.

Atomic center	Energy levels (energy values in a.u. in paranthesis) 63(0.6754)	64(0.6780)	69(0.6940)
14	0.2014	0.2417	-0.3599
15	-0.2984	-0.3293	0.1810
16	0.2644	0.2754	0.0673
17	0.0502	0.0415	0.0402
18	-0.3128	-0.3020	-0.1303
19	0.3133	0.2009	0.0832
20	-0.2169	-0.0489	-0.0268
21	0.0274	-0.1609	-0.0479
22	-0.0065	-0.0000	0.0000
23	0.0274	0.1609	0.0479
24	-0.2169	0.0489	0.0268
25	0.3133	-0.2009	-0.0836
26	-0.3128	0.3020	0.1303
27	0.0502	-0.0415	-0.0402
28	0.2644	-0.2754	-0.0673
29	-0.2984	0.3293	-0.1810
30	0.2014	-0.2417	0.3599
31	-0.0013	0.0368	0.4356
32	0.0101	0.0000	-0.0000
33	-0.0013	-0.0368	0.4356
34	-0.1746	-0.1588	-0.3244
35	0.1531	0.2631	0.0977
36	0.1531	-0.2631	-0.0977
37	-0.1746	0.1588	0.3244

Table III.1 continued.

Atomic center	Energy levels (energy values in a.u. in paranthesis) 78(0.7453)	79(0.7712)	80(0.7720)	84(0.8045)
14	-0.0850	-0.0442	-0.1039	-0.1334
15	0.1501	0.1788	0.1619	0.0018
16	-0.2208	-0.3591	-0.2603	0.1390
17	0.1668	0.3364	0.2813	-0.0944
18	-0.1138	-0.3263	-0.3045	0.0700
19	0.1686	0.1475	0.0941	-0.0259
20	-0.2517	-0.0410	0.0606	0.0025
21	0.4161	-0.0663	0.2733	0.0244
22	-0.3808	-0.0000	0.2444	-0.0221
23	0.4161	0.0663	-0.2733	0.0245
24	-0.2517	0.0410	0.0606	0.0025
25	0.1686	-0.1475	0.0941	-0.0259
26	-0.1138	0.3263	-0.3045	0.0700
27	0.1668	-0.3364	0.2813	-0.0944
28	-0.2208	0.3591	-0.2603	0.1390
29	0.1501	-0.1738	0.1619	0.0018
30	-0.0850	0.0442	-0.1039	-0.1334
31	0.0131	0.0939	0.0611	0.3317
32	-0.0943	0.0000	-0.1368	-0.6177
33	0.0131	-0.0939	0.0611	0.3317
34	0.1099	0.2245	0.0919	-0.2209
35	-0.1515	0.1743	0.2556	-0.0363
36	-0.1515	-0.1743	0.2556	-0.0363
37	0.1099	-0.2245	0.0919	-0.2209

a: only the $2p_z$ of carbon and nitrogen orbital coefficients are included.
The highest occupied orbital belongs to the level no. 56.

Table III. 2.

CNDO/2 molecular orbital energies of phlorin trianion amd porphin dianion.

Phlorin trianion		Porphin dianion	
orbital no.	energy (a.u.)	orbital no.	energy (a.u.)
63	0.6754	63 e_g	0.5351
62	0.6697	62	
61	0.6404	61	0.5284
60	0.4824	60	0.3809
59 (LUMO)	0.4412	59 LUMO e_g	0.2876
58 (HOMO)	0.2082	58	
57	0.1102	57 (HOMO 1)	0.0166
56	0.0519	56 (HOMO 2)	-0.0096

Table III. 3.

Nucleophilic Reactivity parameters of phlorin trianion

Atomic center	Frontier electron density		Superdelocalisability	
	PPP	CNDO/2	PPP	CNDO/2
14	0.0051	0.0214	0.43	0.72
15	0.0575	0.0422	0.62	0.74
16	0.0024	0.0054	0.43	0.66
17	0.1777	0.1610	1.00	1.00
18	0.0035	0.0112	0.50	0.77
19	0.0733	0.0741	0.71	0.94
20	0.0086	0.0359	0.55	0.82
21	0.0854	0.0537	0.71	0.91
22	0.0000	0.0000	0.55	0.55
33	0.0494	0.0225	0.64	0.71
34	0.0142	0.0320	0.25	0.72
35	0.0226	0.0460	0.21	0.53

$$\text{Superdelocalisability (Nucleophilic)} = \sum_{j}^{vac} \frac{C_j^2}{E_j}$$

Table III. 4.

Electrophilic Reacticity Parameters of Phlorin trianion.

Atomic center	Frontier Electron density		Superdelocalisability	
	PPP	CNDO/2	PPP	CNDO/2
14	0.0094	0.0270	0.81	0.62
15	0.0490	0.0270	0.77	0.59
16	0.0330	0.0449	0.76	0.63
17	0.0883	0.0648	0.68	0.53
18	0.0500	0.0341	0.71	0.53
19	0.0074	0.0033	0.71	0.43
20	0.0518	0.0226	0.77	0.51
21	0.0019	0.0042	0.60	0.39
22	0.2056	0.1918	0.92	1.00
33	0.0610	0.0396	0.74	0.64
34	0.0039	0.0137	0.94	0.60
35	0.0405	0.1089	1.00	0.89

Superdelocalisability (Electrophilic) $= \sum_{i}^{occ} \frac{C_i^2}{E_i}$

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CHAPTER IV

CNDO/2 CALCULATIONS ON CORROLES AND TETRADEHYDROCORRINS

IV. 1. Introduction

Corroles and tetradehydrocorrins are related to vitamin B_{12} system.[1,2] Corrole is a macrocyclic conjugated system which contains one methine bridge less than porphyrins (figure 4.1, 4.2, 4.3). Similar to the porphyrin, a corrole can be visualised as 18 membered annulene system. The optical absorption spectrum supports this view. An intense, 'Soret band' is observed around 400 nm and a weak 'visible' band is observed at 500-600 nm range.[3] The nmr data is also indicative of the aromatic character of corrole.[1] However, X-ray structure of corrole has shown appreciable deviation from planarity.[4,5] Corroles form complexes with a number of metals like Cu, Ni, Co, Pd etc.[7,8] Divalent metal ions form N protonated neutral metallocorroles. Complexes of corroles with Ni(II) and Pd(II) are non-aromatic with one of the potentially tautomeric hydrogen atoms being displaced from nitrogen to carbon in such a way as to interrupt the macrocyclic conjugation of the chromophore. The localtion of the displaced proton is still unresolved. The Ni(II) and Pd(II) complexes are paramagnetic.[7] This paramagnetism is due to the presence of radical species in the complexes which arise from the loss of the blocking hydrogen atom. The free radical formed in this manner is a delocalised metallocorrole radical. The metallocorroles can also be easily deprotonated to yield the corresponding aromatic anions.[7,8] Co(III) corrole

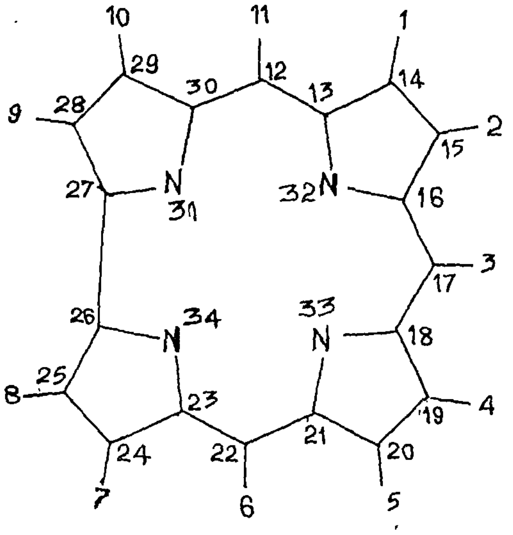


Fig. 4.1

SKELETON FOR CORROLE TRIANION

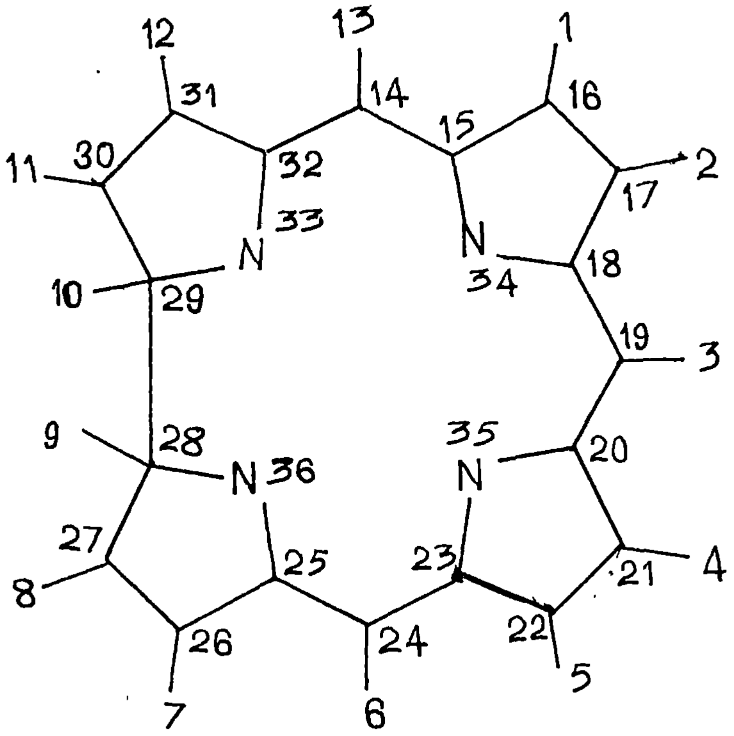
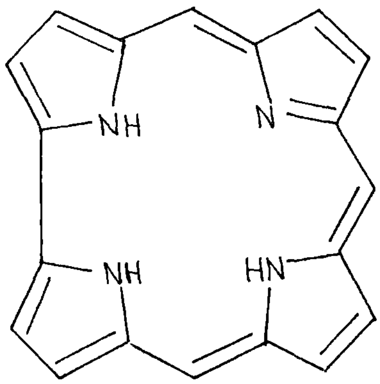
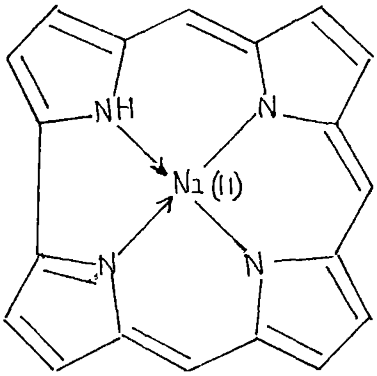


Fig. 4.2

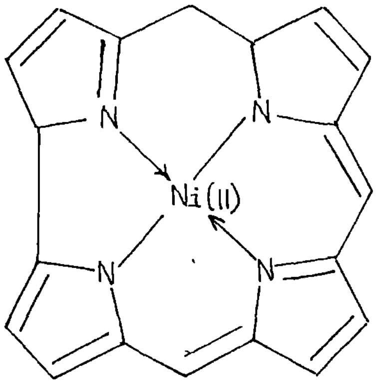
SKELETON FOR TETRADEHYDROCORRIN MONOANION



CORROLE FREEBBASE



N-PROTONATED Ni(II) COMPLEX



Ni(II) - CORROLE MONOANION

Fig° 4.3
SKELETON FOR CORROLE FREE BASE, N-PROTONATED Ni(II) COMPLEX, Ni(II) CORROLE MONOANION

which is a neutral species., has been reduced to Co(II) corrole anion. The electronic spectra of the metallocorrole anions are very similar to the corresponding metalloporphyrins, indicating the aromatic character of the macrocycle. SCF -π electron calculations have been done in the PPP framework, including configuration interaction for corrole trianion. The effect of metal was considered indirectly by changing the nitrogen parameters.[9-11] Reasonable agreement has been obtained between experimental spectra and the results of PPP calculation

The macrocyclic conjugation in corrole is broken down by introducing two hydrogen atoms, to form a tetradehydrocorrin. The structural relationship between a corrole and tetradehydrocorrin is similar to that between a porphyrin and phlorin. The non-aromatic nature of tetradehydrocorrin macrocycle is emphasised by the comparatively high τ- values of the signals due to meso protons.[1] The visible electronic spectrum of a Ni(II) tetradehydrocorrin salt is similar to that of a metallophlorin.[1] The bands at 350 nm and 550 nm have comparable extinction coefficients. Stable Co(II) and Ni(II) salts have been obtained for 1, 19 dialkyl tetradehydrocorrin systems. Electrochemical and ESR studies have indicated[12] that Ni(II) salts are reduced to the radical anions and dianions; whereas Co(II) tetradehydrocorrins are reduced to Co(I) systems and Co(II) dianions. Further studies have shown that in Co(II) corrole anion and Co(II) tetradehydrocorrin cation, the central cobalt atom has different electronic ground states.[13]

IV.2. Methods of Calculation

To our knowledge, calculations beyond the PPP level have not appeared in the literature for corroles and tetradehydrocorrins. We report here CNDO/2 calculations on the ground states of corrole trianion and tetradehydrocorrin anion, which have the same symmetry of their metal complexes (fig. 4.1 and 4.2). Idealised geometry has been used for these two systems. While the PPP and CNDO/2 energy levels and wave functions for corrole trianion are presented in Table IV.1 and IV.2 respectively, the corresponding energy levels and wave functions for tetradehydrocorrin mono anion are summarised in Tables IV.3 and IV.4. The reactivity parameters have been computed in the same manner as we have done for phlorin. (see Tables IV. 5,6,7 and 8).

IV.3. Results and Discussion

A comparison of the energy levels of porphine dianion, phlorin trianion, corrole trianion and tetradehydrocorrin mono anion is made in Table IV. 9. Though the charges on these ions are different they are taken prototypes for their corresponding metal complexes with bivalent metal ions. Thus the corresponding M(II) metal complexes are: M(II) porphyrin, M(II) phlorin anion, M(II) corrole anion, M(II) tetradehydrocorrin cation. The effect of M^{2+} on the orbital energy of the ligand may not be the same for all these four ions but one may expect some approximate correlations of energies between the deprotonated ligands and their corresponding metal complexes. The comparison in Table IV.9. is made with this point of view. Since no ionisation potential data is available, the trends in redox potentials of the metal complexes may be correlated with the trends in the calculated energy values. Ni(II) porphyrin and Ni(II) tetradehydrocorrin have similar reduction potentials, (-1.50 V and -1.60 V vs SCE respectively). Ni(II) corrole is reduced at a much higher value (-2.34 V vs SCE).[13] Though the data for Ni(II) phlorin is not available, metallophlorins undergo one-electron reduction around -1.90 V vs SCE.[14] The orbital energies for LUMO levels for these four ligands also reflect the same trend. The LUMO energy value for corrole trianion and phlorin trianion are high compared with the corresponding values of porphine dianion and tetradehydrocorrin mono anion. Thus the relative orbital energies obtained for these four systems appear to be reasonable.

The reactivity parameters, namely frontier electron density, and superdelocalisability for corrole trianion and tetradehydrocorrin anion obtained from PPP and CNDO/2 methods are compared in Tables IV. 5-9. Regarding the centers for the highest electrophilic or nucleophilic reactivity there is no ambiguity in the reactivity parameters. Thus in the case of corrole trianion, for electrophilic reactivity, both the PPP and CNDO/2 data point to position 17 as the most probable centre. Regarding the centres of next priority for electrophilic reactivity, superdelocalisabilities and frontier electron densities obtained from the same method (PPP or CNDO/2) do not agree. Considering both the CNDO/2 and PPP-data together we have four reactivity parameters for each center for each type of reactivity. The overall order of electrophilic reactivity may be summarised for corrole trianion as follows: The centre of highest reactivity is predicted to be the position '17'. Other centers of comparable reactivities correspond to positions 32, 31, 12 and 29. The limited data on electrophilic substitution reactions in corroles indicate[7,8] that alkylation occurs at positions 32, 31 and 29. No alkylation has been reported in the position 17. No data is available for the nucleophilic reactivity of corroles. Analysis of the reactivity parameters indicates that position 12 is the most probable centre for nucleophilic reactivity. Other centres which are likely to undergo nucleophilic addition correspond to positions 14, 15 and 29.

In the case of tetradehydrocorrin, high electrophilic reactivity is predicted at positions 19 and 14. This is observed experimentally. Bromination occurs at positions 14 and 22 leading to the dibromo derivative.[15] Nitration occurs at positions 14, 19 and 24. Mono- di- and trinitro derivatives are known.[16-18] Formylation occurs only at position 19.

Regarding the nucleophilic reactivity of tetradehydro corrin system, the PPP parameters are at variance from those obtained from CNDO/2 method. Experimental data appears to support the CNDO/2 calculations. The highest nucleophilic reactivity is predicted at positions 14 and 24 (CNDO/2), which is observed experimentally.[16]

IV. 4. Conclusion

In conclusion it can be pointed out that CNDO/2 calculations lead to correct ordering of energy levels for corrole and tetradehydro corrin. The relative orbital energies of the HOMO and LUMO levels of porphine, phlorin, corrole and tetradehydrocorrin also appear to be in the right direction as indicated by the redox potential data. The overall reactivities are also predicted better by the CNDO/2 method than by the PPP approach. It should also be pointed out here that the semi empirical methods in the ZDO framework have severe limitations, particularly when $\sigma - \pi$ interactions are strong. More sophisticated methods are required to treat systems like corrole and tetradehydrocorrins, and related systems.

Table IV.1

LCAO coefficients in the PPP wave function for corrole trianion.

Atomic Center	Energy levels (energy values in a.u in parenthesis) 1(-16.3284)	2(-16.0158)	3(-15.8849)	4(-15.3913)
12	0.1386	0,0363	-0.1708	-0.0563
13	0.1681	0.2178	-0.2859	0.1242
14	0.0811	0.1213	-0.1428	0.0768
15	0.0783	0.1370	-0.1258	0.0840
16	0.1568	0.2815	-0.2201	0.1506
17	0.1028	0.1941	0.0000	-0.0000
18	0.1568	0.2815	0.2201	-0.1506
19	0.0783	0.1370	0.1258	-0.0840
20	0.0811	0.1213	0.1428	-0.0768
21	0.1681	0.2178	0.2859	-0.1242
22	0.1386	0.0363	0.1708	0.0562
23	0.2412	-0.1178	0.1857	0.2765
24	0.1211	-0.0702	0.0834	0.1430
25	0.1332	-0.0932	0.0587	0.1176
26	0.2893	-0.2062	0.0898	0.1845
27	0.2893	-0.2062	-0.0898	-0.1845
28	0.1332	-0.0932	-0.0587	-0.1176
29	0.1211	-0.0702	-0.0834	-0.1430
30	0.2412	-0.1178	-0.1857	-0.2765
31	0.4145	-0.2729	-0.2432	-0.4738
32	0.2528	0.4186	-0.4386	0.2767
33	0.2528	0.4186	0.4386	-0.2767
34	0.4145	-0.2729	0.2432	0.4738

Table IV.1 continued.

Atomic Center	Energy levels (energy values in a.u in parenthesis) 5(-12.4890)	6(-11.5601)	7(-11.3784)	-8(-11.1171)
12	0.3341	0.3349	-0.1110	0.0102
13	0.3002	0.3002	0.0475	0.0702
14	0.1109	0.1109	-0.2630	0.1398
15	-0.1060	-0.1060	-0.3502	0.0932
16	-0.2967	-0.2967	-0.1708	-0.0361
17	-0.3648	-0.3648	-0.2831	-0.0544
18	-0.2967	-0.2967	-0.1708	-0.0363
19	-0.1060	-0.1060	-0.3502	0.0922
20	0.1109	0.1109	-0.2630	0.1389
21	0.3002	0.3002	0.0475	0.0702
22	0.3341	0.3341	-0.1110	0.0104
23	0.2269	0.2269	-0.1784	-0.0708
24	0.0880	0.0880	-0.0646	0.3131
25	-0.0807	-0.0807	0.0877	0.4352
26	-0.2254	-0.2254	0.1802	0.2098
27	-0.2254	-0.2254	0.1802	0.2098
28	-0.0807	-0.0807	0.0877	0.4347
29	0.0880	0.1880	-0.0646	0.3125
30	0.2260	0.2269	-0.1784	-0.0709
31	-0.0597	-0.0597	-0.0302	-0.3513
32	0.0120	0.0120	0.3838	-0.0679
33	0.0120	0.0120	0.3838	-0.0673
34	-0.0597	-0.0597	-0.0302	-0.3517

Table IV.1 continued.

Atomic center	Energy levels (energy values in [illegible] parenthesis) 9(-11.1149)	10(-10.8665)	11(-10.8331)	12(-8.7614)
12	0.0714	-0.0761	-0.2034	-0.0950
13	0.0032	0.1836	-0.1767	0.2765
14	-0.3693	0.3436	0.0738	0.1854
15	-0.4118	0.1963	0.2366	-0.1476
16	-0.1001	-0.1507	0.1890	-0.2890
17	-0.0001	-0.2744	0.0000	0.0000
18	0.1000	-0.1507	-0.1890	0.2890
19	0.4121	0.1963	-0.2366	0.1476
20	0.3697	0.3436	-0.0738	-0.1854
21	-0.0030	0.1836	0.1767	-0.2765
22	-0.0713	-0.0761	0.2034	0.0949
23	-0.0812	-0.2768	0.3780	0.3382
24	-0.2137	-0.3100	-0.3415	0.1118
25	-0.1722	-0.0775	-0.4136	-0.2642
26	0.0119	0.2293	-0.1217	-0.2705
27	-0.0114	0.2293	0.1217	0.2705
28	0.1733	-0.0775	0.4136	0.2642
29	0.2145	-0.3100	0.3415	-0.1118
30	0.0810	-0.2768	-0.3780	-0.3382
31	-0.1722	0.0920	-0.1587	0.0676
32	-0.2582	-0.0620	-0.0335	0.0200
33	-0.2584	-0.0620	0.0335	-0.0200
34	0.1714	0.0920	0.1587	-0.0676

Table IV.1 continued

Atomic center	Energy levels (Energy values in a.u in paranthesis) 13(-8.0867)	14(-3.7974)	15(-3.2145)	16(-0.8838)
12	0.3634	0.4032	0.2760	-0.1634
13	0.1834	-0.0116	-0.2465	-0.1950
14	-0.1257	-0.2531	-0.2242	0.2127
15	-0.2136	0.0713	0.3086	-0.1354
16	0.0620	0.2630	0.1048	-0.0785
17	0.4458	0.0000	-0.4378	0.1430
18	0.0620	-0.2630	0.1048	-0.0785
19	-0.2136	-0.0713	0.3086	-0.1354
20	-0.1257	0.2531	-0.2242	0.2127
21	0.1834	0.0116	-0.2464	-0.0949
22	0.3634	-0.4032	0.2760	-0.1634
23	-0.0862	0.1264	0.1253	0.2849
24	-0.2294	0.2263	-0.1493	0.0881
25	-0.0132	-0.1820	-0.0672	-0.3687
26	0.2305	-0.2281	0.1828	0.3084
27	0.2305	0.2281	0.1828	0.3084
28	-0.0132	0.1820	-0.0672	-0.3687
29	-0.2294	-0.2663	-0.1493	0.0881
30	-0.0862	-0.1264	0.1253	0.2849
31	-0.1268	-0.0638	-0.1716	-0.2432
32	-0.2005	-0.1511	0.0726	0.0721
33	-0.2005	0.1511	0.0726	0.0721
34	-0.1268	0.0638	-0.1716	-0.2432

Table IV.1 continued.

Atomic center	Energy values (energy levels in a.u in paranthesis)			
	17(-0.3179)	18(0.3657)	19(0.4619)	20(1.4865)
12	-0.0996	0.0657	-0.0571	-0.1140
13	0.3224	-0.2898	-0.1358	0.1147
14	-0.0684	0.2770	0.3570	-0.0823
15	-0.2097	-0.1390	-0.4049	0.0449
16	0.3586	-0.0871	0.2597	0.0020
17	-0.0000	0.1226	-0.0000	0.0000
18	-0.3586	-0.0871	-0.2597	-0.0020
19	0.2097	-0.1390	0.4049	-0.1449
20	0.0684	0.2770	-0.3570	0.0823
21	-0.3224	-0.2898	0.1358	-0.1147
22	0.0996	0.0657	0.0571	0.1140
23	0.2044	0.1982	-0.2270	-0.1113
24	-0.2370	-0.3560	0.1930	-0.1340
25	0.0892	0.3220	-0.0642	0.3523
26	0.1328	-0.1106	-0.1043	-0.5180
27	-0.1328	-0.1106	0.1043	0.5180
28	-0.0892	0.3220	0.1643	-0.3523
29	0.2370	-0.3560	-0.1930	0.1340
30	-0.2044	0.1982	0.2270	0.1113
31	0.1312	-0.0330	-0.1170	-0.2022
32	-0.2611	0.1322	-0.0443	-0.0369
33	0.2611	0.1322	0.0443	0.0369
34	-0.1312	-0.1330	0.1170	0.2022

Table IV.1 continued.

Atomic center	Energy values (energy levels in β.u in paranthesis) 21(1.5673)	22(1.5728)	23(1.5962)
12	0.2784	-0.3158	0.1811
13	-0.2723	0.3104	-0.1781
14	0.2650	-0.2130	-0.0379
15	-0.2457	0.1133	0.2350
16	0.2029	0.0033	-0.4304
17	-0.2032	0.0000	0.4394
18	0.2029	-0.0033	-0.4304
19	-0.2458	-0.1133	0.2350
20	0.2650	0.2130	-0.0379
21	-0.2723	-0.3104	-0.1781
22	0.2786	0.3158	0.1811
23	-0.2928	-0.3291	-0.1838
24	0.2170	0.2769	0.1342
25	-0.1200	-0.1956	-0.0739
26	0.0038	0.0846	0.0020
27	0.0038	-0.0846	0.0020
28	-0.1200	0.1957	-0.0739
29	0.2170	-0.2769	0.1342
30	-0.2928	0.3291	-0.1838
31	0.0909	-0.0758	0.0567
32	0.0202	-0.0979	0.1910
33	0.0202	0.0979	0.1910
34	0.0909	0.0758	0.0567

Table IV.2

LCAO coefficients in the CNDO/2 wave functions for Corrole (only the pi orbital functions are included)[a]

Atomic	Energy levels (energy values in a.u in paranthesis)			
Center	20(-0.5187)	22(-0.4648)	24(-0.4609)	29(-0.3640
12	-0.2092	-0.2656	-0,0122	0.0693
13	-0.2428	-0.3150	-0.1510	-0.1464
14	-0.1906	-0.2470	0.1803	-0.2106
15	-0.1904	-0.2151	0.2161	-0.2271
16	-0.2262	-0.1836	0.2664	-0.1872
17	-0.1876	-0.0000	0.2412	0.0000
18	-0.2262	0.1836	0.2664	0.1872
19	-0.1904	0.2151	0.2161	0.2271
20	-0.1906	0.2470	0.1803	0.2106
21	-0.2428	0.3150	0.1510	0.1464
22	-0.2092	0.2656	-0.0122	-0.0693
23	-0.2402	0.2512	-0.1898	-0.2946
24	-0.1794	0.1702	-0.1937	-0.2866
25	-0.1723	0.1205	-0.2202	-0.2405
26	-0.2300	0.0882	-0.2964	-0.1652
27	-0.2300	-0.0882	-0.2964	0.1652
28	-0.1723	-0.1205	-0.2202	0.2405
29	-0.1794	-0.1702	-0.1937	0.2866
30	-0.2402	-0.2512	-0.1898	0.2946
31	-0.2048	-0.1552	-0.2235	0.2381
32	-0.2038	-0.2253	0.1947	-0.1791
33	0.2038	-0.2253	0.1947	0.1791
34	-0.2048	0.1552	-0.2235	-0.2381

Table IV.2 continued

Atomic Center	Energy levels (energy values in a.u in paranthesis) 33(-0.2151)	40(-0.1016)	44(-0.0809)	47(-0.0253)
12	0.3499	0.3704	-0.1311	-0.0505
13	0.2913	0.2498	0.0681	-0.1501
14	0.1127	-0.1138	0.3841	0.1494
15	-0.0913	-0.3019	0.2746	0.2146
16	-0.2719	-0.1938	-0.1825	0.0040
17	-0.3889	0.0000	-0.3631	0.0587
18	-0.2719	0.1938	-0.1825	0.0040
19	-0.0913	0.3019	0.2746	0.2146
20	0.1127	0.1138	0.3841	0.1494
21	0.2913	-0.2498	0.0681	-0.1501
22	0.3499	-0.3704	-0.1311	-0.0505
23	0.1843	-0.1252	-0.2236	0.1086
24	0.0156	0.1753	-0.1502	0.3958
25	-0.1504	0.2995	0.0666	0.2094
26	-0.2491	0.1479	0.2379	-0.2612
27	-0.2491	-0.1479	0.2379	-0.2612
28	-0.1504	-0.2995	0.0666	0.2094
29	0.0156	-0.1753	-0.1502	0.3958
30	0.1843	0.1252	-0.2236	0.1086
31	-0.0557	-0.0245	0.0255	-0.2478
32	-0.0123	0.0128	-0.1474	-0.2508
33	-0.0123	-0.0128	-0.1474	-0.2508
34	-0.0557	0.0245	0.0255	-0.2478

Table IV.2 continued

Atomic Center	Energy levels (energy values in a.u in paranthesis) 50(-0.0099)	52(0.0185)	53(0.0324)	54(0.14435)
12	0.0796	-0.0615	0.0942	0.0545
13	-0.0297	0.1957	0.1528	-0.2618
14	0.3545	-0.0726	0.0661	-0.1456
15	0.2398	-0.1835	-0.0860	0.1688
16	-0.2381	-0.0418	-0.1345	0.2226
17	0.0000	-0.2025	0.0000	0.0000
18	0.2381	-0.0418	0.1345	-0.2226
19	-0.2398	-0.1835	0.0860	-0.1688
20	-0.3545	-0.0726	-0.0661	0.1456
21	0.0297	0.1957	-0.1528	0.2618
22	-0.0796	-0.0615	-0.0942	-0.0545
23	-0.0728	-0.2493	0.1202	-0.3098
24	0.0430	0.1567	-0.2944	-0.2194
25	0.1001	0.3301	-0.2755	0.2425
26	0.0333	0.0585	0.1370	0.3096
27	-0.0333	0.0585	-0.1370	-0.3096
28	-0.1001	0.3301	0.2755	-0.2425
29	-0.0430	0.1567	0.2944	0.2194
30	0.0728	-0.2493	-0.1202	0.3098
31	0.0362	-0.3035	-0.4895	-0.1734
32	-0.4830	0.3248	-0.0504	-0.0219
33	0.4830	0.3248	0.0504	0.0219
34	-0.0362	-0.3035	0.4895	0.1734

Table IV.2 continued

Atomic Center	Energy levels (energy values in a.u in paranthesis 55(0.1820)	56(0.4366)	57(0.4734)	58(0.6325)
12	0.3013	-0.3931	-0.3209	-0.0495
13	0.1545	0.0879	0.2058	-0.1093
14	0.0059	0.2623	0.2962	0.1565
15	-0.1386	-0.1759	-0.3289	-0.1078
16	-0.0138	-0.2246	-0.1226	-0.0246
17	0.4801	0.0000	0.3537	0.0452
18	-0.0138	0.2246	-0.1226	-0.0246
19	-0.1385	0.1759	-0.3289	-0.1078
20	0.0059	-0.2623	0.2962	0.1565
21	0.1545	-0.0879	0.2058	-0.1093
22	0.3013	0.3931	-0.3209	-0.0495
23	-0.1583	-0.1090	-0.0256	0.1820
24	-0.1314	-0.2382	0.1356	0.1463
25	0.1219	0.2057	-0.0493	-0.3668
26	0.1603	0.1578	-0.1227	0.3470
27	0.1603	-0.1578	-0.1227	0.3470
28	0.1219	-0.2057	-0.0493	-0.3668
29	-0.1314	0.2382	0.1396	0.1463
30	-0.1583	0.1090	-0.0256	0.1820
31	-0.1963	0.1039	-0.2063	-0.3629
32	-0.3595	0.2023	-0.0319	0.0818
33	-0.3595	-0.2023	-0.0319	0.0818
34	-0.1963	-0.1039	0.2063	-0.3629

Table IV.2 continued

Atomic	Energy levels (energy values in a.u in parenthesis)			
Center	59(0.6656)	60(0.6729)	61(0.6309)	72(0.7537)
12	0.0920	0.0798	-0.0034	-0.3189
13	-0.3476	-0.3152	-0.0770	0.2855
14	0.2044	0.3012	0.3102	-0.1856
15	-0.0100	-0.1892	-0.4278	0.1337
16	-0.2189	-0.0270	0.4121	-0.0887
17	0.0000	0.0540	0.0000	0.0808
18	0.2189	-0.0270	-0.4121	-0.0887
19	0.0100	-0.1892	0.4278	0.1337
20	-0.2044	0.3012	-0.3102	-0.1856
21	0.3476	-0.3152	0.0770	0.2855
22	-0.0920	0.0798	0.0034	-0.3189
23	-0.2385	0.2114	-0.0709	0.3747
24	0.2719	-0.3241	0.0677	-0.2781
25	-0.1581	0.2752	-0.0373	0.1186
26	-0.0532	-0.0856	-0.0123	0.0203
27	0.0532	-0.0856	0.0123	0.0203
28	0.1581	0.2752	0.0373	0.1186
29	-0.2719	-0.3241	-0.0677	-0.2481
30	0.2385	0.2114	0.0709	0.3747
31	-0.1802	-0.0719	-0.0430	-0.1793
32	0.2997	0.1661	-0.1788	-0.0690
33	-0.2997	0.1661	0.1788	-0.0690
34	0.1802	-0.0719	0.0430	-0.1793

Table IV.2

Atomic	Energy levels (energy values in a.u in paranthesis)		
Center	73(0.7541)	75(0.7771)	76(0.7807)
12	0.3115	-0.0960	0.0765
13	-0.2900	0.0745	-0.0946
14	0.1496	-0.0355	-0.0767
15	-0.0582	0.0136	0.2469
16	-0.0339	0.0070	-0.4944
17	0.0000	0.0000	0.4605
18	0.0339	-0.0070	-0.4944
19	0.0582	-0.0136	0.2469
20	-0.1496	0.0355	-0.0767
21	0.2900	-0.0745	-0.0946
22	-0.3115	0.0960	0.0765
23	0.3539	-0.1404	-0.0663
24	-0.2851	-0.0706	0.0385
25	0.2089	0.2844	-0.0172
26	-0.1181	-0.5344	-0.0027
27	0.1181	0.5344	-0.0027
28	-0.2089	-0.2844	-0.0172
29	0.2851	0.0706	0.0385
30	-0.3539	0.1404	-0.0663
31	0.1034	-0.3030	0.0265
32	0.1309	-0.0289	0.2470
33	-0.1309	0.0289	0.2470
34	-0.1034	0.3030	0.0265

Aa: Only the $2P_z$ of carbon and nitrogen orbital coefficients are included.

The highest occupied orbital belongs to the level **no**.55.

Table IV.3

LCAO coefficients in the PPP wave function for Tetradehydro Corrin monoanion.

Atomic Center	Energy levels (energy values in a.u in parenthesis) 1(-16.6997)	2(-16.4577)	3(-15.0935)
14	0.0938	-0.1075	0.1302
15	0.2435	-0.2633	0.0222
16	0.1154	-0.1218	0.0019
17	0.1234	-0.1140	-0.0202
18	0.2759	-0.2300	-0.0556
19	0.1734	-0.0000	-0.0440
20	0.2759	0.2300	-0.0556
21	0.1234	0.1140	-0.0202
22	0.1154	0.1218	0.0019
23	0.2435	0.2633	0.0222
24	0.0938	0.1075	0.1301
25	0.0499	0.0621	0.3361
26	0.0171	0.0217	0.1478
27	0.0061	0.0074	0.0618
30	0.0061	-0.0074	0.0618
31	0.0171	-0.0217	0.1478
32	0.0499	-0.0621	0.3361
33	0.0462	-0.0594	0.5776
34	0.5543	-0.5748	-0.0767
35	0.5543	0.5748	-0.0767
36	0.0462	0.0594	0.5776

Table IV.3 continued.

Atomic center	Energy levels (energy values in a.u in paranthesis) 4(-15.0737)	5(-11.8433)	6(-11.6943)
14	-0.1259	-0.1729	0.2393
15	-0.0072	-0.1841	0.2083
16	0.0045	0.1376	0.3488
17	0.0201	0.3268	0.2564
18	0.0486	0.3293	-0.0343
19	-0.0000	0.4506	-0.0417
20	-0.0486	0.3293	-0.0343
21	-0.0201	0.3268	0.2565
22	-0.0045	0.1376	0.3490
23	0.0072	-0.1841	0.2083
24	0.1260	-0.1729	0.2393
25	0.3358	-0.0671	0.1212
26	0.1472	-0.1127	0.2235
27	0.0605	-0.0891	0.1791
30	-0.0605	-0.0891	0.1791
31	-0.1472	-0.1127	0.2235
32	-0.3357	-0.0671	0.1212
33	-0.5764	0.1532	-0.2375
34	0.1046	-0.2279	-0.2380
35	-0.1046	-0.2279	-0.2381
36	0.5765	0.1531	-0.2375

Table IV.3 continued.

Atomic center	Energy levels (energy values in a.u in paranthesis)		
	7(-11.6841)	8(-11.3512)	9(-11.0852)
14	0.2114	-0.1046	-0.1067
15	-0.1813	-0.0087	-0.2045
16	-0.3723	0.2525	-0.2393
17	-0.2987	0.2665	-0.0907
18	+0.0022	0.1023	0.1695
19	0.0000	0.0000	0.2755
20	-0.0022	-0.1023	0.1695
21	0.2986	-0.2965	-0.0907
22	0.3722	-0.2525	-0.2393
23	0.1883	0.0087	-0.2045
24	0.2114	0.1046	-0.1067
25	0.1056	0.1360	0.0886
26	0.2010	0.3727	0.3961
27	0.1627	0.3194	0.3603
30	-0.1627	-0.3194	0.3603
31	-0.2011	-0.3727	0.3981
32	-0.1056	-0.1360	0.0886
33	0.2129	0.2299	-0.1307
34	0.2622	-0.1206	0.0372
35	0.2621	0.1206	-0.0372
36	-0.2129	-0.2299	-0.1307

Table IV.3 continued.

Atomic Center	Energy levels (energy values in a.u in paranthesis) 10(-10.1909)	11(-8.8561)	12 (-4.6932)
14	0.3854	0.4042	0.2739
15	0.3821	0.0940	-0.2186
16	-0.0164	-0.2172	-0.2930
17	-0.2596	-0.2010	0.1750
18	0.2464	0.1355	0.3527
19	0.0000	0.4539	-0.0000
20	0.2464	0.1355	-0.3527
21	0.2596	-0.2010	-0.1750
22	0.0164	-0.2172	0.2930
23	-0.3021	0.0940	0.2186
24	-0.3854	0.4041	-0.2740
25	-0.0611	0.1575	-0.2518
26	0.2362	-0.1220	0.0216
27	0.2547	-0.1944	0.2070
30	-0.2547	-0.1944	-0.2070
31	-0.2363	-0.1220	-0.0216
32	0.0611	-0.1576	0.2518
33	-0.0744	-0.1310	-0.1562
34	-0.0436	-0.1556	-0.0724
35	0.0436	-0.1556	0.0724
36	0.0744	-0.1310	0.1562

Table IV.3 continued.

Atomic Center	Energy levels (energy values in a.u in parenthesis) 13(-3.3437)	14(-2.0894)	15(-1.7251)
14	0.0798	-0.2324	0.2817
15	-0.2974	-0.1160	-0.0306
16	-0.1596	0.1873	-0.2662
17	0.2763	-0.0295	0.2339
18	0.0657	-0.1981	0.0961
19	-0.3872	-0.0000	-0.2513
20	0.0657	0.1981	0.0961
21	0.2563	0.0295	0.2339
22	-0.1596	-0.1873	-0.2662
23	-0.2974	0.1160	-0.0306
24	0.0798	0.2324	0.2817
25	0.3068	-0.2957	-0.1943
26	0.0710	-0.2476	-0.2642
27	-0.2807	0.4199	0.3716
30	-0.2807	-0.4199	0.3716
31	0.0710	0.2476	-0.2642
32	0.3068	0.2957	-0.1942
33	-0.1577	-0.1336	0.0840
34	0.0987	0.1200	-0.0249
35	0.0987	-0.1200	-0.0249
36	-0.1577	0.1336	0.0840

Table IV.3 continued.

Atomic center	Energy levels (energy values in a.u. in paranthesis). 16(-0.0196)	17(0.4083)	18(0. 6188)
14	-0.1225	0.0358	-0.0232
15	0.2944	-0.3182	-0.1901
16	0.0008	0.2888	0.3438
17	-0.2574	-0.1474	-0.3654
18	0.3875	-0.0838	0.2443
19	0.0000	0.1194	0.0000
20	-0.3875	-0.0838	-0.2443
21	0.2573	-0.1474	0.3654
22	-0.0008	0.2888	-0.3438
23	-0.2944	-0.3182	0.1901
24	0.1225	0.0358	0.0233
25	0.1510	0.2825	-0.2356
26	-0.2620	-0.3424	0.2501
27	0.2067	0.2415	-0.1668
30	-0.2067	0.2415	0.1668
31	0.2620	-0.3424	-0.2501
32	-0.1510	0.2825	0.2356
33	0.0510	-0.0922	-0.0760
34	-0.2123	0.1196	-0.0171
35	0.2123	0.1196	0.0171
36	-0.0510	-0.0922	0.0760

Table IV.3 continued.

Atomic center	Energy levels (energy values in a.u in paranthesis)		
	19(1.8032)	20(1.8369)	21 (1.8422)
14	0.1027	-0.3519	0.3389
15	-0.1004	0.3461	-0.3340
16	0.2054	-0.2085	0.1413
17	-0.3141	0.1041	0.0169
18	0.4534	0.0056	-0.1948
19	-0.4621	-0.0000	0.2012
20	0.4534	-0.0057	-0.1948
21	-0.3141	-0.1041	0.0169
22	0.2045	0.2085	0.1414
23	-0.1004	-0.3461	-0.3340
24	0.1027	0.3518	0.3389
25	-0.1050	-0.3476	-0.3316
26	0.0679	0.2230	0.2125
27	-0.0350	-0.1149	-0.1097
30	-0.0350	0.1149	-0.1097
31	0.0679	-0.2230	0.2125
32	-0.1050	0.3477	-0.3316
33	0.0301	-0.0992	0.0942
34	-0.0941	-0.0918	0.1383
35	-0.0941	0.0918	0.1384
36	0.0301	0.0992	0.0942

Table IV.4

LCAO coefficients in the CNDO/2 wave function for Tetradehydro Corrin monoanion.
(The highest ten occupied levels and the lowest ten vacant levels are listed here).

Energy value (level)	Atomic orbital coefficients^a					
-0.3370(46)	H(1S)	0.0063	-0.0073	0.0000	0.0073	-0.0063
		0.0120	0.0162	-0.0078	-0.0129	0.0129
		0.0078	-0.0162	-0.0120	-	-
	C(2S)	0.0022	-0.0021	-0.0058	0.0071	0.0048
		-0.0000	-0.0048	-0.0071	0.0058	0.0021
		-0.0022	0.0007	-0.0090	-0.0004	0.0097
		-0.0097	-0.0004	0.0090	-0.0007	-
	N(2S)	0.0069	-0.0034	0.0034	-0.0069	-
	C(2P$_x$)	0.0189	-0.0225	0.0110	-0.0085	-0.0072
		0.0000	0.0072	0.0085	-0.0110	0.0225
		-0.0189	0.0189	-0.0185	0.0062	0.0067
		0.0067	-0.0062	0.0185	-0.0189	-
	N(2P$_y$)	0.0194	0.0092	-0.0092	-0.0194	-
	C(2P$_y$)	-0.0090	0.0081	0.0074	-0.0100	0.0185
		-0.0198	0.0185	-0.0100	0.0074	0.0081
		-0.0090	0.0135	-0.0101	0.0071	-0.0101
		-0101	0.0071	-0.0101	0.0135	-
	N(2P$_y$)	-0.0229	-0.0071	-0.0071	-0.0229	-
	C(2P$_z$)	0.1466	-0.0171	-0.3078	-0.2485	0.1254
		0.2578	0.1254	-0.2485	-0.3078	-0.0171
		0.1166	0.1535	-0.2277	-0.3138	0.0291
		0.0291	-0.3138	-0.2277	0.1535	-
	N(2P$_z$)	0.2859	0.1376	0.1376	0.2859	-

Table IV.4 continued.

Energy value (level)		Atomic orbital coefficients				
-0.3318(47)	H(1S)	-0.0770	0.0105	0.1950	0.0105	-0.0770
		-0.2058	-0.0540	-0.0332	-0.0495	-0.0495
		-0.0332	-0.0540	-0.2058	-	-
	C(2S)	0.0271	-0.0242	0.0089	0.0340	-0.0032
		-0.0730	-0.0032	0.0340	0.0089	-0.0242
		0.0271	-0.0152	0.0409	0.0710	-0.0210
		0.0210	0.0710	0.0409	-0.0152	-
	N(2S)	0.0820	0.9453	0.0453	0.0820	-
	C(2P_x)	0.0647	-0.0772	-0.0326	-0.0245	-0.1227
		0.2001	-0.1227	-0.0245	-0.0326	-0.0772
		0.0647	-0.0132	0.0884	0.0785	-0.0529
		-0.0529	0.0785	0.0884	-0.0132	-
	N(2P_x)	0.1717	0.0785	0.0785	0.1717	-
	C(2P_y)	-0.1608	0.2272	-0.0512	0.0128	0.0764
		-0.0000	-0.0764	-0.0128	0.0512	-0.2272
		0.1608	-0.1873	0.0301	0.0742	-0.1051
		0.1051	-0.0742	-0.0301	0.1873	-
	N(2P_y)	-0.2737	-0.2713	0.2713	0.2737	-
	C(2P_z)	-0.0339	-0.0250	0.0153	0.0304	0.0136
		-0.0000	-0.0136	-0.0304	-0.0153	0.0250
		0.0339	0.0024	-0.0827	-0.0620	0.0408
		-0.0408	0.0620	0.0827	-0.0024	-
	N(2P_z)	-0.0497	0.0094	0.0094	0.0497	-

Table IV.4 continued

Energy value (level)		Atomic orbital coefficients^a				
-0.3099(48)	H(1S)	-0.0068	0.0429	0.0000	-0.0429	0.0068
		-0.0946	-0.0959	-0.0636	-0.0205	0.0205
		0.0636	0.0959	0.0946	-	-
	C(2S)	0.0091	0.0213	0.0167	-0.0580	-0.0131
		-0.0000	0.0131	0.0580	-0.0167	-0.0213
		-0.0091	-0.0423	0.0944	0.0774	-0.0275
		0.0275	-0.0774	-0.0944	0.0423	-
	N(2S)	-0.1591	-0.0114	0.0114	0.1591	-
	C(2P$_x$)	-0.1111	0.1103	-0.0273	0.0569	0.0234
		0.0000	-0.0234	-0.0569	0.0273	-0.1103
		0.1111	-0.1129	0.1369	0.0939	-0.1653
		0.1653	-0.0939	-0.1369	0.1129	-
	N(2P$_x$)	-0.3957	0.0048	-0.0048	0.3957	-
	C(2P$_y$)	0.0489	-0.1022	-0.0142	0.0708	-0.1150
		0.1314	-0.1146	0.0708	-0.0142	-0.1022
		0.0489	-0.1527	0.0774	0.0618	0.0389
		0.0389	0.0618	0.0774	-0.1527	-
	N(2P$_y$)	0.2787	0.1235	0.1235	0.2787	-
	C(2P$_z$)	0.0277	0.0166	-0.0453	-0.0422	0.0115
		0.0228	0.0115	-0.0466	-0.0453	0.0166
		0.0277	0.0067	-0.0067	-0.0106	-0.0065
		-0.0065	-0.0106	-0.0067	0.0067	-
	N(2P$_z$)	-0.0223	0.0342	0.0342	-0.0223	-

Table IV.4 continued

Energy value (level)		Atomic orbital coefficients[a]				
-0.3057(49)	H(1S)	0.0149	0.0179	0.0061	0.0179	0.0149
		0.0300	0.0260	-0.0178	-0.1383	-0.1383
		-0.0178	0.0260	0.0300	-	-
	C(2S)	0.0057	0.0260	-0.0101	-0.0158	0.0016
		0.0119	0.0052	-0.0158	-0.0101	0.0052
		0.0057	0.0016	-0.0084	0.0047	0.0954
		0.0954	0.0044	-0.0084	0.0040	-
	N(2S)	-0.0119	0.0047	-0.0219	-0.0119	-
	C($2P_x$)	-0.0150	-0.0219	0.0049	0.0206	-0.0189
		-0.0050	0.0130	0.0206	0.0049	0.0130
		-0.0150	-0.0189	-0.0365	0.0160	-0.0044
		-0.0044	0.0224	-0.0365	0.0224	-
	N($2P_x$)	-0.0703	0.0160	0.0422	-0.0703	-
	C($2P_y$)	0.0145	0.0422	0.0160	0.0111	-0.0098
		-0.0000	-0.0388	-0.0111	-0.0157	0.0388
		-0.0145	0.0098	-0.0046	0.0087	0.0654
		-0.0654	0.0431	0.0046	-0.0431	-
	N($2P_y$)	0.0492	-0.0087	-0.0030	-0.0492	-
	C($2P_z$)	0.0389	0.0636	0.0075	-0.0166	-0.0255
		-0.0000	0.0302	0.0166	-0.0075	-0.0302
		-0.0389	0.0255	-0.3692	-0.2563	0.2637
		-0.2637	0.0091	0.3692	-0.0091	-
	N($2P_z$)	-0.4098	0.2536	0.0151	0.4098	-

Table IV.4

Energy value (level) Y	Atomic orbital coefficients^{a}					
-0.2707(50)	H(1S)	-0.0691	-0.0762	-0.1433	-0.0762	-0.0691
		-0.0265	0.0187	0.0055	0.0225	0.0225
		0.0055	0.0187	-0.0265	-	-
	C(2S)	-0.0248	-0.0554	0.0940	0.0724	-0.0494
		-0.0364	-0.0494	0.0724	0.0940	-0.0554
		-0.0248	0.0324	-0.0346	-0.0086	0.0214
		0.0214	-0.0086	-0.0346	0.0324	-
	N(2S)	-0.0685	0.1763	0.1763	-0.0685	-
	C($2P_x$)	-0.0974	0.0887	-0.1107	-0.0740	0.2129
		-0.0646	0.2129	-0.0740	-0.1107	0.0887
		-0.0974	0.0747	-0.0549	-0.0106	0.0497
		0.0497	-0.0106	-0.0549	0.0747	-
	N($2P_x$)	-0.1047	-0.3750	-0.3750	-0.1047	-
	C($2P_y$)	-0.0045	-0.1281	-0.0926	-0.0913	-0.0015
		0.0000	-0.0015	0.0913	0.0926	-0.1281
		0.0045	0.0045	-0.0150	-0.0209	-0.0200
		0.0200	0.0209	0.0150	-0.0045	-
	N($2P_y$)	0.0671	-0.3090	0.3090	-0.0671	-
	C($2P_z$)	0.0236	0.0490	-0.0816	-0.0875	0.0290
		0.0000	-0.0290	0.0875	0.0816	-0.0490
		-0.0236	0.0372	-0.0112	-0.0397	-0.0033
		0.0033	0.0397	0.0112	-0.0372	-
	N($2P_z$)	-0.0702	0.1111	-0.1111	0.0702	-

Table IV.4 continued.

Energy value (level)		Atomic orbital coefficients[a]				
-0.2691(51)	H(1S)	-0.0036	-0.0089	-0.0000	0.0089	0.0037
		0.0047	0.0115	0.0056	-0.0417	0.0417
		-0.0056	-0.0115	-0.0047	-	-
	C(2S)	-0.0060	-0.0092	0.0039	0.0121	-0.0067
		-0.0000	0.0067	-0.0121	-0.0039	0.0092
		0.0060	-0.0028	-0.0100	0.0026	0.0126
		-0.0126	-0.0026	0.0100	0.0028	
	N(2S)	0.0057	0.0187	-0.0187	-0.0056	-
	C(2P$_x$)	0.0072	-0.0031	-0.0064	-0.0106	0.0107
		-0.0000	-0.0007	0.0106	0.0064	0.0031
		-0.0072	0.0086	-0.0094	-0.0003	0.0229
		-0.0229	0.0003	0.0094	-0.0086	-
	N(2P$_x$)	0.0437	-0.0293	0.0293	-0.0437	-
	C(2P$_y$)	0.0018	0.0207	-0.0041	-0.0162	0.0185
		-0.0205	0.0185	-0.0162	-0.0041	0.9207
		0.0018	0.0039	-0.0092	0.0090	-0.0166
		-0.0166	0.0090	-0.0092	0.0039	-
	N(2P$_y$)	-0.0060	-0.0375	-0.0375	-0.0060	-
	C(2P$_z$)	0.1095	0.2388	-0.1971	-0.2966	-0.0033
		-0.0745	-0.0033	-0.2966	-0.1971	0.2388
		0.1095	-0.1969	0.0288	0.1969	0.0588
		0.0588	0.1969	0.0288	-0.1969	-
	N(2P$_z$)	-0.3036	0.3426	0.3426	-0.3036	-

Table IV.4 continued.

Energy value (level)		Atomic orbital coefficients[a]				
-0.2651(52)	H(1S)	0.0169	0.0180	0.0371	0.0180	0.0169
		0.0127	-0.0115	0.0015	0.0097	0.0397
		-0.0015	0.0115	0.0027	-	-
	C(2S)	0.0047	0.0150	-0.0244	-0.0174	0.0136
		0.0084	0.0136	-0.0174	-0.0244	0.0150
		0.0047	-0.0113	0.0120	0.0010	-0.0357
		-0.0357	-0.0010	0.0120	-0.0113	-
	N(2S)	0.0249	-0.0458	0.0458	0.0249	-
	C($2P_x$)	0.0301	-0.0265	0.0298	0.0171	-0.0549
		0.0172	-0.0540	0.0170	0.0299	-0.0265
		0.0301	-0.0265	0.0238	-0.0013	-0.0178
		-0.0178	-0.0013	0.0239	-0.0260	-
	N($2P_x$)	0.0510	0.0961	0.0961	0.0510	-
	C($2P_x$)	0.0001	-0.0298	0.0231	0.0232	0.0008
		-0.0000	-0.0008	-0.0232	-0.0231	0.0298
		-0.0001	-0.0116	0.0048	0.0016	-0.0147
		0.0147	-0.0016	0.0048	0.0116	-
	N($2P_y$)	0.0311	0.0763	-0.0763	0.0311	-
	C($2P_z$)	0.0116	0.1059	-0.3226	-0.2794	0.1817
		-0.0000	-0.1817	0.2794	0.3226	-0.1059
		0.0116	0.1129	0.0346	-0.0835	-0.0800
		0.0800	0.0335	-0.0346	-0.1129	-
	N($2P_z$)	-0.0539	0.4538	-0.4538	0.0537	-

Table IV.4 continued.

Energy value (level)		Atomic orbital coefficients[a]				
-0.2459(53)	H(1S)	-0.0458	-0.0653	-0.0000	0.0653	0.0458
		0.0609	-0.0190	-0.1044	-0.0093	0.0093
		0.0144	0.0100	-0.0609	-	-
	C(2S)	-0.0077	-0.0909	0.0673	0.1016	-0.0872
		-0.0000	0.0872	-0.1016	-0.0673	0.0909
		0.0077	-0.0369	0.0292	0.0158	-0.0231
		0.0231	-0.0158	0.0292	0.0369	-
	N(2S)	-0.0656	0.2105	-0.2105	0.0656	-
	C($2P_x$)	-0.0647	0.0395	-0.1118	-0.0777	0.1299
		-0.0000	-0.1299	0.0777	0.1118	-0.0395
		0.0647	-0.0655	0.0430	0.0991	-0.0667
		0.0667	-0.0191	-0.0430	0.0655	
	N($2P_x$)	-0.1240	-0.3224	0.3224	0.1240	-
	C($2P_y$)	-0.0324	0.1355	-0.0570	-0.1445	0.1368
		-0.1588	0.1368	-0.1445	-0.0570	0.1855
		-0.0324	0.0056	0.0102	0.0323	0.0159
		0.0159	0.0323	0.0102	0.0056	0.0450
	N($2P_y$)	-0.3720	-0.3720	0.0450	-0.0003	-
	C($2P_z$)	-0.0194	0.0096	0.0194	0.0024	
		0.0131	0.0024	0.0194	0.0095	0.0194
		-0.0003	0.0223	0.0021	-0.0191	-0.0145
		-0.0145	-0.0191	0.0021	0.0223	-
	N($2P_z$)	0.0121	-0.0289	-0.0289	0.0121	

Table IV.4 continued

Energy value (level)		Atomic orbital coefficients[a]				
-0.2030(54)	H(1S)	-0.0015	-0.0011	-0.0053	-0.0011	-0.0015
		0.0037	0.0151	-0.0096	-0.1374	-0.1374
		-0.0096	0.0151	0.0037	-	-
	C(2S)	0.0040	-0.0039	0.0042	0.0013	-0.0032
		-0.0003	-0.0032	0.0013	0.0042	-0.0039
		0.0040	0.0040	-0.0066	0.0154	0.0819
		0.0819	0.0154	-0.0066	0.0060	-
	N(2S)	-0.0110	0.0079	0.0079	-0.0110	-
	C(2P$_x$)	-0.0124	0.0081	-0.0060	-0.0007	0.0083
		-0.0025	0.0083	-0.0007	-0.0060	0.0081
		-0.0124	0.0145	-0.0190	0.0160	0.0088
		0.0088	0.0160	-0.0190	0.0145	-
	N(2P$_x$)	-0. 0559	-0.0136	-0.0136	-0.0559	-
	C(2P$_y$)	-0.0013	0.0010	-0.0028	-0.0032	-0.0012
		-0.0000	0.0012	0.0032	0.0028	-0.0010
		0.0013	0.0178	0.0001	0.0177	0.0486
		-0.0486	-0.0177	-0.0001	-0.0178	-
	N(2P$_y$)	0.0194	-0.0089	0.0089	-0.0194	-
	C(2P$_z$)	-0.2116	0.2786	-0.0435	0.1283	0.2772
		-0.0000	-0.2772	-0.1283	0.1435	0.2786
		0.2116	-0.2616	-0.1635	0.1744	0.2264
		-0.2264	-0.1744	0.1635	0.2516	-
	N(2P$_z$)	0.1967	0.1374	-0.1374	-0.1967	-

Table IV.4 continued.

Energy value (level)		Atomic orbital coefficients[a]				
-0.1101(55)	H(1S)	0.0003	-0.0000	-0.0000	0.0000	-0.0003
		-0.0038	0.0113	-0.0005	-0.0715	0.0715
		0.0005	-0.0113	0.0038	-	-
	C(2S)	-0.0050	0.0006	-0.0015	-0.0003	0.0012
		-0.0000	-0.0012	0.0003	0.0015	-0.0006
		0.0050	-0.0051	-0.0090	0.0135	0.0108
		-0.0108	-0.1035	0.0090	0.0051	-
	N(2S)	-0.0042	-0.0019	0.0019	0.0042	-
	C($2P_x$)	0.0072	-0.0014	0.0021	0.0000	-0.0014
		-0.0000	0.0014	-0.0000	-0.0021	0.0014
		-0.0072	0.0074	-0.0044	0.0116	0.0121
		-0.0121	-0.0116	0.0044	-0.0074	-
	N($2P_x$)	0.0287	0.0024	-0.0024	-0.0287	-
	C($2P_y$)	0.0045	-0.0007	0.0007	0.0010	-0.0001
		0.0004	-0.0002	0.0010	0.0007	-0.0007
		0.0045	-0.0043	-0.0058	0.0205	-0.0255
		-0.0255	0.0205	-0.0058	-0.0043	-
	N($2P_y$)	0.0072	0.0030	0.0030	0.0072	-
	C($2P_z$)	0.3613	0.0388	-0.0205	-0.0440	0.0099
		0.4473	0.0099	-0.0440	-0.0205	0.0388
		0.3613	-0.0218	-0.0854	0.0207	0.0772
		0.0772	0.0207	-0.0854	-0.0218	-
	N($2P_z$)	-0.2592	-0.4195	-0.4195	-0.2592	-

Table IV.4 continued.

Energy value (level)		Atomic orbital coefficients^{a}				
0.1455(56)	H(1S)	-0.0001	-0.0000	-0.0007	-0.0000	-0.0001
		-0.0001	0.0088	-0.0062	-0.0882	-0.0882
		-0.0062	0.0088	-0.0001	-	-
	C(2S)	0.0029	-0.0008	0.0009	0.0000	-0.0007
		0.0000	-0.0007	0.0000	0.0009	-0.0008
		0.0029	0.0018	-0.0046	0.0163	0.0411
		0.0411	0.0163	-0.0046	0.0018	-
	N(2S)	-0.0004	0.0014	0.0014	-0.0004	-
	C(2p$_x$)	-0.0040	0.0015	-0.0011	0.0000	0.0012
		-0.0000	0.0012	0.0001	-0.0012	0.0015
		-0.0040	0.0030	-0.0043	0.0107	0.0063
		0.0063	0.0107	-0.0043	0.0030	-
	N(2P$_x$)	-0.0222	-0.0016	-0.0016	-0.0222	-
	C(2P$_y$)	-0.0017	-0.0002	-0.0004	-0.0004	-0.0003
		0.0000	0.0003	0.0005	0.0004	0.0002
		0.0017	0.0051	0.0024	0.0171	0.0238
		-0.0238	-0.0171	-0.0024	-0.0051	-
	N(2P$_y$)	0.0003	-0.0014	0.0014	-0.0003	-
	C(2P$_z$)	-0.3609	0.1987	0.2782	-0.2145	0.2849
		0.0000	0.2849	0.2145	-0.2782	-0.1987
		0.3609	0.0501	-0.1334	0.0334	0.0986
		-0.0986	-0.0334	0.1334	-0.0501	-
	N(2P$_z$)	0.2182	0.1883	-0.1884	-0.2182	-

Table IV.4 continued.

Energy value (level)		Atomic orbital coefficients^a				
0.2062(57)	H(1S)	0.0001	-0.0001	0.0000	0.0001	-0.0001
		-0.0075	0.0271	-0.0040	-0.1451	0.1451
		0.0040	-0.0271	0.0075	-	-
	C(2S)	-0.0107	0.0004	-0.0016	-0.0001	0.0012
		-0.0000	-0.0012	0.0001	0.0016	-0.0004
		0.0107	-0.0134	-0.0219	0.0394	-0.0147
		0.0147	-0.0394	0.0219	0.0134	-
	N(2S)	-0.0182	-0.0017	0.0017	0.0182	-
	C($2P_x$)	0.0113	-0.0009	0.0019	-0.0001	-0.0012
		0.0000	0.0012	0.0001	-0.0019	0.0009
		-0.0113	0.0075	0.0002	0.0298	0.0186
		-0.0186	-0.0298	-0.0002	-0.0075	-
	N($2P_x$)	0.0433	0.0016	-0.0016	-0.0433	-
	C($2P_y$)	0.0054	-0.0000	0.0006	0.0008	0.0001
		0.0001	0.0001	0.0008	0.0006	-0.0000
		0.0054	-0.0094	-0.0046	0.0459	-0.0586
		0.0586	0.0459	-0.0046	-0.0094	-
	N($2P_y$)	0.0161	0.0023	0.0023	0.0161	-
	C($2P_z$)	0.1523	-0.2354	-0.2254	0.2849	0.1167
		-0.3616	0.1167	0.2849	-0.2254	-0.2354
		9.1523	0.1735	0.0630	-0.2007	0.0758
		0.0758	-0.2007	0.0630	0.1735	-
	N($2P_z$)	-0.2931	0.1021	0.1021	-0.2931	-

Table IV.4 continued.

Energy value (level)	Atomic orbital coefficients^a					
0.2579(58)	H(1S)	-0.0000	-0.0002	0.0000	0.0002	0.0000
		-0.0100	0.0370	-0.0082	-0.1724	0.1724
		0.0082	-0.0370	0.0100	-	-
	C(2S)	-0.0148	0.0006	-0.0018	0.0002	0.0013
		-0.0000	-0.0013	-0.0002	0.0018	-0.0006
		0.0148	-0.0193	-0.0289	0.0543	-0.0366
		0.0366	-0.0543	0.0289	0.0193	-
	N(2S)	-0.0281	-0.0014	0.0014	0.0281	-
	C(2P$_x$)	0.0133	-0.0005	0.0016	-0.0001	-0.0011
		-0.0000	0.0011	0.0001	-0.0016	0.0005
		-0.0133	0.0071	0.0048	0.0380	0.0167
		-0.0167	-0.9380	-0.0048	-0.0071	-
	N(2P$_x$)	0.0510	0.0006	-0.0006	-0.0510	-
	C(2P$_y$)	0.0059	0.0007	0.0006	0.0008	0.0002
		-0.0001	0.0002	0.0008	0.0006	0.0007
		0.0059	-0.0114	-0.0032	0.0583	-0.0745
		-0.0745	0.0583	-0.0032	-0.0114	-
	N(2P$_y$)	0.0210	0.0016	0.0016	0.0210	-
	C(2P$_z$)	-0.2079	0.0928	0.2065	-0.2095	-0.0804
		0.1984	-0.0804	-0.2095	0.2065	0.0928
		-0.2079	0.0793	0.3188	-0.3627	0.0589
		0.0589	-0.3827	0.3188	0.0793	-
	N(2P$_z$)	-0.1598	0.0128	0.0128	-0.1598	-

TableIV.4 continued.

Energy value (level)		Atomic orbital coefficients[a]				
0.2941(59)	H(1S)	-0.0001	0.0002	-0.0012	0.0002	-0.0001
		-0.0016	0.0314	-0.0335	-0.2617	[illegible]
		-0.0335	0.0314	-0.0016	-	-
	C(2S)	0.0099	-0.0025	0.0020	-0.0003	-0.0017
		0.0005	-0.0017	-0.0003	0.0020	-0.0025
		0.0099	0.0028	-0.0169	0.0598	0.1053
		0.1053	0.0598	-0.0169	0.0028	-
	N(2S)	0.0126	0.0024	0.0024	0.0126	-
	C($2P_x$)	-0.0090	0.0022	-0.0018	0.0002	0.0019
		0.0002	0.0019	0.0002	-0.0018	0.0022
		-0.0090	0.0048	-0.0049	0.0232	0.0052
		0.0052	0.0232	-0.0049	0.0048	-
	N($2P_x$)	-0.0608	-0.0011	-0.0011	-0.0608	-
	C($2P_y$)	-0.0058	-0.0013	-0.0008	-0.0009	-0.0005
		-0.0000	0.0005	0.0009	0.0008	0.0013
		0.0058	0.0124	0.0091	0.0550	0.0626
		-0.0626	-0.0550	-0.0091	-0.0124	-
	N($2P_y$)	-0.0134	-0.0017	0.0017	0.0134	-
	C($2P_z$)	0.0780	0.0255	-0.0610	0.0314	0.0403
		0.0000	-0.0403	-0.0314	0.0610	-0.0255
		-0.0780	0.1151	0.2793	-0.4177	0.1973
		-0.1973	0.4177	-0.2793	-0.1151	-
	N($2P_z$)	0.2849	-0.0590	0.0590	-0.2849	-

Table IV.4 continued.

Energy value (level)		Atomic orbital coefficients[a]				
0.3674(60)	H(1S)	-0.0016	0.0032	0.0000	-0.0032	0.0016
		-0.0542	0.1921	-0.1229	-0.1973	0.1973
		0.1229	-0.1921	0 .0542	-	-
	C(2S)	-0.0493	-0.0040	0.0024	-0.0016	0.0041
		-0.0000	-0.0041	0.0016	-0.0024	0.0040
		0.0493	-0.0215	-0.1910	0.0833	-0.3402
		0.3402	-0.2833	0.1910	0.0215	-
	N(2S)	-0.0856	-0.0068	0.0068	0.0856	-
	C($2P_x$)	0.0274	0.0002	-0.0029	-0.0017	-0.0041
		0.0000	0.0041	0.0017	0.0028	-0.0002
		-0.0274	-0.0325	-0.0690	0.0530	0.0930
		-0.0930	-0.0530	-0.0690	0.0325	-
	N($2P_x$)	0.1199	0.0008	-0.0008	-0.1199	-
	C($2P_y$)	-0.0121	-0.0018	-0.0004	-0.0000	0.0002
		-0.0020	-0.0002	-0.0000	-0.0004	-0.0018
		-0.0121	-0.0377	0.0405	0.1270	-0.1324
		-0.1324	0.1270	0.0405	-0.0377	-
	N($2P_y$)	0.0442	-0.0018	-0.0018	0.0442	-
	C($2P_z$)	-0.0054	-0.0095	0.0154	-0.0107	-0.0040
		0.0077	-0.0040	-0.0107	0.0154	-0.0095
		-0.0054	0.0209	-0.1034	0.0497	-0.2264
		-0.2264	0.1497	-0.1034	0.0209	-
	N($2P_z$)	0.0818	0.0059	0.0059	0.0818	

Table IV.4 continued.

energy value (level)		Atomic orbital coefficients^a				
0.3912(61)	H(1S)	-0.0007	0.0087	0.0004	0.0087	-0.0007
		-0.0004	-0.0508	0.2351	0.0232	0.0232
		0.2351	-0.0508	-0.0004	-	-
	C(2S)	0.0255	-0.0132	0.0091	-0.0068	0.0001
		0.0002	0.0001	-0.0068	0.0091	-0.0132
		0.0255	-0.0623	0.1021	-0.2381	0.0571
		0.0571	-0.2381	0.1021	-0.0623	-
	N(2S)	0.0049	-0.0026	-0.0026	0.0049	
	C(2P$_x$)	-0.0168	0.0052	-0. 0069	-0.0035	-0.0006
		-0.0005	-0.0006	-0.0035	-0.0069	0.0052
		-0.0168	0.0267	-0.0321	0.1156	-0.0632
		-0.0632	0.1156	-0.0321	0.0267	-
	N(2P$_x$)	0.0257	-0.0005	-0.0005	0.0257	-
	C(2P$_y$)	-0.0141	-0.0071	-0.0035	-0.0032	0.0002
		0.0000	-0.0002	0.0032	0.0035	0.0071
		0.0141	0.0036	0.0186	-0.0310	-0.0626
		0.0626	0.0310	-0.0186	-0.0036	-
	N(2P$_y$)	0.0003	0.0017	0.0017	-0.0002	-
	C(2P$_z$)	-0.0289	-0.2113	0.1642	-0.0452	-0.1235
		0.0000	0.1235	0.0454	-0.1642	0.2113
		0.0289	-0.3024	0.2667	-0.1556	0.0304
		-0.0305	0.1556	-0.2667	0.3024	-
	N(2P$_z$)	-0.1610	0.1929	-0.1929	0.1610	-

Table IV.4 continued.

Energy value (level)	Atomic orbital coefficients^a					
0.3944(62)	H(1S)	0.0019	-0.0147	-0.0015	-0.0147	0.0019
		-0.0076	0.0222	-0.3677	-0.0033	-0.0033
		-0.3677	0.0222	-0.0076	-	-
	C(2S)	-0.0334	0.0213	-0.0158	0.0115	-0.0006
		0.0005	-0.0006	0.0115	-0.0158	0.0213
		-0.0334	0.0781	-0.1140	0.3323	-0.0899
		-0.0899	0.3323	-0.1140	0.0781	-
	N(2S)	0.0201	0.0047	0.0047	0.0201	-
	C(2P$_x$)	0.0242	-0.0075	0.0116	0.0060	0.0013
		0.0009	0.0013	0.0060	0.0116	-0.0075
		0.0242	-0.0383	0.0358	-0.2059	0.0552
		0.0552	-0.2059	0.0358	-0.0383	-
	N(2P$_x$)	-0.0520	0.0009	0.0009	-0.0520	-
	C(2P$_y$)	0.0257	0.0116	0.0055	+0.0054	-0.0003
		0.0000	0.0003	-0.0054	-0.0054	-0.0116
		-0.0257	-0.0152	-0.0583	+0.0290	0.0709
		-0.0709	-0.0290	0.0583	0.0152	-
	N(2P$_y$)	0.0030	0.0036	-0.0036	-0.0030	-
	C(2P$_z$)	-0.0157	-0.1530	0.1155	-0.0306	-0.0878
		0.0000	0.0878	0.0306	-0.1155	0.1530
		0.0157	-0.2096	0.1602	-0.0633	-0.0537
		0.0537	0.0633	-0.1602	0.2096	-
	N(2P$_z$)	-0.1442	0.1378	-0.1378	0.1442	-

Table IV.4 continued.

Energy value (level)		Atomic orbital coefficients^a				
0. 3948(63)	H(1S)	0.0010	-0.0035	0.0000	0.0935	-0.0010
		0.0074	0.0024	0.0897	0.0051	-0.0061
		-0.0897	-0.0024	-0.0074	-	-
	C(2S)	-0.0018	0.0047	-0.0041	0.0027	-0.0007
		-0.0000	0.0007	-0.0027	0.0041	-0.0047
		0.0018	-0.0098	0.0198	-0.0764	0.0316
		-0.0316	0.0764	-0.0198	0.0098	-
	N(2S)	0.0132	0.0016	-0.0016	-0.0182	-
	C(2P$_x$)	0.0032	-0.0011	0.0029	0.0014	0.0007
		-0.0000	-0.0007	-0.0014	0.0029	0.0011
		-0.0032	0.0092	-0.0073	0.0513	0.0001
		-0.0001	-0.0513	0.0073	-0.0091	-
	N(2P$_x$)	-0.0226	0.0002	-0.0002	0.0226	-
	C(2P$_y$)	0.0077	0.0026	0.0010	0.0012	0.0000
		0.0004	0.0000	0.0012	0.0010	0.0026
		0.0077	0.0067	0.0188	-0.0080	0.0071
		-0.0071	-0.0080	0.0188	0.0067	-
	N(2P$_y$)	-0.0007	0.0013	0.0013	-0.0007	-
	C(2P$_z$)	-0.0529	-0.2336	0.2800	-0.1874	-0.0345
		0.0645	-0.0345	-0.1874	0.2800	-0.2336
		-0.0529	0.3617	-0.2970	0.1519	0.0191
		0.0191	0.0519	-0.2970	0.3617	-
	N(2P$_z$)	-0.2042	0.1479	0.1479	-0.2042	-

Table IV.4 continued.

Energy value (level)	Atomic orbital coefficients^a					
0.4010(64)	H(1S)	-0.0022	0.0209	-0.0000	-0.0209	0.0022
		0.0131	-0.1732	-0.4395	0.0569	-0.0569
		0.4395	0.1732	-0.0131	-	-
	C(2S)	0.0669	-0.0295	0.0210	-0.0175	0.0002
		0.0000	-0.0002	0.0175	-0.0210	0.0295
		-0.0669	0.0933	0.0198	-0.2677	0.0762
		-0.0762	-0.2677	-0.0198	-0.0933	-
	N(2S)	-0.0168	-0.0033	0.0033	0.0168	-
	C(2P$_x$)	-0.0406	0.0108	-0.0137	-0.0086	0.0002
		0.0000	-0.0002	0.0086	0.0138	-0.0108
		0.0406	-0.0240	-0.0254	-0.3334	0.0107
		-0.0107	0.3334	0.0254	0.0240	-
	N(2P$_x$)	0.0512	-0.0015	0.0015	-0.0512	-
	C(2P$_y$)	-0.0263	-0.0150	-0.0074	-0.0070	0.0010
		0.0013	0.0010	-0.0070	-0.0074	-0.0150
		-0.0263	-0.0172	0.1609	-0.0252	0.1232
		0.1232	-0.0252	-0.1601	-0.0172	-
	N(2P$_y$)	-0.0323	-0.0027	-0.0027	-0.0323	-
	C(2P$_z$)	-0.0061	-0.0453	-0.0512	-0.0340	-0.0052
		0.0099	-0.0052	-0.0339	0.0512	-0.0453
		-0.0061	0.0632	-0.0334	-0.9047	+0.0596
		0.0596	-0.0047	-0.0334	0.0632	
	N(2P$_z$)	-0.0581	0.0278	0.0278	-0.0581	-

Table IV.4 continued.

Energy value (level)		Atomic orbital coefficients[a]				
0.4206(65)	H(1S)	0.0010	0.0008	0.0042	0.0008	0.0010
		0.0091	0.4509	0.1380	-0.0142	-0.0142
		0.1380	0.4509	0.0091	-	-
	C(2S)	-0.0070	+0.0028	-0.0013	+0.0001	0.0022
		-0.0032	0.0022	0.0001	-0.0013	0.0028
		-0.0070	0.0897	-0.3362	0.0384	-0.0433
		-0.0433	0.0384	-0.3362	0.0897	-
	N(2S)	-0.0815	-0.0040	0.0040	-0.0815	-
	C($2P_x$)	0.0014	-0.0015	0.0000	-0.0009	-0.0022
		-0.0019	-0.0022	-0.0009	-0.0000	-0.0014
		0.0014	-0.0524	0.1127	0.1745	0.0571
		0.0571	0.1745	0.1127	-0.0524	-
	N($2P_x$)	0.0759	-0.0005	-0.0005	0.0759	-
	C($2P_y$)	-0.0030	-0.0001	-0.0003	0.0002	-0.0002
		-0.0000	0.0002	-0.0002	0.0003	0.0001
		0.0030	0.0224	0.2730	-0.0313	0.0700
		-0.0700	0.0313	-0.2730	-0.0224	-
	N($2P_y$)	-0.0724	-0.0006	0.0006	0.0725	-
	C($2P_z$)	0.0061	-0.0277	0.0106	0.0067	-0.0236
		-0.0000	0.0236	-0.0067	-0.0106	-0.0277
		-0.0061	-0.0221	0.0117	0.0172	-0.0359
		0.0359	-0.0072	-0.0117	0.0221	-
	N($2P_z$)	-0.0296	+0.0276	-0.0276	0.0296	

(The highest ten occupied levels and the lowest ten vacant levels are listed here, the energy values are in au).

[a] The orbital coefficients are arranged as follows: The hydrogen a.o'sare listed first, next all the carbon 2S followed by nitrogen 2S are given. Then follow $2P_x$ orbitals of all the carbon atoms and nitrogen atoms. The $2P_y$ and $2P_z$ orbitals are then labeled in the same way.

Table IV. 5.

Nucleophilic Reactivity Parameters of Corrole trianion.

Atomic Centre	Frontier electron density		Superdelocalisability	
	PPP	CNDO/2	PPP	CNDO/2
12	0.1626	0.1545	1.0000	1.0000
13	0.0001	0.0077	0.6173	0.5854
14	0.0640	0.0688	0.7527	0.8072
15	0.0051	0.0310	0.6687	0.7149
16	0.0692	0.0504	0.0721	0.4606
17	0.0000	0.0000	0.0761	0.5238
27	0.0520	0.0249	0.6999	0.5618
28	0.0331	0.0423	0.6136	0.5692
29	0.0709	0.0568	0.7055	0.6221
30	0.0160	0.0119	0.5854	0.4831
31	0.0041	0.0108	0.2651	0.4879
32	0.0228	0.0409	0.1417	0.3969

Table IV. 6.
Electrophilic reactivity parameters for Corrole trianion.

Atomic center	Frontier electron density		Superdelocalisability	
	PPP	CNDO/2	PPP	CNDO/2
12	0.1321	0.0908	0.8225	0.5789
13	0.0336	0.0239	0.6721	0.5454
14	0.0158	0.0003	0.6937	0.4760
15	0.0456	0.0192	0.7559	0.5379
16	0.0026	0.0002	0.5929	0.4133
17	0.1987	0.2305	1.0000	1.0000
27	0.0531	0.0257	0.7135	0.5969
28	0.0132	0.0149	0.7478	0.6508
29	0.0526	0.0173	0.7666	0.6205
30	0.0074	0.0251	0.6802	0.6114
31	0.0161	0.0386	0.7642	0.7741
32	0.0402	0.1292	0.8282	0.9527

Table IV. 7.

Nucleophilic Reactivity Parameter of Tetradehydro Corrin Anion.

Atomic center	Frontier electron density		Superdelocalisability	
	PPP	CNDO/2	PPP	CNDO/2
14	0.0750	0.1302	0.5873	1.0000
15	0.0478	0.0395	0.6792	0.8892
16	0.0858	0.0774	0.6695	0.9939
17	0.0306	0.0460	1.0000	0.9320
18	0.1244	0.0811	0.7955	0.9534
19	0.0000	0.0000	0.5331	0.4853
29		0.0097		0.5194
30	0.0428	0.0011	0.7900	0.9220
31	0.0005	0.0178	0.4571	0.8118
32	0.0634	0.0025	0.8162	0.7356
33	0.0244	0.0254	0.1753	0.8620
34	0.0052	0.0355	0.1308	0.5018

Table IV.8.
Electrophilic Reactivity Parameters of Tetradehydro Corrin Anion.

Atomic center	Frontier electron density		Superdelocalisability	
	PPP	CNDO/2	PPP	CNDO/2
14	0.1633	0.1305	0.9962	0.5024
15	0.0088	0.0015	0.4781	0.3100
16	0.0472	0.0042	0.6835	0.3546
17	0.0404	0.0019	0.7228	0.3569
18	0.0184	0.0001	0.4369	0.2827
19	0.2060	0.1998	1.0000	0.6615
29		0.0060		0.1233
30	0.0378	0.0004	0.6486	0.3506
31	0.0149	0.0073	0.7290	0.3683
32	0.0248	0.0005	0.3296	0.3147
33	0.0172	0.0672	0.8202	0.5491
34	0.0242	0.1760	0.7403	1.0000

Table IV.9

A comparison of the HOMO and LUMO levels of porphine dianion(I), phlorin trianion(II) Corrole trianion(III) and tetradehydrocorrin monoanion(IV). (energies are expressed in a.u.).

I		II		III		IV	
Orbital No.	Energy	Orbital No.	Energy	Orbital No.	Energy	Orbital No.	Energy
63 62 } e_g	0.5351	63	0.6754	59	0.6656	59	0.2941
61	0.5284	62	0.6697	58	0.6325	58	0.2579
60	0.3809	61	0.6404	57	0.4734	57	0.2062
59	0.2876	60	0.4824	56(LUMO)	0.4366	56(LUMO)	0.1459
58		59(LUMO)	0.4412	55(HOMO)	0.1819	55(HOMO)	-0.1100
57(HOMO I)	0.0166	58(HOMO)	0.2082	54	0.1443	54	-0.2030
56(HOMO II)	-0.0096	57	0.1102	53	0.0324	53	-0.2458
		56	0.0519	52	0.0185	52	-0.2691

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SUMMARY

The scope of the thesis is to find rational explanations for some of the observed physicochemical data on metalloporphyrins 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. Emphesis is laid on the literature that has appeared during the past eight years. A comparative evaluation is made on the various methods used for theoritical calculations, based on how well the results of these calculations explain the experimental data. Extended Huckel approach (EHT) and Pariser-Parr-Pople π-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 CNDO/2, CNDO/3S, INDO are more promising, but the multiplicity of the approach is discouraging the theoritical chemists and it is difficult to choose among the plethora of various modifications of CNDO/2 and INDO formalisms. SCF-X-α 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 π energy levels of porphyrins is estimated using SCF perturbation theory. CNDO/2 and PPP wave functions of porphine dianion are used as zeroeth 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 bee 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_{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 zeroeth 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 PPP 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 II. The relevant expressions are presented here for the sake of understanding the computer programmes.

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

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

$$H^{(1)}_{\mu\mu} = - \frac{ze^2}{r_\mu} \qquad (A.1.)$$

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

and $$H_{\mu\nu} = 0 \quad \text{if} \quad \mu \neq \nu \qquad (A.2.)$$

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

$$F^{(1)}_{\mu\mu} = H^{(1)}_{\mu\mu} + \frac{1}{2} P^{(1)}_{\mu\mu}\gamma_{\mu\mu} + \sum_{\mu\neq\nu} P^{(1)}_{\nu\nu}\gamma_{\mu\nu} \qquad (A.3.)$$

and

$$F^{(1)}_{\mu\nu} = -\frac{1}{2} P^{(1)}_{\mu\nu} \gamma_{\mu\nu} \qquad \text{(A. 4.)}$$

To start with $F^{(1)}_{\mu\nu}$ is set equal to $H^{(1)}_{\mu\nu}$.
Then $F'^{(1)}_{ij}$ is calculated by the expression

$$F'^{(1)}_{ij} = \sum_{\mu} \sum_{\nu} C^{(0)}_{\mu i} F^{(1)}_{\mu\nu} C^{(0)}_{\nu j} \qquad \text{(A.5.)}$$

where the indices μ and ν refer to the atomic orbitals and i and j refer to the energy levels.

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

The elements of the matrix A are given by

$$A_{ik} = F'^{(1)}_{ik} \Big/ (E_k^{(0)} - E_i^{(0)}) \qquad \text{(A.6.)}$$

The first order change in the charge density matrix $P^{(1)}$ is now expressed in terms of 'A' matrix.

$$P^{(1)}_{\mu\nu} = 2 \sum_{i}^{occ} \sum_{k}^{vac} A_{ki} \left(C^{(0)}_{\mu i} C^{(0)}_{\nu k} + C^{(0)}_{\mu k} C^{(0)}_{\nu i} \right) \qquad \text{(A.7.)}$$

Now, the first order correction to the total energy is given by

$$W^{(1)} = \left(\frac{1}{2}\right) \sum_{\mu} \sum_{\nu} \left\{ P^{(0)}_{\mu\nu} \left(H^{(0)}_{\mu\nu} + F^{(1)}_{\mu\nu} \right) + P^{(1)}_{\mu\nu} H^{(0)}_{\mu\nu} \right\} \qquad \text{(A.8.)}$$

Also, the first order change in the orbital energies are given by the diagonal elements of the $F^{(1)}$ matrix:

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

The $P_{\mu\nu}^{(1)}$ 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 bondorder, 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 LCAO coefficients of the zeroeth order wave functions.
File No. 26 Title 'MATRIXE':	It contains zeroeth order orbital energies.
File No. 27 Title 'MATRIXR':	It contains repulsion integrals.
File No. 29 Title 'MATRIXP3':	It contains zeroeth 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.)

$$H^{core}_{\mu\mu} = U_{\mu\mu} - \sum_{\nu} Z_{\nu} \gamma_{\mu\nu} \qquad (A.10.)$$

The data to be read are: $F^{core}_{\mu\nu} = \beta_{\mu\nu}$ (A.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, TOL and MIXT in F 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 itereations 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 NPOS 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.I.1.

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

$$F^{(1)}_{\mu\mu} = H^{(1)}_{\mu\mu} + (\tfrac{1}{2})\, P^{(1)}_{\mu\mu}\, \gamma_{AA} + \sum_{B} Q^{(1)}_{B}\, \gamma_{AB} \qquad (A.\ 12.)$$

$$F^{(1)}_{\mu\nu} = -\, (\tfrac{1}{2})\, P^{(1)}_{\mu\nu}\, \gamma_{AB} \qquad (A.\ 13.)$$

Expressions for first order changes in the bond order ($P^{(1)}_{\mu\nu}$), total energy change ($W^{(1)}$) 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. 79 Title 'LOCATOM' : 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 Hamiltomian 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 zeroeth order wave function.

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

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

$$H_{\mu\mu} = -1/2\ (I_{\mu} + A_{\mu}) + 1/2\ \gamma_{AA} - \sum_{B \neq A} Z_B\, \gamma_{AB} \qquad (A.\ 14)$$

$$H_{\mu\nu} = \beta^{0}_{AB}\ S_{\mu\nu} \qquad (A.\ 15)$$

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 F 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 itereations 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.

COMPUTER PROGRAMS FOR SCF PERTURBATION CALCULATIONS

```
FILE  25(KIND=DISK,TITLE="MATRIXV", FILETYPE=7)
FILE  26(KIND=DISK,TITLE="MATRIXE", FILETYPE=7)
FILE  27(KIND=DISK,TITLE="MATRIXR", FILETYPE=7)
FILE  28(KIND=DISK,TITLE="MATRIXP3", FILETYPE=7)
FILE  29(KIND=DISK, TITLE="MATRIXH", FILETYPE=7)
FILE  5(KIND=READER)
FILE  6(KIND=PRINTER)


      DIMENSION H1(35,35),F1(35,35),XC(35),YC(35),ZC(35),DIST(35)
      DIMENSION FMO(35,35),C(35,35),P1(35,35),A(35,35),R(35,35),P(35,35)
      DIMENSION H(35,35),E(35),G(35),W1(35),TITLE(13),PERTB(10)
C
C
C     FIRST ORDER PERTURBATION CALCULATION
C     THIS PROGRAM CALCULATES THE FIRST ORDER CHANGES IN ENERGY AND
C      BONDORDER USING S.C.F PERTURBATION APPROACH (REF: SANYBY.D.P.
C     IN ELECTRONIC STRUCTER OF POLYMER AND MOLECULAR CRYSTALS.
C     J.ANDRE AND J.LADIK. EDS. NEWYORK PLENUM PRESS 1975. )
C     PPP    WAVEFUNCTIONS ARE USED  AS THE ZEROTH ORDER FUNCTION
C     THE PERTURBATION  ARISES FROM  A SIMPLE COULOMBIC INTERACTION.
C
      READ (5,8) TITLE
8     FORMAT(13A6)
      WRITE(6,9) TITLE
9     FORMAT (1H1/36X, "PERTURBATIONS S.C.F M.O CALCULATIONS"/1X,13A6//)
      READ (5,10) NA,NOCC,NUM,NCENT
10    FORMAT (4I4)
      WRITE (6,15) NA,NOCC,NUM,NCENT
15    FORMAT (3X,"NA,NOCC,NUM,NCENT"/, 4I5)
C
      READ(25) ((C(I,J),J=1,NA),I=1,NA)
      READ(26) (E(K),K=1,NA)
      READ(27) ((R(M,N),N=1,NA), M=1,NA)
      READ(28)  ((P(I,J), J=1,NA), I=1,NA)
      READ(29) ((H(K,L), L=1,NA), K=1,NA)
C
C     TO CALCULATE H1(MU,MU)= -ZP(MU)/DIST(MU) AND
C     SETTING H1(MU,MU)= F1(MU,MU)
C     NA IS THE TOTAL NO OF PI ATOMIC ORBITALS
C     NOCC IS THE NO OF OCCUPIED PI ELECTRON LEVELS
C
      READ (5,20) TOL,MIXT
20    FORMAT (F10.5,I5)
      WRITE (6,25) TOL,MIXT
25    FORMAT (3X,"TOLERANCE AND MAXINUM NO OF ITEREATIONS"/, F10.5,I5)
      DO 35 MU = 1,NA
      DO 30 NU = 1,NA
      H1(MU,NU)=0.0
      F1(MU,NU)=0.0
```

```
      FMO(MU,NJ) = 0.0
30    CONTINUE
35    CONTINUE
      READ(5,40)(XC(MU),YC(MU),ZC(MU),MU=1,NA)
      DO 36  NFR = 1,NCENT
      READ (5,40) (XP,YP,ZP)
40    FORMAT (3F15.8)
      READ (5,10) NPOS
      WRITE (6,41) NPOS,XP,YP,ZP
41    FORMAT (//1X,"THE PERTUBING CENTER IS=",I3,//1X,"THE CO-ORDINATES
     1 OF THE PERTUBING CENTER ARE=", 3F15.8)
      READ(5,45) (PERTB(I), I=1,NUM)
45    FORMAT (8F10.3)
      DO 500 IRUN = 1,NUM
      CHARGE = PERTB(IRUN)
      DO 50 MU = 1,NA
      DIST(MU) = SQRT(( (XC(MU)-XP )**2) + ((YC(MU)-YP)**2) +
     1 ((ZC(MU)-ZP)**2))
      H1(MU,MU) = -(CHARGE * 14.3933)/DIST(MU)
      F1(MU,MU)= H1(MU,MU)
50    CONTINUE
      WRITE (6,55)
55    FORMAT (//1X,'DISTANCES OF ATOMS FROM PERTUBING CENTER'/)
      WRITE(6,60) (DIST(MU), MU=1,NA)
60    FORMAT (5X,8F15.8)
      WRITE (6,65)
65    FORMAT (//1X, 'THE CHARGE IS=          '/)
      WRITE (6,70) CHARGE
70    FORMAT(5X, F15.6)
      WRITE (6,75)
75     FORMAT(//1X, 'THE F1DIGONAL MATRIX'/)
      WRITE (6,85) (F1(MU,MU), MU=1,NA)
85    FORMAT (2X,10F11.6)
      KOUNT=0
90    KOUNT=KOUNT+1
C
C
C     TO CALCULATE BIG F(K,I) FROM THE RELATION
C     SIGMA(MU),SIGMA(NU) C(0)(MU,I)*C(0)(NU,K)*F1(MU,NU)
C     NOCC IS THE NUMBER OF OCCUPIED LEVEL
C     I IS OCCUPIED ORBITAL , K IS VACCANT ORBITAL
      DO 95 I =1,NOCC
      DO 95 K = NOCC+1,NA
      FMO(K,I) = 0.0
       DO 100 MU = 1,NA
      DO 100 NU = 1,NA
      FMO(K,I)  = FMO(K,I) + C(K,MU)*F1(MU,NU)*C(I,NU)
100   CONTINUE
      FMO(K,I) = FMO(K,I)/(E(I) - E(K))
95    CONTINUE
      DO 120 I = 1,NA
      FMO(I,I) = 0.0
      DO 121 MU = 1,NA
      DO 121 NU = 1,NA
      FMO(I,I) = FMO(I,I) + C(I,MU)*F1(MU,NU)*C(I,NU)
```

```
121     CONTINUE
120     CONTINUE
C
C
C       TO CALCULATE P1(MU,NU)= 2* SIGMA I TO OCC SIGMA K TO VAC
C       A(K,I)(C(0)(MU,I)*C(0)(NU,K) + C(0)(MU,K)*C(0)(NU,I))
        DO 140 MU = 1,NA
        DO 140 NU = MU,NA
        P1 (MU,NU)= 0.0
        DO 145 I = 1,NOCC
        DO 145 K = NOCC+1,NA
        P1(MU,NU) = P1(MU,NU)+2*FMO(K,I)*(C(K,MU)*C(I,NU)+C(K,NU)*C(I,MU))
145     CONTINUE
        P1(NU,MU) = P1(MU,NU)
140     CONTINUE
C
C
C       TO CALCULATE F1(MU,MU)=H1(MU,MU)+ SIGMA NU TO N P1(NU,NU)*
C       GAMA(MU,NU)- 0.5*P1(MU,MU)*GAMA(MU,MU)
        DO 170 MU = 1,NA
        F1(MU,MU) = H1(MU,MU)-0.5*P1(MU,MU) *R(MU,MU)
        DO 175 NU = 1,NA
        F1(MU,MU) = F1(MU,MU) + P1(NU,NU)*R(MU,NU)
175     CONTINUE
C       TO CALCULATE F1(MU,NU) = -0.5* P1(MU,NU) * GAMA(MU,NU)
        DO 170 NU = MU+1,NA
        F1(MU,NU) = -0.5*P1(MU,NU)*R(MU,NU)
        F1(NU,MU) =F1(MU,NU)
170     CONTINUE
C
C
C       TO CALCULATE W1FROM THE RELATION W1= 0.5 SIGMA MU TO NA SIGMA
C       NU TO NA (P(0)(MU,NU)(H1(MU,NU)+F1(MU,NU)*H(MU,NU))
        W1(KOUNT)=0.0
        DO 195 MU= 1,NA
        DO 200 NU= 1,NA
        W1(KOUNT) = W1(KOUNT) + (P(MU,NU)*(H1(MU,NU)+F1(MU,NU))) +
       1(P1(MU,NU)*H(MU,NU))
200     CONTINUE
195     CONTINUE
        W1(KOUNT) = 0.5*W1(KOUNT)
        WRITE (6,210)
210     FORMAT (//1X, 'THE KOUNTS AND W1(KOUNTS)'/)
        WRITE (6,215) KOUNT,W1(KOUNT)
215     FORMAT (2X, I5, F11.6)
C
C
C       TO CALCULATE E(1)FROM THE RELATION E1(I)=BIGF(I,I)
        WRITE (6,225)
225     FORMAT (//1X, 'THE E1 MATRIX'/)
        WRITE (6,230) (FMO(I,I), I=1,NA)
230     FORMAT(2X,10F11.6)
        KMIN=KOUNT-1
         IF (KMIN) 235,235,240
240     DIFF = ABS(W1(KOUNT)-W1(KMIN))
```

```
      IF (DIFF-TOL)255,255,250
250   IF (KOUNT-MIXT)235,260,260
235   GO TO 90
260   WRITE (6,265)
265   FORMAT (1X, 'UNABLE TO REACH SELF CONSISTENCY')
255   WRITE (6,270)
270   FORMAT (//1X, 'THE PEPTURB ENERGY W1'/)
      WRITE (6,275) W1(KOUNT)
275   FORMAT (2X,F11.6)
      WRITE (6,280)
280   FORMAT (//1X, 'THE ORBITAL ENERGY CORRESPONDING TO FIRST ORDER'/)
      WRITE (6,285) (FMO(I,I), I=1,NA)
285   FORMAT (2X, 10F11.6)
      WRITE (6,290)
290   FORMAT (//1X,'THE BONDORDER MATRIX P1')
      DO 295 MU = 1, NA
295   WRITE (6,296) (P1(MU,NU), NU= 1,NA)
296   FORMAT (2X, 10F11.6)
500   CONTINUE
36    CONTINUE
      END
      002:0210:0  IS THE LOCATION FOR EXCEPTIONAL ACTION ON THE I/O STATEMENT A
      002:021E:2  IS THE LOCATION FOR EXCEPTIONAL ACTION ON THE I/O STATEMENT A
      002:021F:4  IS THE LOCATION FOR EXCEPTIONAL ACTION ON THE I/O STATEMENT A
      002:0221:0  IS THE LOCATION FOR EXCEPTIONAL ACTION ON THE I/O STATEMENT A
      002:0222:2  IS THE LOCATION FOR EXCEPTIONAL ACTION ON THE I/O STATEMENT A
```

```
                 B6700  FORTRAN  COMPILATION  MARK  2.9.110
                                                 SCFPERTURABATION 2

FILE  79 (KIND = DISK, TITLE ="LOCATN", FILETYPE=7)
FILE  81 (KIND = DISK, TITLE ="HIJ", FILETYPE=7)
FILE  82 (KIND = DISK, TITLE ="HII", FILETYPE=7)
FILE  83 (KIND=DISK, TITLE="GAMMA", FILETYPE=7)
FILE  86 (KIND = DISK, TITLE ="LCAO", FILETYPE=7)
FILE  87 (KIND = DISK, TITLE ="EENRGY", FILETYPE=7)
FILE  89 (KIND = DISK, TITLE ="BONDORDER", FILETYPE=7)


      DIMENSION H1(110),F1(110,110),XC(40),YC(40),ZC(40),DIST(110),
     1FMO(65,65),C(110,110),P1(110,110),R(40,40),E1(110),P(110,110),
     1H(110,110),E(110),W1(110),LOCATN(110),TITLE(13)
C
C
C     FIRST ORDER ALL VALENCE PERTURBATION CALCULATION
C     THIS PROGRAM CALCULATES THE FIRST ORDER CHANGES IN ENERGY AND
C     BONDORDER USING S.C.F PERTURBATION APPROACH (REF: SANYAL.D.P.
C     IN ELECTRONIC STRUCTER OF POLYMER AND MOLECULAR CRYSTALS.
C     J.ANDRE AND J.LADIK. EDS. NEWYORK PLENUM PRESS 1975. )
C     CNDO/2 WAVEFUNCTIONS ARE USED  AS THE ZEROTH ORDER FUNCTION
C     THE PERTURBATION ARISES FROM A SIMPLE COULOMBIC INTERACTION.
C
      READ(5,8) TITLE

8     FORMAT(13A6)
      WRITE(6,9) TITLE

9     FORMAT(1H1/36X,'ALL VALENCE PERTURBATIONS SCF M.O CALCULATIONS'/1X
     1, 13A6//)
      READ (5,10) NA,NATOMS,NOCC,NCUT,INDEX,NBOND
10    FORMAT(10I4)
C     NA IS THE TOTAL NUMBER OF VALENCE ORBITALS
C     NATOMS IS THE TOTAL NO OF ATOMS
C     NOCC IS THE NUMBER OF OCCUPIED LEVEL
C     NCUT IS FOR CUTTING OUT ENERGY LEVELS
C     INDEX = NA/2 IF NA IS EVEN
C     INDEX = NA-1/2 IF NA IS ODD
C     NBOND IS FOR CONTROLLING BONDORDER MATRIX
C     WHEN NBOND = 0 BONDORDER MATRIX IS NOT PRINTED
C     WHEN NBOND GREATER THAN ZERO BONDORDER MATRIX IS PRINTED
C
      WRITE (6,15) NA,NATOMS,NOCC,NCUT,INDEX,NBOND
15    FORMAT (3X, 'NA=',I3,3X,'NATOMS=',I3,3X,'NOCC=',I3,3X,'NCUT=',I3,
     13X,'INDEX=',I3,3X,'NBOND=',I3, //)
      READ (5,20) TOL,MIXT
20    FORMAT (F10.5,I5)
      WRITE (6,25) TOL,MIXT
25    FORMAT (3X,'TOLERANCE AND MAXIMUM NO OF ITEREATIONS'/, F10.5,I5)
      LUMO = NOCC+ 1
C
```

```
C
      READ (79) (LOCATN(I), I=1,NA)
      DO 124 I = 1,NA-1
124   READ (81) (H(I,J), J=I+1,NA)
      READ(82)  (H(I,I),I=1,NA)
      READ(83) ((R(I,J), J=1,NATOMS), I=1,NATOMS)
      DO 125 I = 1,NA
125   READ (86) (C(I,J), J=1,NA)
      READ(87) (E(I), I=1,NA)
      DO 126 I = 1,NA
126   READ (89) (P(I,J), J=1,NA)
C
C     THESE CARDS ARE INSERTED TO INVERT THE ORDERING OF CNDO ENERGY
C      LEVELS AND THE CORRESPONDING EIGEN VECTORS
      DO 400 I=1,INDEX
      EE = E(I)
      INA = NA-I+1
      EE1 = E(INA)
      E(I) = EE1
      E(INA) = EE
400   CONTINUE
      DO 450 I = 1,NA
      DO 450 J = 1,INDEX
      LNA = NA-J+1
      CIJ = C(I,J)
      CNA = C(I,LNA)
      C(I,J) = CNA
      C(I,LNA) = CIJ
450   CONTINUE
C     TO CALCULATE H1(MU,NU)= -ZP(MU)/DIST(MU) AND
C
C     SETTING H1(MU,MU)= F1(MU,MU)
C     AFTER READING FILE 81 AND FILE82 ALL ELEMENTS OF H COMPLETED
      DO 35 MU = 1,NA
      DO 30 NU = 1,NA
      H(NU,MU) = H(MU,NU)
30    CONTINUE
35    CONTINUE
      READ(5,40)(XC(MU),YC(MU),ZC(MU),MU=1,NATOMS)
      READ (5,40) XP,YP,ZP
40    FORMAT(3F15.8 )
      READ (5,45)  CHARGE
45    FORMAT (F13.8)
      DO 50 MU = 1,NA
      MU1 = LOCATN(MU)
      DIST(MU) = SQRT(((XC(MU1)-XP)**2) + ((YC(MU1)-YP)**2) +
     1  ((ZC(MU1)-ZP)**2))
      H1(MU) = -(CHARGE * 0.529)/DIST(MU)
         F1 (MU,MU) = H1(MU)
50    CONTINUE
      WRITE (6,55)
55    FORMAT(//1X, 'THE DISTANCES OF ATOMIC ORBITALS FROM ORIGIN'/)
      WRITE(6,60) (DIST(MU), MU=1,NA)
60    FORMAT (5X,8F15.8)
      WRITE (6,65) CHARGE
```

```
65      FORMAT(//5X, 'THE CHARGE OF THE METAL CONSIDERED IS=', F10.5)
        WRITE (6,75)
75       FORMAT(//1X, 'THE F1 DIGONAL MATRIX'/)
        WRITE(6,85) (F1(MU,MU), MU=1,NA)
85      FORMAT (2X,10F11.6)
        KOUNT=0
90      KOUNT=KOUNT+1
C
C
C       TO CALCULATE BIG F(K,I) FROM THE RELATION
C       SIGMA(MU),SIGMA(NU) C(0)(MU,I)*C(0)(NU,K)*F1(MU,NU)
C       MU AND NU ARE ORBITAL INDEX
C       I IS THE INDEX FOR OCCUPIED LEVEL
C       J IS THE INDEX FOR UNOCCUPIED LEVEL
        NINL = NCUT + 1
        NFIL = NA - NCUT
        DO 95 I = NINL,NOCC
        E1(I)  = 0.0
        NVAC = NFIL - I + NINL
        IF (NVAC-LUMO)405,402,402
402     E1(NVAC)=0.0
405     CONTINUE
        DO 96 K = NOCC+1,NFIL
        KK = K - NOCC
        FMO(KK,I) = 0.0
        DO 100 MU = 1,NA
        DO 100 NU = 1,NA
        FMO(KK,I) = FMO(KK,I) + C(MU,K)*F1(MU,NU)*C(NU,I)
        IF (K - NFIL) 100,101,100
101     E1(I) = E1(I) + C(MU,I)*F1(MU,NU)*C(NU,I)
        IF (NVAC - LUMO) 100,1011,1011
1011    E1(NVAC) = E1(NVAC) + C(MU,NVAC)*F1(MU,NU)*C(NU,NVAC)
100     CONTINUE
        FMO(KK,I) = FMO(KK,I)/(E(I) - E(K))
96      CONTINUE
95      CONTINUE
C
C
C       TO CALCULATE P1(MU,NU)= 2* SIGMA I TO OCC SIGMA K TO VAC
C       A(K,I)(C(0)(MU,I)*C(0)(NU,K) + C(0)(MU,K)*C(0)(NU,I))
        DO 140 MU = 1,NA
        DO 140 NU = MU,NA
        P1 (MU,NU)= 0.0
        DO 145 I = NINL,NOCC
        DO 145 K = NOCC+1,NFIL
         KK = K - NOCC
        P1(MU,NU) = P1(MU,NU) + 2*FMO(KK,I)* (C(MU,K)*C(NU,I) + C(NU,K)*
       1 C(MU,I))
145     CONTINUE
        P1(NU,MU) = P1(MU,NU)
140     CONTINUE
C
C
C       TO CALCULATE F1(MU,MU)=H1(MU,MU)+ SIGMA NU TO N P1(NU,NU)*
C       GAMA(MU,NU)- 0.5*P1(MU,MU)*GAMA(MU,MU)
```

```
      DO 170 MU = 1,NA
      MU1 = LOCATM(MU)
          F1(MU,MU) = H1(MU) - 0.5 * P1( MU,MU )*R(MU1,MJ1)
      DO 175 NU = 1,NA
      NU1 = LOCATM(NU)
      F1(MU,MU) = F1(MU,MU) + P1(NU,NU)*R( MU1,NU1)
175   CONTINUE
170   CONTINUE
C     TO CALCULATE F1(MU,NU) = -0.5* P1( MU,NU) * GAM
      NMIN = NA - 1
      DO 176 MU = 1,NMIN
      DO 176 NU = MU+1,NA
      MU1 = LOCATM(MU)
      NU1 = LOCATM(NU)
      F1(MU,NU) = -0.5*P1(MU,NU)*R( MU1,NU1)
      F1(NU,MU) =F1(MU,NU)
176   CONTINUE
C
C
C     TO CALCULATE H1FROM THE RELATION H1= 0.5 SIGMA MU TO NA SIG=1
C     NU TO NA (P(0)(MU,NU)(H1(MU,NU)+F1(MU,NU)*H(MU,NJ))
      H1(KOUNT)=0.
      DO 195 MU= 1,NA
      H1(KOUNT) = H1(KOUNT) +((P(MU,MU)*(H1(MU)+F1(MU,MU))) + (P1(MU,MU)
     1 *H(MU,MU)))*0.5
       DO 200 NU = MU+1,NA
      H1(KOUNT) = H1(KOUNT) + (P(MU,NU)*F1(MU,NU)) +(P1(MU,NU)*H(MU,NU))
200   CONTINUE
195    CONTINUE
      WRITE (6,210)
210   FORMAT (//1X, 'THE KOUNTS AND H1(KOUNTS)'/)
      WRITE (6,215) KOUNT,H1(KOUNT)
215   FORMAT (2X, I5, F11.6)
C
C
C     TO CALCULATE E(1)FROM THE RELATION E1(I)=BIGF(I,I)
      WRITE (6,225)
225   FORMAT (//1X, 'THE E1 MATRIX'/)
      WRITE (6,230) (E1(I), I=NIML,NFIL)
230   FORMAT(2X,10F11.6)
      KMIN=KOUNT-1
       IF (KMIN) 235,235,240
240   DIFF = ABS(H1(KOUNT)-H1(KMIN))
      IF (DIFF-TOL)255,255,250
250   IF (KOUNT-NIXT)235,260,260
235   GO TO  90
260   WRITE (6,265)
265   FORMAT (1X, 'UNABLE TO REACH SELF CONSISTENCY')
255   WRITE (6,270)
270   FORMAT (//1X, 'THE PERTURB ENERGY H1'/)
      WRITE (6,275) H1(KOUNT)
275   FORMAT (2X,F11.6)
      WRITE (6,280)
280   FORMAT (//1X, 'THE ORBITAL ENERGY CORRESPONDING TO FIRST ORDER'/)
      WRITE (6,285) (I,E1(I), I=NIML,NFIL)
```

```
                              PERTURBATIONS S.C.F M-O CALCULATIONS
PORPHINE DI-ANION SCF CALCULATION

NA ,NOCC, NUH
 24   13    2
TOLERANCE AND MAXIMUM NO OF ITERATIONS
 0.00100   10

DISTANCES OF ATOMS FROM PERTUBING CENTER

      4.27163318   3.04393249   3.45633795   3.04393249   4.27163318   4.27163318   3.04393249   3.45633795
      3.04393249   4.27163318   4.27163318   3.04393249   3.45533795   3.04393249   4.27163318   4.27163318
      3.04393249   3.45633795   3.04393249   4.27163318   2.05400000   2.05400000   2.05400000   2.05400000

THE CHARGE IS=
        0.520000

THE DIAGONAL MATRIX

    -1.684754  -2.364261  -2.082160  -2.364261  -1.684754  -1.684754  -2.364261  -2.082160  -2.364261  -1.684754
    -1.684754  -2.364261  -2.082160  -2.364261  -1.684754  -1.684754  -2.364261  -2.082160  -2.364261  -1.684754
    -3.503724  -3.503724  -3.503724  -3.503724

THE KOUNTS AND H1(KOUNTS)

    1 -60.287232

THE E1 MATRIX

    -2.416013  -2.405892  -2.405892  -2.412140  -2.187152  -2.002859  -2.002860  -2.091726  -2.193537  -2.533330
    -2.533330  -2.157413  -2.599431  -2.157253  -2.157258  -1.870576  -1.891602  -2.112276  -2.112275  -2.747061
    -2.073408  -2.472300  -2.472299  -2.525729

THE KOUNTS AND H1(KOUNTS)

    2 -60.287232

THE E1 MATRIX

    -2.416013  -2.405892  -2.405892  -2.412140  -2.187152  -2.002859  -2.002860  -2.091726  -2.193537  -2.533330
    -2.533330  -2.157413  -2.599431  -2.157258  -2.157258  -1.870576  -1.891602  -2.112276  -2.112276  -2.747061
    -2.073408  -2.472300  -2.472299  -2.525729

THE PERTURB ENERGY H1

  -60.287232

THE ORBITAL ENERGY CORRESPONDING TO FIRST ORDER

    -2.416013  -2.405892  -2.405892  -2.412140  -2.187152  -2.002359  -2.002860  -2.091726  -2.193537  -2.533330
    -2.533330  -2.157413  -2.599431  -2.157258  -2.157258  -1.870576  -1.891602  -2.112276  -2.112276  -2.747061

    -2.073408  -2.472300  -2.472299  -2.525729
```

```
                         ALL VALENCE PERTURBATIONS SCF M.O CALCULATIONS
 PORPHYRIN DI-ANION MOLECULE
   NA=100   NATOMS= 36   NOCC= 57   NCUT= 31   INDEX= 54   NBDHO= 0
   TOLERANCE AND MAXIMUM NO OF ITERATIONS
   0.00100     1
 THE DISTANCES OF ATOMIC ORBITALS FROM ORIGIN
      5.25382537   4.53679711   5.25382537   5.25382537   4.53679711   5.25382537   5.25382537   4.53679711
      5.25382537   5.25382537   4.53679711   5.25382537   4.27163318   3.04393249   3.45633795   3.04393249
      4.27163318   4.27163318   3.04393249   3.45633795   3.04393249   4.27163318   4.27163318   3.04393245
      3.45633795   3.04393249   4.27163318   4.27163318   3.04393249   3.45633795   3.04393249   4.27163318
      2.05400000   2.05400000   2.05400000   2.05400000   4.27163318   3.04393249   3.45633795   3.04393245
      4.27163318   4.27163318   3.04393249   3.45633795   3.04393249   4.27163318   4.27163318   3.04393245
      3.45633795   3.04393249   4.27163318   4.27163318   3.04393249   3.45633795   3.04393249   4.27163318
      2.05400000   2.05400000   2.05400000   2.05400000   4.27163318   3.04393249   3.45633795   3.04393245
      4.27163318   4.27163318   3.04393249   3.45633795   3.04393249   4.27163318   4.27163318   3.04393245
      3.45633795   3.04393249   4.27163318   4.27163318   3.04393249   3.45633795   3.04393249   4.27163318
      2.05400000   2.05400000   2.05400000   2.05400000   4.27163318   3.04393249   3.45633795   3.04393249
      4.27163318   4.27163318   3.04393249   3.45633795   3.04393249   4.27163318   4.27163313   3.04393245
      3.45633795   3.04393249   4.27163318   4.27163313   3.04393249   3.45633795   3.04393249   4.27163318
      2.05400000   2.05400000   2.05400000   2.05400000
   THE CHARGE OF THE METAL CONSIDERED IS=   1.00000
 THE FIDUCIAL MATRIX
    -0.100689 -0.116602 -0.100689 -0.100689 -0.116602 -0.100689 -0.100689 -0.116602 -0.101689 -0.100689
    -0.116602 -0.100689 -0.123840 -0.173788 -0.153052 -0.173788 -0.123840 -0.123840 -0.173788 -0.153052
    -0.173788 -0.123840 -0.123840 -0.173788 -0.153052 -0.173788 -0.123840 -0.123840 -0.173788 -0.153052
    -0.173788 -0.123840 -0.257546 -0.257546 -0.257546 -0.257546 -0.123840 -0.173788 -0.153052 -0.173788
    -0.123840 -0.123840 -0.173788 -0.153052 -0.173788 -0.123840 -0.123840 -0.173788 -0.153052 -0.173788
    -0.123840 -0.123840 -0.173788 -0.153052 -0.173788 -0.123840 -0.257546 -0.257546 -0.257546 -0.257546
    -0.123840 -0.173788 -0.153052 -0.173788 -0.123840 -0.123840 -0.173788 -0.153052 -0.173788 -0.123840
    -0.123840 -0.173788 -0.153052 -0.173788 -0.123840 -0.123840 -0.173788 -0.153052 -0.173788 -0.123840
    -0.257546 -0.257546 -0.257546 -0.257546 -0.123840 -0.173788 -0.153052 -0.173788 -0.123840 -0.123840
    -0.173788 -0.153052 -0.173788 -0.123840 -0.123840 -0.173788 -0.153052 -0.173788 -0.123840 -0.123840
    -0.173788 -0.153052 -0.173788 -0.123840 -0.257546 -0.257546 -0.257546 -0.257546
  THE KOUNTS AND W1(KOUNTS)
     1  -18.746075
  THE EI MATRIX
    -0.163440 -0.161382 -0.125419 -0.135310 -0.135310 -0.178183 -0.135993 -0.179103 -0.179103 -0.149919
    -0.147704 -0.147704 -0.162206 -0.162206 -0.178376 -0.152232 -0.149937 -0.217186 -0.186580 -0.201378
    -0.201378 -0.194497 -0.194497 -0.210468 -0.161453 -0.202085 -0.164894 -0.164894 -0.137935 -0.203124
    -0.155913 -0.155913 -0.136175 -0.140394 -0.124463 -0.127907 -0.127907 -0.120063 -0.120060 -0.123314
    -0.115712 -0.123708 -0.139514 -0.139914 -0.144569 -0.151360
  THE KOUNTS AND W1(KOUNTS)
```

```
  2 -18.746010

 THE E1 MATRIX

   -0.143725  -0.141733  -0.128091  -0.132307  -0.132307  -0.153219  -0.131735  -0.152426  -0.152426  -0.139746
   -0.134344  -0.134344  -0.145035  -0.145035  -0.151307  -0.139104  -0.137703  -0.173770  -0.163588  -0.165146
   -0.165146  -0.167392  -0.167392  -0.170047  -0.139119  -0.174533  -0.146896  -0.146896  -0.128901  -0.170816
   -0.141072  -0.141072  -0.129344  -0.130158  -0.125322  -0.126545  -0.126545  -0.122904  -0.122904  -0.125218
   -0.121650  -0.125614  -0.131975  -0.131975  -0.133299  -0.137481

 THE PERTURB ENERGY H1

   -18.746010

 THE ORBITAL ENERGY CORRESPONDING TO FIRST ORDER

   32 -0.143725   33 -0.141733   34 -0.128091   35 -0.132307   36 -0.132307   37 -0.153219   38 -0.131735   39 -0.152426
   40 -0.152426   41 -0.139746   42 -0.134344   43 -0.134344   44 -0.145035   45 -0.145035   46 -0.151307   47 -0.139104
   48 -0.137703   49 -0.173770   50 -0.163588   51 -0.165146   52 -0.165146   53 -0.167392   54 -0.167392   55 -0.170047
   56 -0.139119   57 -0.174533   58 -0.146896   59 -0.146896   60 -0.128901   61 -0.170816   62 -0.141072   63 -0.141072
   64 -0.129344   65 -0.130158   66 -0.125322   67 -0.126545   68 -0.126545   69 -0.122904   70 -0.122904   71 -0.125218
   72 -0.121650   73 -0.125614   74 -0.131975   75 -0.131975   76 -0.133299   77 -0.137481

 THE ZERO ORDER ENERGIES

    1 -1.668846    2 -1.651878    3 -1.651878    4 -1.633153    5 -1.307041    6 -1.248341    7 -1.248341    8 -1.163506
    9 -1.065755   10 -1.046192   11 -1.046192   12 -1.012779   13 -0.993728   14 -0.885087   15 -0.885087   16 -0.842307
   17 -0.760423   18 -0.760423   19 -0.756024   20 -0.722932   21 -0.666274   22 -0.616243   23 -0.616243   24 -0.607211
   25 -0.604925   26 -0.604925   27 -0.597672   28 -0.579351   29 -0.532548   30 -0.504046   31 -0.504046   32 -0.432589
   33 -0.377293   34 -0.374918   35 -0.359086   36 -0.359086   37 -0.353329   38 -0.326532   39 -0.284795   40 -0.284795
   41 -0.277138   42 -0.259722   43 -0.259722   44 -0.242488   45 -0.242488   46 -0.238955   47 -0.203097   48 -0.196936
   49 -0.196886   50 -0.158258   51 -0.152710   52 -0.152710   53 -0.145587   54 -0.145587   55 -0.137449   56 -0.009592
   57  0.016565   58  0.287594   59  0.287594   60  0.380920   61  0.528375   62  0.535087   63  0.535087   64  0.538592
   65  0.557143   66  0.560175   67  0.562877   68  0.562877   69  0.566054   70  0.566054   71  0.568157   72  0.569243
   73  0.571531   74  0.576110   75  0.576110   76  0.588709   77  0.602105   78  0.618444   79  0.618444   80  0.632452
   81  0.637735   82  0.656334   83  0.656334   84  0.658597   85  0.692942   86  0.697673   87  0.697673   88  0.717331
   89  0.717871   90  0.737420   91  0.740687   92  0.740687   93  0.749004   94  0.749004   95  0.758674   96  0.759468
   97  0.805126   98  0.809934   99  0.810268  100  0.810264  101  0.810884  102  0.829784  103  0.829784  104  0.850128
  105  0.860898  106  0.865251  107  0.865251  108  0.867538
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