CHAPTER II

SCF PERTURBATION CALCULATION ON METALLOPORPHYRINS
The past twenty years have witnessed accumulation of extensive data on the physicochemical properties of porphyrins and related systems. Progress on parallel lines has also taken place in the theoretical calculations at varying levels of sophistication on the ground and excited states of porphyrins. 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. 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. Recent results on the photoelectron spectroscopic studies on porphyrins have also been interpreted on this basis. 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, $E' = (-Ze^2/r)$, 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.\textsuperscript{15,16} The wave functions for
the unperturbed system have been calculated by PPP-pi electron
method as well as by CNDO/2 method.\textsuperscript{17} The results are
electrifying and we have obtained good correlations between
the oxidation potential of the pi ligand and the charge on
the metal ion.

II.2. \textbf{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.\textsuperscript{15,16} Though this method
is well documented,\textsuperscript{15,16} for the sake of completeness, a brief
account of this approach relevant 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{align}
F &= F^{(0)} + F^{(1)} \\
S &= S^{(0)} + S^{(1)} \\
C &= C^{(0)} + C^{(1)} \quad (II.1.)
\end{align}
The superscript \((0)\) refers to the operators in the unperturbed system. Starting with Roothen's equation,

\[
FC = SCE
\]  

(II. 2)

it is expanded in a perturbation series to first order. Since our zeroth order wave functions have been obtained using zero differential overlap approximation, (PFP and CND0/2 methods), we can ignore \(S^{(1)}\). Expanding II.2 to first order and collecting terms by the order, we get

\[
F(0) C(0) = S(0) C(0) E(0) \tag{II. 3}
\]

\[
F(1) C(0) + F(0) C(1) = S(0) C(0) E(1) + S(0) C(1) E(0) \tag{II. 4}
\]

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

\[
C(1) = C(0) \Lambda \tag{II.5}
\]

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

\[
F'(1) + E(0) \Lambda = E(1) + \Lambda E(0) \tag{II.6}
\]

where

\[
F'(1) = \tilde{C}(0) F(1) C(0) \tag{II.7}
\]
The elements of $F^{'}(1)$ matrix are given by,

$$F_{\mu\nu}^{'}(1) = \sum_{\mu} \sum_{\nu} C^{(0)}_{\mu i} E^{(1)}_{\mu i} C^{(0)}_{\nu j}$$

(II.8.)

where the indices $\mu$ and $\nu$ 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.

$$F_{\mu\mu}^{'}(1) = E_{\mu i}^{(1)} = \sum_{\mu} \sum_{\nu} C^{(0)}_{\mu i} E^{(1)}_{\mu i} C^{(0)}_{\nu i}$$

(II.9.)

The elements of the $A$ matrix are:

$$A_{\mu\nu} = F^{'}_{\mu\nu} / (E_{\mu}^{(0)} - E_{\nu}^{(0)})$$

(II.10)

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

$$P^{(1)}_{\mu\nu} = 2 \sum_{\mu\nu} A_{\mu\nu} C^{(0)}_{\mu i} C^{(0)}_{\nu j}$$

(II.11)

A nice feature of this expression is that only those $A_{\mu\nu}$ 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,

\[ W^{(1)} = \frac{1}{2} \sum_{\mu} \sum_{\nu} p^{(0)}_{\mu \nu} \left( H^{(0)}_{\mu \nu} + F^{(1)}_{\mu \nu} \right) \]

\[ + p^{(1)}_{\mu \nu} H^{(0)}_{\mu \nu} \]  

(II.12)

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

\[ H^{(1)}_{\mu \mu} = \left( - \frac{Z}{R_{\mu}} \right) \]

\[ \text{in a.u.} \]

and

\[ H^{(1)}_{\mu \nu} = 0 \ (\text{for} \ \mu \neq \nu) \]  

(II.13)

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

\[ F^{(1)}_{\mu \mu} = H^{(1)}_{\mu \mu} + \frac{1}{2} F^{(1)}_{\mu \mu} + \sum_{\mu \neq \nu} p^{(1)}_{\mu \nu} \gamma_{\mu \nu} \]

(II.14).

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

(II.15).

In the CNDO/2 formalism, these elements are:

\[ F^{(1)}_{\mu \mu} = H^{(1)}_{\mu \mu} + \frac{1}{2} F^{(1)}_{\mu \mu} \gamma_{AA} + \sum_{B} q^{(1)}_{B} \gamma_{AB} \]

(II.16).

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

(II.17)
The zeroth order functions have been obtained for porphyrin
dianion with $D_{4h}$ symmetry, using the coordinates given by
Zerner and Gouterman.\textsuperscript{18} (fig 2.1). In the first cycle of
SCF perturbation calculations, $F^{(1)}$ is set equal to $H^{(1)}$
and $F^{(1)}$ 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.\textsuperscript{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. 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, $a_{1u}(\pi)$, $a_{2u}(\pi^*)$, and $e_g(\pi)$ 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 PPP wavefunctions.
Fig. 2.3 Energies of HOMO and LUMO levels of Porphin dianion obtained by SCF perturbation method using CNDO/2 wavefunctions.
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. 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:

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

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 on the metal ions in various metalloporphyrins, using figures 2.1 and 2.2 as pointed out earlier these charges may be considered as residual charges on the metal ion. A value of 1.34 (PFF) and 1.5 (CNDO/2) for Mg leads to an ionic character of 65% to 75% in the Mg-N C 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 zeroth 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 \( \pi - \pi^* \) 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 \( E^{(0X)}_{1/2} \) values. The following expression is obtained with standard deviation and linear correlation coefficient being 0.154 and 0.978 respectively.

\[
\text{IP (eV)} = 1.4453 \ E^{(0X)}_{1/2} + 6.1880 \quad (\text{II.19})
\]

where \( E^{(0X)}_{1/2} \) 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, McMaster 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 \(^{CP 71.2}\) (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).

<table>
<thead>
<tr>
<th>System</th>
<th>Charge (PPP)</th>
<th>Charge (CND$\chi_2$)</th>
<th>$E^{\text{OX}}_{1/2}$ (volts) (vs SCE)</th>
<th>IP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(II)OEP</td>
<td>1.30</td>
<td>1.52</td>
<td>0.54</td>
<td>6.21</td>
</tr>
<tr>
<td>Zn(II)OEP</td>
<td>1.31</td>
<td>1.56</td>
<td>0.63</td>
<td>6.26</td>
</tr>
<tr>
<td>Ni(II)OEP</td>
<td>1.32</td>
<td>1.58</td>
<td>0.73</td>
<td>6.32</td>
</tr>
<tr>
<td>H$_2$OEP</td>
<td>1.34</td>
<td>1.59</td>
<td>0.81</td>
<td>6.36</td>
</tr>
<tr>
<td>Ag(iI)OEP</td>
<td>1.38</td>
<td>1.63</td>
<td>1.10</td>
<td>6.53</td>
</tr>
<tr>
<td>Al(III)OEP(OH)</td>
<td>1.36</td>
<td>1.61</td>
<td>0.95</td>
<td>6.44$^b$</td>
</tr>
<tr>
<td>Sn(IV)OEP(OH)$_2$</td>
<td>1.43</td>
<td>1.68</td>
<td>1.40</td>
<td>6.70$^b$</td>
</tr>
</tbody>
</table>

$^a$ $E_{1/2}$ 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).
REFERENCES


