SCF perturbation calculations on metalloporphyrins

K K BHATTACHARJEE, J SUBRAMANIAN*, D P SANTRY**
and J-H FUHRHOP†

Department of Chemistry, North-Eastern Hill University, Shillong 793 003, India
** Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1
† Institut für Organische Chemie FB21 WE02, Freie Universität Berlin, 3 Takustrasse,
1000 Berlin 33, Federal Republic of Germany

Abstract. The influence of metal ion on the oxidation and ionisation potentials of metalloporphyrins is investigated by the simple electrostatic model using SCF perturbation theory. The zero order wavefunctions are obtained from PPP and CNDO/2 methods. The wide variations in redox potentials with metal and the relative insensitivity of the optical transitions with metal are very well accounted for by the perturbation approach.

Keywords. SCF perturbation calculations; metalloporphyrins; CNDO perturbation calculations.

1. Introduction

Metalloporphyrins occur as chromophores in many biological systems. Hence a considerable number of studies have been made on the various physicochemical aspects of these systems (Smith 1975; Dolphin 1978). A number of molecular orbital calculations have been made on metalloporphyrins and related systems in varying levels of sophistication (Maggiora 1973; Gouterman 1978; Almlöf 1974; Maggiora and Weiman 1974; Sangler et al 1977; Case and Karplus 1977; Petke et al 1978; Christofferson 1979; Ohno 1979; Dedieu et al 1982; Edward and Zerner 1983; Rawlings et al 1984).[§] It has been noticed that with a few exceptions, in the metalloporphyrins the redox potentials are very sensitive to the nature of the metal ion but the visible electronic spectra are relatively independent (Fuhrhop et al 1973; Felton 1978; Davis 1978) of the metal ion. This behaviour has been qualitatively interpreted as arising from the coulombic perturbation of the π electron energy levels of the porphyrin ligand by the metal ion (Felton 1978; Davis 1978). Recent results of photoelectron spectroscopic studies on metalloporphyrins have also been interpreted on this basis (Kitagawa et al 1979). An attempt has been made in this work to investigate this model 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 nuclear 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 (Stevens et al 1963; Geralt and Mills 1968; Pople et al 1968; Santry 1974, 1976). The wave function for the

---

* To whom all correspondence should be addressed
§ Only a few representative references are given. The literature cited is by no means exhaustive.

unperturbed system have been calculated by the PPP-π electron method as well as by the CNDO/2 method. The results are encouraging and we obtained good correlations between the oxidation potential of the π-ligand and the charges on the metal ion.

2. Methods of calculation

The SCF perturbation theory is well-documented (Santry 1974, 1976), and only the salient features are presented here for the sake of continuity. This method aims at calculating the first order corrections, namely $E^{(1)}$ and $W^{(1)}$ to the molecular orbital energy matrix and the total energy respectively, in the presence of a perturbation, $H^{(1)}$. The zeroth order Fock, overlap and coefficient matrices are given by $F^{(0)}$, $S^{(0)}$ and $C^{(0)}$. The corresponding matrices for the first order correction are respectively $F^{(1)}$, $S^{(1)}$ and $C^{(1)}$. Starting with Roothan's matrix equations,

$$FC = SCE \tag{1}$$

it is expanded in a perturbation series to first order. Our zeroth order functions are calculated in the ZDO framework and hence $S^{(1)}$ is ignored. The first order corrections to the m.o. energies are given by

$$E_i^{(1)} = \mathscr{F}_{ii} = \sum_\mu \sum_\nu C_{\mu i}^{(0)} F_{\mu\nu}^{(1)} C_{\nu i}^{(0)}, \tag{2}$$

where i, j, k etc. refer to the m.o. energy levels and μ, ν to the atomic orbitals. The corresponding coefficient matrix $C^{(1)}$ is given by

$$C^{(1)} = C^{(0)}A, \tag{3}$$

where the mixing matrix A is given by

$$A_{ik} = \mathscr{F}_{ik}/(E_k^{(0)} - E_i^{(0)}), \tag{4}$$

and

$$A_{ii} = 0.$$

The first order correction to the bond-order matrix is

$$P^{(1)} = 2 \sum_i^{occ} \sum_k^{vac} A_{ki} (C_{\mu i}^{(0)} C_{\nu k}^{(0)} + C_{\mu k}^{(0)} C_{\nu i}^{(0)}) \tag{5}$$

Only those A_{ki} terms are involved for which the i belong to the occupied levels and the k to the vacant ones. The first order correction to the total energy is given by

$$W^{(1)} = (\tfrac{1}{2}) \sum_\mu \sum_\nu \{P_{\mu\nu}^{(0)} (H_{\mu\nu}^{(1)} + F_{\mu\nu}^{(1)}) + P_{\mu\nu}^{(1)} H_{\mu\nu}^{(0)} \}. \tag{6}$$

The expressions (2) to (6) are obtained by putting $S^{(1)} = 0$ in the general equation

given by Santry (1974). $W^{(1)}$ is calculated by an iterative procedure using the dependence of $F^{(1)}$ on $P^{(1)}$. In the first cycle of calculations, $F^{(1)}$ is set equal to $H^{(1)}$. The $H^{(1)}$ matrix is given by

$$H^{(1)}_{\mu\mu} = (-Z/R_\mu) \text{ in au,} \tag{7}$$

and

$$H^{(1)}_{\mu\nu} = 0 \text{(for } \mu \neq \nu) \tag{8}$$

where R_μ is the distance of the atomic orbital μ from the central metal ion. The zeroth order functions have been obtained for porphin dianion with D_{4h} symmetry. The geometry used is that of Zerner and Gouterman (1966). In the PPP method, the elements of the $F^{(1)}$ matrix are given by

$$F^{(1)}_{\mu\mu} = H^{(1)}_{\mu\mu} + (\tfrac{1}{2}) P^{(1)}_{\mu\mu} \gamma_{\mu\mu} + \sum_{\mu \neq \nu} P^{(1)}_{\nu\nu} \gamma_{\mu\nu},$$

$$F^{(1)}_{\mu\nu} = -(\tfrac{1}{2}) P^{(1)}_{\mu\nu} \gamma_{\mu\nu}, \tag{9}$$

and the corresponding elements in the CNDO/2 formalism are

$$F^{(1)}_{\mu\mu} = H^{(1)}_{\mu\mu} + (\tfrac{1}{2}) P^{(1)}_{\mu\mu} \gamma_{AA} + \sum_B Q^{(1)}_B \gamma_{AB},$$

$$F^{(1)}_{\mu\nu} = -(\tfrac{1}{2}) P^{(1)}_{\mu\nu} \gamma_{AB}. \tag{10}$$

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 π 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 π levels are considered to arise out of the perturbation of the π 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 π electrons in the porphyrin dianion. We have taken the results of CNDO/2 calculation on porphyrin dianion as the starting point (Maggiora 1973). The changes in the π m.o. energies (2) and the total energy of the system (6) as functions of perturbing charge were calculated (table 1). The total orbital energies, $E_i^{(0)} + E_i^{(1)}$ as functions of perturbing charges are presented in figure 1 for the HOMO and LUMO levels. Similar calculations were done using the PPP wavefunctions. In the PPP formalism, it is not possible to distinguish explicitly between a porphyrin dianion and a metalloporphyrin. In choosing the "standard parameters" for PPP-calculations on a metalloporphyrin, Weiss *et al* (1965) adjusted the nitrogen parameters to obtain the best fit with the electronic spectrum of zinc porphyrin. Taking the CNDO/2 energy levels of the porphyrin 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

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

| System	Charge (PPP)	Charge (CNDO/2)	$E_{1/2}^{(OX)}$ (volts) (vs SCE)	IP (eV)
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] $E_{1/2}^{(OX)}$ values are taken from reference (Fuhrhop *et al* 1973).
[b] *IP* values are estimated using (11); other values are experimental data from Kitagawa *et al* 1979).
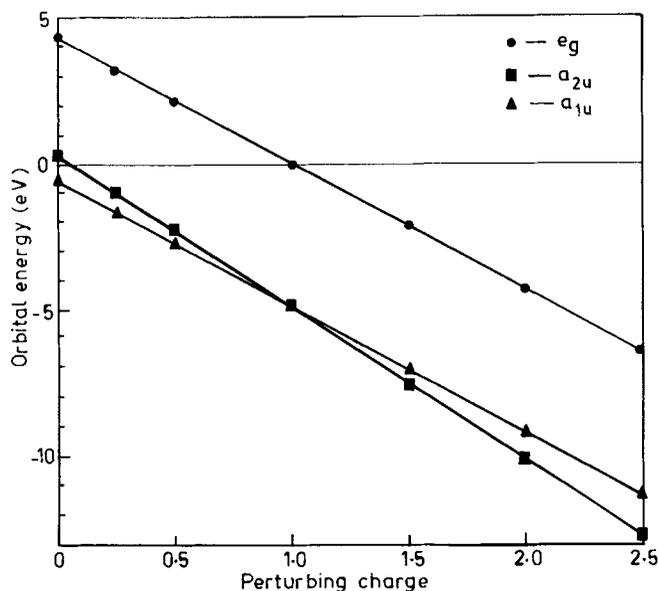
Figure 1. Energies of HOMO and LUMO levels of porphyrin dianion obtained by SCF perturbation method using PPP wavefunctions.

the orbital energy, $E_i^{(0)} + E_i^{(1)}$ vs the perturbing charge using the PPP-data is presented in figure 2. 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
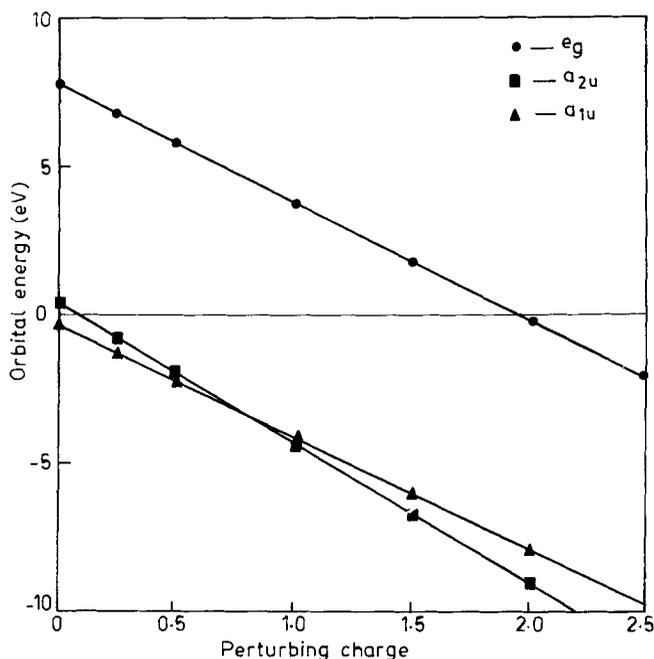
Figure 2. Energies of HOMO and LUMO levels of porphyrin dianion obtained by SCF perturbation method using CNDO/2 wavefunctions.

(a_{1u} and a_{2u}) (Dolphin *et al* 1971; Hanson *et al* 1981). The presence of the counter-ion 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 (Kitigawa *et al* 1979) have observed a linear correlation of the experimental ionisation potentials and oxidation potentials of metallo-octaethyl porphyrins. Hence we have fitted the available ionisation potential values of metallo-octaethyl porphyrins with their corresponding $E_{1/2}^{(OX)}$ values as follows:

$$IP \text{ (eV)} = 5.896 + 0.5766 \ E_{1/2}^{(OX)}, \tag{11}$$

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 (11)], using Koopman's theorem we have obtained the charges on the metal ions in various metalloporphyrins, using figures 1 and 2. As 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 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 π m.o. levels. Hence one does not expect much 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 electrostatic model, to a limited extent, does explain the observed trends in the electronic spectra and oxidation potentials of metalloporphyrins.

Acknowledgements

References

Almlöf J 1974 *Int. J. Quantum Chem.* **8** 915
Case D A and Karplus M 1977 *J. Am. Chem. Soc.* **99** 6182
Christofferson R E 1979 *Int. J. Quantum Chem.* **16** 573
Davis D G 1978 in *Porphyrins* (ed.) D Dolphin (New York: Academic Press) vol. 5, p. 127
Dedieu A, Rohmer M and Veillard A 1982 *Adv. Quantum Chem.* **16** 43
Dolphin D (ed.) 1978 in *Porphyrins* (New York: Academic Press) vol. 1–7
Dolphin D, Forman A, Borg D C, Fajer J and Felton R H 1971 *Proc. Natl. Acad. Sci. USA,* **68** 614
Edward W D and Zerner M C 1983 *Int. J. Quantum Chem.* **23** 1407
Felton R H F 1978 in *Porphyrins* (ed.) D Dolphin (New York: Academic Press) vol. 5
Fuhrhop J H, Kadish K M and Davis D G 1973 *J. Am. Chem. Soc.* **91** 5140
Geralt J Mills I M 1968 *J. Chem. Phys.* **49** 1719
Gouterman M 1978 in *Porphyrins* (ed.) D Dolphin (New York: Academic Press) vol. 3, pp 1–156
Hanson L K, Chang C K, Davis M S and Fajer J 1981 *J. Am. Chem. Soc.* **103** 663
Kitagawa S, Morishima I, Yonezawa J and Sato N 1979 *Inorg. Chem.* **18** 1345
Maggiora G M 1973 *J. Am. Chem. Soc.* **95** 6555
Maggiora G M and Weiman L J 1974 *Int. J. Quantum Chem., Quantum Biology Symp.* **1** 179
Ohno K 1979 in *Horizons of quantum chemistry* (eds.) K Fukui and B Pullman (Dordrecht: Reidel) p. 245
Petke J D, Maggiora G M, Shipman L L and Christofferson R E 1978 *J. Mol. Spectrosc.* **71** 64
Pople J A, Mciverjr J W and Ostlund N S 1968 *J. Chem. Phys.* **49** 2960, 2965
Rawlings D C, Davidson E R and Gouterman M 1984 *Int. J. Quantum Chem.* **26** 237
Sangler D, Maggiora G M, Shipman L L and Christofferson R E 1977 *J. Am. Chem. Soc.* **99** 7470, 7487
Santry D P 1974 in *Electronic structure of polymers and molecular crystals* (eds.) J M Andre and J Ladik (New York: Plenum) p. 479
Santry D P 1976 *Theor. Chim. Acta* **42** 67
Smith K M (ed.) 1975 in *Porphyrins and metalloporphyrins* (Amsterdam: Elsevier)
Stevens R H, Pitzer R M and Lipscomb W N 1963 *J. Chem. Phys.* **38** 550
Weiss C, Kobayashi H and Gouterman M 1965 *J. Mol. Spectrosc.* **16** 6415
Zerner M and Gouterman M 1966 *Theor. Chim. Acta* **4** 44