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Porphyrins

IV. Extended Hückel Calculations on Transition Metal Complexes

By

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The extended Hückel model is applied to porphyrin systems with metals Mn, Fe, Co, Ni, Cu, Zn and to the diprotic acid. A single method for choosing parameters is detailed. The model is used to discuss magnetic state, coupling of ring and metal, electronic transitions, and the effect of non-planarity.

Die erweiterte Hückel Theorie wird auf das Porphyrin-System mit den Metallen Mn, Fe, Co, Ni, Cu und Zn sowie auf die zweifach protonierte Säure angewendet. Die Parameter werden dabei einheitlich gewählt. Anhand dieses Modells werden magnetische Eigenschaften, Kopplung zwischen Ring und Metall, Elektronenübergänge und der Einfluß der Abweichung von planarer Anordnung diskutiert.

Le modèle étendu de Hückel est appliqué aux complexes du porphyrine avec les métaux Mn, Fe, Co, Ni, Cu et Zn, et à l'acide diprotonique. On présente en detail une méthode unifiée pour obtenir les paramètres. L'état magnétique, le couplage cycle-métal, les transitions électroniques et l'effet de la non-planeïté sont discutés à l'aide de ce modèle.

Introduction

The first three papers [*17*, *18*, *41*] of this series are concerned with the π electronic spectra of the porphyrins. Paper I presented experimental facts and simple models of a free electron nature. Paper II attempted to refine these models to more quantitative accuracy. Finally Paper III applied to the porphyrin π system the Self-Consistent-Molecular-Orbital Pariser-Parr-Pople (SCMO-PPP) theory, which reproduced spectroscopic data quite satisfactorily. In effect the heuristic free electron model was justified on the basis of the most sophisticated π electron theory now available for large aromatic molecules.

In this paper we attempt to move one step forward in understanding the electronic structure of porphyrins and in encompassing broader data at the expense, however, of some sophistication. The most interesting of porphyrins, those that enter in biology, have metals present: Mg, Fe, and sometimes Cu. Yet π electron theory is as yet incapable of including these metals except as perturbations. Over the past years a model, known as the extended Hückel model or the Wolfsberg-Helmholtz model [*43*], has been used to study the molecular orbitals of all the electrons in a large molecule. Hoffmann applied the model to a variety of organic molecules [*20*, *21*]. Ballhausen and Gray [*1*, *2*] used the model to study ligand field splittings in various transition metal complexes. Pullman, Berthier and

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SPANJAARD [*31*] as well as OHNO, TANABE and SASAKI [*28*] applied the method to iron porphyrin. However, both of these latter works made use of a limited basis set including only π electron orbitals, sp^2 hybrids on the central N atoms, and the $3d$, $4s$, $4p$ orbitals of the metal*.

The extended Hückel calculations to be reported here include all the valence orbitals of H, C and N atoms and the $3d$, $4s$, $4p$ orbitals of the metal. We report here calculations on the six transition metals Mn through Zn and the diprotic acid. In the present paper we use the model to accomplish the following objectives:

a) to order the energies of the d orbitals with respect to the π in such a way as to account for the ground state magnetic properties;

b) to show that the coupling of the metal orbitals to the π system is weak in agreement with the spectra [*16*];

c) to give an account of the π electron transitions that accords with the now "established" SCMO-PPP treatment;

d) to seek the effects of the known non-planarity of the ring.

In the present paper we present the model and show that it does fulfill all these objectives reasonably well. In later papers we hope to extend the work to other metals, to a more detailed study of d-π interactions, and to a consideration of the effect of ligands on the ring.

Apology

If quantum chemistry is to say something about the functioning of porphyrins, the relation of the metal orbitals to the π orbitals must be understood. However, for these systems even so inexact a solution to the Schrödinger equation as a minimal basis set SCF wave function is far beyond present technology [*10*]. For some time to come our "knowledge" of the electronic structure of metal porphyrins must be based on models.

The present paper works with the MO model. Originally used to obtain symmetries of ground and excited electronic states and applied widely to electronic spectroscopy, MO's have more recently been used for explaining ESR and NMR spectra as well as geometric configurations and chemical reactivities. But do they really exist? Certainly they can be defined theoretically as the eigenfunctions of Hartree-Fock one electron Hamiltonians [*35*]; that is, they are the best one electron orbitals for a Slater determinant type wave function. If account is taken of the special problems of the open shell, such orbitals have well defined energies and well defined expansion coefficients in terms of a limited basis set. It is to these orbitals that we hope our calculations relate. But even in H_2, the one electron Slater determinant solution does not give a good description of the ground state and becomes very bad near dissociation [*38*].

Thus the MO's which we are striving to obtain have but a limited relation to reality. Since we obtain these orbitals through a semi-empirical Hamiltonian, might we not be dealing with shadows on the wall? In the last analysis *such shadows are of interest insofar as they fruitfully aid the work and thinking of experimentalists.* As outlined in the Introduction, the present model attempts to relate to only a limited number of experimental facts. It is to be expected that as the model is used to encompass more experimental facts some modifications of its assumptions may be needed. Yet at all points of contact with reality, we may expect that, because of semi-empirical calibration, our model will give as good or better agreement with observables than the limited basis set SCF, which we imagine we are calculating. A final rationale for exploring the extended Hückel model is the fact the model is a quantitative expression of much of the qualitative reasoning presently being used to explain many chemical phenomena.

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* Recently BERTHIER, G., P. MILLIE, and A. VEILLARD: J. chim. Physique **62**, 8 (1965) and MILLIE, P., and A. VEILLARD: J. chim. Physique **62**, 20 (1965) have develepod a model and applied it to Fe (II) porphyrin using a similar basis.

Method

We seek solutions to the molecular equation

$$H_{\text{eff}}\, \varphi_j = w_j\, \varphi_j \tag{1}$$

where the MO φ_j is expanded on a minimal basis set of atomic orbitals.

$$\varphi_j = \sum_p \chi_p\, c_{pj}\,. \tag{2}$$

The coefficients c_{pj} and the MO energies are obtained in usual fashion from the secular equation,

$$\det\ \left| H_{pq} - w S_{pq} \right| = 0\,. \tag{3}$$

In this S_{pq} is the basis set overlap. $H_{pp} = \langle \chi_p \mid H_{\text{eff}} \mid \chi_p \rangle$ is the energy expectation value of an effective one electron molecular Hamiltonian for our basis. WOLFSBERG and HELMHOLTZ [*43*] suggested an atoms-in-molecules method which uses for H_{pp} the atomic orbital ionization potential (AOIP) of a free atom. H_{pq}, which is related to the Hückel "resonance" integral, is given by

$$H_{pq} = \langle \chi_p \mid H_{\text{eff}} \mid \chi_q \rangle = \tfrac{1}{2}\,(H_{pp} + H_{qq})\, S_{pq}\, [\varkappa + (1 - \varkappa)\, S_{pq}]\,, \tag{4}$$

where $\varkappa$ is an interaction parameter. Included in the expansion of φ_j are all the valence orbitals of the H, C and N atoms and the 3*d*, 4*s*, 4*p* orbitals of the transition metal.

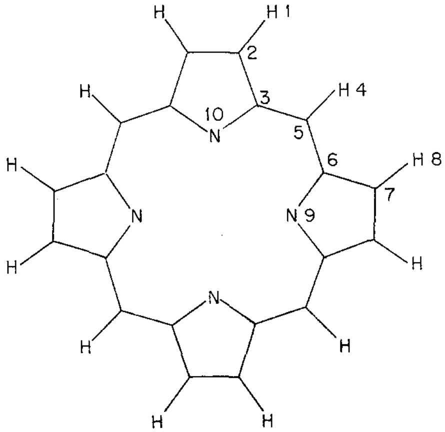

Fig. 1. Geometry and Labeling of Planar Porphin

The assumed geometry for planar porphin, shown in Fig. 1 and given in Tab. 1, is a planar projection of the tetraphenyl porphin coordinates determined by HOARD, HAMOR and HAMOR [*19*]. The metal nitrogen bond lengths, taken from the *X*-ray work of FLEISCHER, MILLER and WEBB [*14*], and from extrapolation using covalent radii as a guide, are presented in Tab. 2, and are introduced into the calculation by a simple radial displacement of the nitrogens from their positions in Fig. 1. The non-planar geometries are those of FLEISCHER, MILLER, and WEBB and HOARD, HAMOR and HAMOR. The coordinates of Ni etioporphyrin [*13*] and "typical" tetraphenylporphin are also given in Tab. 1.

The computations are carried out on an IBM 7094. Computation time is kept down by assuming the existence of two planes of symmetry. The method of including this group theory is described elsewhere [*44*], as a result of which the time for a complete run, including the self consistent charge procedure to be described below, is reduced by a factor of 6 to 10.

Three choices must be made for the Wolfsberg-Helmholz Hamiltonian: a) choice of the atomic orbitals, b) choice of a procedure to evaluate H_{pp}, and c) choice of $\varkappa$.

The very form of the semi-empirical Hamiltonian always exists as an additional choice. BALLHAUSEN and GRAY [*1*], for example, use the geometric mean $(H_{pp}\, H_{qq})^{\frac{1}{2}}$ rather than the arithmetic mean $\frac{1}{2}(H_{pp} + H_{qq})$ as in eq. (4). Should H_{pq} be set proportional to the overlap S, or to $S(1 + 2 \mid S \mid)$ as suggested from an examination of resonance integrals?* In the final analysis the choice must be made from an examination of the results obtained. We have tried these alternatives and have found no great differences. We find the form of eq. (4) most easy to compare with more exact methods, and so choose to develop it.

Table 1. *Coordinates (X, Y, Z) of Porphyrins in* Å

	D_{4h}-Planar Projected[a]	S_4-Ni Etio[b]	S_4-Tetraphenyl[c]
H (1)	1.325, 5.084, 0	1.302, 5.027. −0.086	
C (2)	0.681, 4.217, 0	0.667, 4.158, 0.000	0.672, 4.174, 0.183
C (3)	1.098, 2.839, 0	1.106, 2.806, 0.133	1.070, 2.821, 0.029
H (4)	3.208, 3.208, 0	3.229, 3.229, 0.248	
C (5)	2.444, 2.444, 0	2.465, 2.465, 0.248	2.384, 2.384, −0.135
C (6)	2.839, 1.098, 0	2.806, 1.106, 0.363	2.797, 1.052, 0.039
C (7)	4.217, 0.681, 0	4.158, 0.667, 0.500	4.174, 0.627, 0.028
H (8)	5.084, 1.325, 0	5.027, 1.302, 0.581	
N (9)	2.054, 0.000, 0	1.957, 0.000, 0.317	2.052, 0.000, 0.289
N (10)	0.000, 2.054, 0	0.000, 1.957, 0.179	0.000, 2.052, 0.207
M	0.000, 0.000, 0	0.000, 0.000, 0.248	0.000, 0.000, 0.248

[a] Planar projection of tetraphenyl porphyrins from Ref. [*19*] with special attention to bond lengths. C-H bonds set at 1.08 Å.

[b] Fleischer: J. Amer. chem. Soc. 85, 146 (1962), with C-H bond lengths set at 1.08 Å.

[c] Ref. [*19*], for a "typical" metal tetraphenylporphin.

Table 2. *Nitrogen Metal Bond in* Å

Mn[b]	Fe[a]	Co[b]	Ni[a]	Cu[a]	Zn[a]	H[b]
2.040	2.030	1.962	1.957	1.981	2.042	1.000

[a] Ref. [*14*]

[b] Estimated from covalent radii

a) Choice of Orbitals

Speed in calculating overlap integrals limits the complexity or the orbitals χ_p that should be used. We use a single Slater orbital of the form

$$\chi(n, l, m) = N r^{n-1} \exp(-\zeta r)\, Y_l^m(\theta, \Phi) \tag{5}$$

where N is a normalizing constant. Thus our only freedom is in the choice of ζ. The original Slater values for ζ have often been used in Wolfsberg-Helmholtz calculations [*36*]. However, the values recently obtained by Clementi [*9*] for minimal basis set SCF calculations seem more appropriate. For H and the first row elements there is no serious discrepancy between the Slater and Clementi values, and we use the latter. With increasing atomic number Clementi's ζ values become increasingly larger than Slater's. Preliminary calculations showed Clementi's $3d$ exponents gave too small a ligand field splitting, Slater's values, too large.

The problem is that the orbital form (5) is too simple. Clementi [*8*, *9*] showed that a linear combination of exponentials gives energies very much closer to the

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* This suggestion by Hiroshi Kobayashi. A form proportional to $S(1 - \mid S \mid)$ has been suggested by Ruedenberg in R. G. Parr, Quantum Theory of Molecular Electronic Structure. New York: W. A. Benjamin, Inc. 1963; $S(2 - \mid S \mid)$ has been suggested by L. Chopin Cusachs.

Hartree-Fock energy than does a single exponential. However, use of such more complicated orbitals would extend the calculations to unjustifiable lengths.

Since the interaction of the $3d$ orbitals with the neighboring N atoms is the most important for the porphyrin ligand field, we want these overlaps to be as accurate as possible. Accordingly, we calculated the non-zero overlaps between the best available atomic $3d$ orbitals, those of WATSON [*40*], and the neighboring N atoms. We then use in our calculations that ζ which best reproduced these. The results are shown in Tab. 4 for Zn. In general we find that a single ζ, lying intermediate in value between the Clementi and Slater numbers, reproduces all the various overlaps of the Watson d functions and the neighboring N orbitals at the distance present in porphin. This ζ presents a very satisfactory ligand field picture. We use the same procedure for the metal $4s$ orbital.

The transition metal $4p$ orbitals present a different problem. The $4p$ orbitals are unoccupied in the ground configurations of these atoms, and calculations of $4p$ orbitals of comparable accuracy to those of Watson are not available for fitting as we did with the $4s$ and $3d$. Indeed, even if such orbitals were available, the applicability of $4p$ exponents from such highly excited atomic states in molecular problems is questionable. The $4p$ functions of RICHARDSON, POWELL and NIEUWPOORT [*33*], for example, proved too diffuse, leading in many case to negative orbital electronic populations.

We have set the $4p$ exponent equal to the $4s$ reasoning from the analogy with such molecules as Be_2, Li_2, LiH, etc. In these cases the $2p$ orbital is unoccupied in the atom as is the $4p$ orbital in the transition metal. The "Best Limited L.C.A.O." calculations of RANSIL [*32*] for these molecules show that the optimized $2s$ and $2p$ exponents are nearly equal to each other and to the $2s$ exponent of the free atom.

Table 3. *Basis Set Exponentials*

	s	*p*	*d*
H[a]	1.0000		
C[a]	1.6083	1.5679	
N[a]	1.9237	1.9170	
Mn	1.360	1.360	2.600
Fe	1.370	1.370	2.722
Co	1.423	1.423	2.830
Ni	1.473	1.473	2.960
Cu	1.482	1.482	3.080
Zn	1.509	1.509	3.200

[a] Ref. [*22*]

The exponents which result are shown in Tab. 3.

b) *Evaluation of H_{pp}*

H_{pp} is the diagonal term of an effective one electron molecular Hamiltonian expanded on an atomic basis set. In an atoms-in-molecules model H_{pp} represents the energy of an electron in a specific atomic orbital moving in the field of a shielded atomic nucleus. Traditionally valence state ionization potentials (VSIP) have been used for estimating H_{pp}'s, at least for the second row elements. The ionization potential of a hydrogen $1s$ electron is a well known number. The ionization potentials for other atoms are not as simple. They depend on the electron and the configuration of the atom and ion being considered. For example, for carbon, one has such reasonable processes to consider as [*30*]

Table 4. Zn *Nitrogen Overlap*[a]

Overlap Type	Watson-Metal Overlap	Single Zn Exponent	Slater Zn Overlap $\zeta_{3d} = 2.95$, $\zeta_{4p} = 1.18$	Best Single, Averaged[b] $\zeta_{3d} = 3.20$, $\zeta_{4p} = 1.51$	Clementi Zn Overlap $\zeta_{3d} = 4.626$, $\zeta_{4p} = 1.491$
$(2s \mid 3d_{x^2-y^2})$	0.03689	3.16	0.0462	0.0384	0.00913
$(2p_x \mid 3d_{x^2-y^2})$	0.04979	3.26	0.0667	0.0526	0.01523
$(2p_z \mid 3d_{xz})$	0.02285	3.15	0.0280	0.0210	0.00521
$(2s \mid 3d_{z^2})$	0.02153	3.13	0.0267	0.0201	0.00527
$(2p_x \mid 3d_{z^2})$	0.02902	3.25	0.0385	0.0304	0.00879
$(2s \mid 4s)$	0.2719	1.52	0.302	0.274	0.277
$(2p_x \mid 4s)$	0.1690	1.48	0.115	0.178	0.174

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[a] 2.054 Å is assumed for Zn-nitrogen distance. Nitrogen exponents in Tab. 3. The internuclear axis is X. ζ_i is the appropriate exponential constant, in reciprocal Bohr radii.

[b] The average is weighted by overlap.

Table 5. H_{pp} for H, C and N[a]

	$A^- \rightarrow A + e$		$A \rightarrow A^+ + e$		$A^+ \rightarrow A^{+2} + e$	
H	$s^2 \rightarrow s + (s)$	− 0.7569	$s \rightarrow (s)$	−13.595		−15.357[b]
C	$s^2xyz \rightarrow sxyz + (s)$	− 8.890	$sxyz \rightarrow xyz + (s)$	−20.776	$s^2x \rightarrow sx + (s)$	−31.649
	$sx^2yz \rightarrow sxyz + (p)$	− 0.870	$sxyz \rightarrow sxy + (p)$	−11.316	$s^2x \rightarrow s^2 + (p)$	−23.608
N	$s^2x^2yz \rightarrow sx^2yz + (s)$	−13.800	$s^2xyz \rightarrow sxyz + (s)$	−25.157	$s^2xy \rightarrow sxy + (s)$	−39.986
	$s^2x^2yz \rightarrow s^2xyz + (p)$	− 1.080	$s^2xyz \rightarrow s^2xyz + (p)$	−14.158	$s^2xy \rightarrow s^2x + (p)$	−29.651

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[a] All numbers in this table are from Ref. [*30*], or are obtained from data in this reference and atomic spectra.

[b] This value from applying the extended Hückel model to H_2^+ and extrapolating.

$$\mathrm{C} \to \mathrm{C}^+ + \mathrm{e} + \mathrm{I.\,P}$$
$$sxyz \to xyz + (s) - 20.78\ \mathrm{eV}$$
$$s^2xy \to sxy + (s) - 19.10\ \mathrm{eV}$$
$$\text{etc.}$$
$$sxyz \to sxy + (p) - 11.32\ \mathrm{eV}$$
$$s^2xy \to s^2x + (p) - 11.36\ \mathrm{eV}$$
$$\text{etc.}$$

The transition elements have many more possibilities. We adopt the following model in aiding our choice of H_{pp}.

If we consider that an atom in a molecule is essentially a weakly perturbed atom in the ground configuration, then ionization processes from the ground configuration will be important in estimating H_{pp}. However, such ionization processes, especially in the transition elements, often lead to highly excited configurations of the ion. If either of these species, the atom or our hypothetical ion-in-the-molecule, can exist in excited configurations (the so called "promotion energy"), it would certainly be the atom [*42*] and not the ion which exists at a much higher energy. Thus we might expect that ionization processes which lead to the ground configuration of the ion should be important. We consider a linear

Table 6. H_{pp} *(Potential in eV)*

	Mn	Fe	Co	Ni	Cu	Zn
			$\mathrm{M} \to \mathrm{M}^+ + (\mathrm{e})$			
(s)	10.05	7.90	7.45	7.55	7.75	9.40
(p)	4.90	4.55	4.23	3.95	3.95	5.00
(d)	10.45	8.70	7.18	7.90	10.60	17.35
			Process[a]			
(s)	$d^5s^2 \to d^5s$	$d^7s \to d^7$ $d^6s^2 \to d^6s$	$d^8s \to d^8$	$d^9s \to d^9$	$d^{10}s \to d^{10}$	$d^{10}s^2 \to d^{10}s$
(p)	$d^5sp \to d^5s$	$d^7p \to d^7$ $d^6sp \to d^6s$	$d^8p \to d^8$ $d^7sp \to d^7s$	$d^9p \to d^9$	$d^{10}p \to d^{10}$	$d^{10}sp \to d^{10}s$
(d)	$d^6s \to d^5s$ $d^5s^2 \to d^4s^2$	$d^8 \to d^7$ $d^6s^2 \to d^5s^2$	$d^9 \to d^8$ $d^8s \to d^7s$	$d^{10} \to d^9$ $d^9s \to d^8s$	$d^{10}s \to d^9s$	$d^{10}s^2 \to d^{10}s$
			$\mathrm{M}^+ \to \mathrm{M}^{++} + (\mathrm{e})$			
(s)	16.10	15.85	16.40	16.92	17.45	18.00
(p)	11.40	11.40	11.40	11.50	11.70	11.90
(d)	18.40	20.03	18.20	18.80	20.10	28.00
			Process[a]			
(s)	$d^5s \to d^5$	$d^6s \to d^6$	$d^7s \to d^7$	$d^8s \to d^8$	$d^9s \to d^9$	$d^{10}s \to d^{10}$
(p)	$d^5p \to d^5$	$d^6p \to d^6$	$d^7p \to d^7$	$d^8p \to d^8$	$d^9p \to d^9$	$d^{10}p \to d^{10}$
(d)	$d^6 \to d^5$ $d^5s \to d\text{-}s$	$d^7 \to d^6$ $d^6s \to d^5s$	$d^8 \to d^7$	$d^9 \to d^8$	$d^{10} \to d^9$	$d^{10}s \to d^9s$

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[a] First AOIP is to lowest configuration of ion, second is from lowest configuration of atom. Where an entry is missing, the processes are the same.

average of these two types of processes, which is roughly analogous to averaging the ionization potential of the atom and the electron affinity of the ion. For C, N and O these two processes are the same; for the transition elements they can greatly differ.

One additional point should be noted. We use VSIP's for the first row elements where they have been carefully investigated [*30*]. For the transition series we use ionization processes from average atomic configurations, which we will call atomic orbital ionization potentials (AOIP) to distinguish them from VSIP's.

The processes which we consider, and the H_{pp} which we use are given in Tab. 5 and 6. A more detailed account of these numbers is in preparation.

The fact that the H_{pp} values are highly dependent on whether the atom is neutral or ionic has been handled in various ways. We adopt a self consistent procedure, using for the N^{th} iteration

$$\begin{aligned} H^N_{pp} &= (H^{\pm}_{pp} - H^0_{pp})\, \Delta^N_p + H^0_{pp} \\ \Delta^N_p &= \Delta^{N-1}_p + (q^{N-1}_p - \Delta^{N-1}_p)\, \lambda\,. \end{aligned} \tag{6}$$

Here H^0_{pp} is the AOIP for the neutral species, q^{N-1} is the net charge calculated using the Mulliken population analysis [*27*] for the $(N-1)^{\text{th}}$ iteration, and λ is a constant less than unity. H^+_{pp}, used if Δ^N_p is positive, is the AOIP for the cation obtained in the same manner as H^0_{pp}; H^-_{pp}, used if Δ^N_p is negative, is the electron affinity*. For the first iteration Δ^0_p are set to zero. Iterations are repeated until $|\Delta^N_p - \Delta^{N-1}_p| \leq 0.02$ for all p. This self-consistent procedure greatly moderates charge build up, and positions the ligand field orbitals properly.

c) *Interaction Parameter $\varkappa$*

From the point of view of simplicity a single $\varkappa$ value in eq. (4) is desirable. MULLIKEN [*26*], who anticipated the development of such a model, indicated that different $\varkappa$ values for σ and π electrons are to be expected. However, such different $\varkappa$ values would lead to confusion in cases where σ-π separation breaks down, and these are just the cases where interest in the extended Hückel model is the greatest. Such confusion is anticipated in non-planar porphyrins and in porphyrins when ligands are introduced. Rather than overparameterize our model and destroy its simplicity, we choose, for the present, one value for $\varkappa$.

HOFFMANN [*5*] showed that when $\varkappa \gtrsim 1.75$, charge densities become more or less independent of $\varkappa$**. Beyond that, the meaning of $\varkappa$ may be determined by the use to which the calculations are put. Two possibilities immediately suggest themselves: *i*) $\varkappa$ can be chosen so that the energies w_i correspond roughly to SCF energies such as those of Ref. [*41*] or ii) $\varkappa$ can be set so that differences $w_j - w_i$ between filled and empty orbitals correspond roughly to transition energies. These

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* Electron affinities for the first row elements are from Ref. [*30*]. The less known electron affinities of the transition elements are never needed as the metal always converges with a net positive charge.

** We find this not be be quite true. For most molecular systems, with or without the self consistent charge procedure discussed in the text, charge densities do vary with $\varkappa$ for all reasonable values. What does appear to be generally true is that the variation of charge densities with $\varkappa$ decreases with increasing $\varkappa$ values. For our porphin calculations all atomic charge densities have stabilized before $\varkappa = 1.89$ except those on the central metal and nitrogens. The nitrogens vary about -0.01 electron/$\varkappa$, and the metal, $+0.04$ electrons/$\varkappa$, for $\varkappa = 1.89$.

two possibilities give very different values. For a closed shell ground state, the excitation energy from a filled orbital i to an empty orbital j is given by [*35*]

$$^{1,3}\Delta E_{ji} = \varepsilon_j - \varepsilon_i - J_{ij} + \binom{2}{0} K_{ij}\,. \tag{7}$$

Here ε_j and ε_i are SCF energies, J_{ij} is the Coulomb integral between the hole i and the electron j, and K_{ij} is the exchange integral. For porphyrin $^{1,3}\Delta E_{ji}$, both experimental and theoretical [*16*, *41*], lies between 1.7 and 3.2 eV while $\varepsilon_j - \varepsilon_i$, a theoretical number only, lies between 5.1 and 5.4 eV.

We set $\varkappa = 1.89$ to match the observed average of the singlet and triplet energies. Thus we wish to make the correspondence

$$w_j - w_i \longleftrightarrow \varepsilon_j - \varepsilon_i - J_{ij} + K_{ij}\,. \tag{8}$$

This procedure recommends itself over attempting to match SCF energies ε_j for three reasons. First, $\varkappa \approx 2$ is traditional for Wolfsberg-Helmholtz calculation. Second, the high energies of SCF empty orbitals stem from the fact that they are determined, in effect, as orbitals for the extra electron of the negative ion. An effective Hamiltonian of the type we are using would not be expected to generate such ionic orbitals. Third, and perhaps most important, a simple orbital energy diagram with gaps corresponding to spectral transitions, is probably the most valuable for the experimentalist.

One point should be stressed. We fit the $\pi \rightarrow \pi^*$ excitations. We expect that one of the most valuable eventual uses of this model may be to determine the relation of other transitions to the $\pi \rightarrow \pi^*$, in particular charge transfers transitions, $n \rightarrow \pi^*$ transitions and $d \rightarrow d$ transitions. To estimate these accurately, two extensions of the model may be necessary: 1. use of several interaction factors $\varkappa$ and 2. development of a systematic procedure for combining energy gaps $w_j - w_i$ with Coulomb and exchange integrals. With the present simplest model, the energy gaps for other than $\pi \rightarrow \pi^*$ transitions may or may not prove to relate well to experiment.

Results

a) Ordering of the d energy levels; magnetic state

Fig. 2 shows the orbital energy diagram obtained for the transition metal porphyrins. After we assign electrons to the d levels by a comparison of the d-d electronic energy gaps and the electronic repulsion estimated from atomic spectra*, a number of points become apparent: Zn and Ni are predicted to be diamagnetic. Cu and Co are, of course, paramagnetic; Co is predicted to have low spin. The ground configuration of Co is predicted to be $(b_{2g})^2\,(e_g)^4\,a_{1g}$. The temperature dependence of the magnetic susceptibility found for the Co compound [*23*] can be attributed to movement of the electron hole among the four metal d orbitals which have been split less than 0.04 eV by the porphyrin ligand field. Our calculations make Ni porphyrin paramagnetic upon the addition of one pyridine 2 Å

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* The calculated energy gap, $w_j - w_i$ (*i. e.* eq. 8) represents a transition energy which realizes no spin; that is, it is a transition between two states each at the average energy of all its multiplets. With this model it is necessary to combine this average energy with electronic exchange and repulsion terms to calculate the lowest energy electronic assignment. The various integrals which arise are calculated from Racah coefficients which we obtain from H. A. SKINNER and F. H. SUMNER, J. Inorg. Nucl. Chem. **4**, 245 (1957).

above the metal. This has the effect of raising the $3d_{z^2}$ orbital energy and lowering that of the $3d_{x^2-y^2}$ below that of the porphyrin e_g. Ni porphyrins are known to be paramagnetic in pyridine solutions [*6*]. Fe (ferrous) is predicted to exist in a triplet state. Whether this latter should be observed experimentally depends on the molecules which occupy the fifth and six coordinate positions. It is not yet clear which experimental ligands most approximate the ideal free compound of this calculations. The addition of ligands can easily make ferrous porphyrin diamagnetic. A more detailed investigation of the effects of ligands on ferric and ferrous porphyrins is now in progress. Mn (II) porphin is predicted to exist as a quartet in the "free compound". Ligands will also be important here. The order of the metal *d* orbitals and the electronic assignments that we have calculated from this model are in good agreement with those concluded by LEVER [*23*] from a study of EPR and magnetic susceptibility measurements on phthalocyanines*. We attribute the complex experimental behavior of the Mn (II) and Fe (II) porphyrins to the intertangling of the metal *d* orbitals with the porphyrin a_{2u} (π) MO.

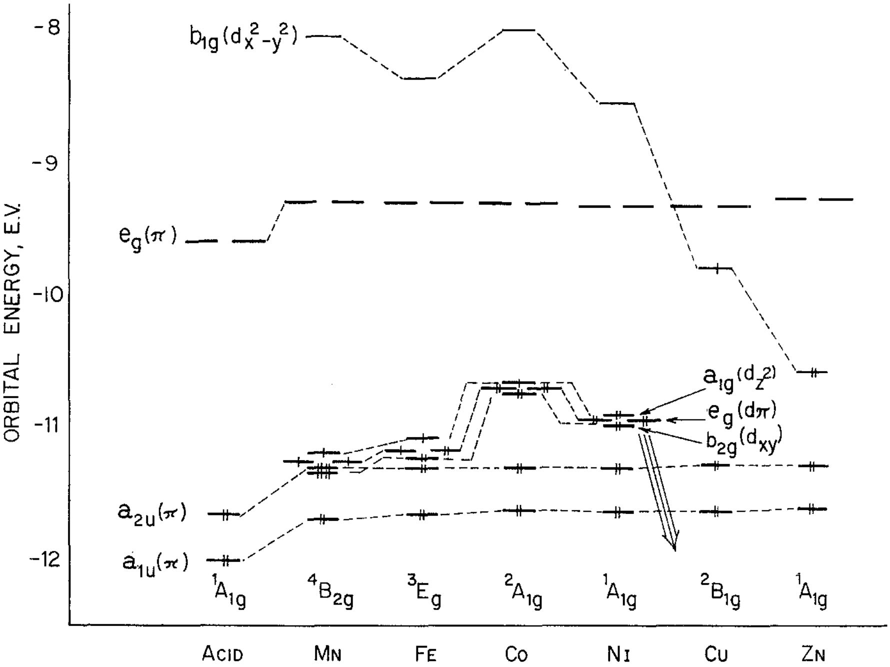

Fig. 2. Calculated Energies of the top filled and lowest empty orbitals

An important point is the self-consistant procedure to be used in these open shell cases. In Cu there is no accidental orbital degeneracy, and the odd electron clearly occupies the b_{1g} ($d_{x^2-y^2}$) orbital whose charge distribution is symmetrical. In this case there is no difficulty for the self-consistant procedure. For Co the metal *d* orbitals fall well above the porphyrin a_{2u} (π), and again there is no difficulty. The odd electron is placed in the highest *d* level. Again the odd electron

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* Preliminary calculations on phthalocyanines seem to indicate that the order and ligand field splitting of the metal *d* orbitals is almost identical to that of porphin.

a_{1g} (d_{z^2}) sets up a symmetric field. In ferrous two holes must be assigned to the nearly degenerate orbitals a_{1g} (d_{z^2}), e_g (d_π), b_{2g} (d_{xy}) and a_{2u} (π). Based on the fact that ferrous porphyrins spectra appear to preserve the normal π structure, we assume the a_{2u} (π) is doubly occupied. However, it is reasonable to expect that the two holes occupy the highest two orbitals among the nearly degenerate d set. Thus we assign electrons $(a_{2u})^2\,(b_{2g})^2\,(e_g)^3\,(a_{1g})$, Fig. 2.

This Fe (II) electron assignment raises a new difficulty. An electron assignment such as $(e_{gx})^2\,(e_{gy})$ sets up a non symmetrical field. For the self-consistant procedure, we symmetrize this field by assigning $\frac{3}{2}$ of an electron to each e_g orbital. There are two reasons for adopting this procedure. First, SLATER [*37*] showed that for atoms the total energy is rather insensitive to whether the calculation minimizes the "average energy" of a configuration or minimizes the individual terms. Second, the non-symmetric charge distribution suggests that there should be nuclear distortion [*22*]. If such distortions are small, the molecule tunnels between various displaced minima in the course of the zero point motion thus averaging out the non-symmetry. Thus it seems improper to use these non-symmetrical charges without simultaneously introducing nuclear displacements. (It might prove possible to use the non symmetrical charge distribution to estimate the size of molecular distortions*.)

b) Coupling of Metal and Porphyrin

The original spectroscopic studies showed that, except for small shifts in energy and intensity, the spectra of the various metal porphyrins are much the same [*16*]. Thus the various metal orbitals must be weakly interacting with the porphyrin π system. The present calculations give a clear picture of how this works as shown by Fig. 2 and Tab. 7.

For Zn the d orbitals lie at low energy and are so thoroughly mixed with the ring orbitals that it is difficult to identify MO's as atomic d orbitals in a ligand field. The highest filled orbital is b_{1g} and is largely porphyrin σ in character.

In Cu the high b_{1g} orbital has more $d_{x^2-y^2}$ character than that of Zn. This orbital lies close to but below the empty porphyrin e_g (π). The other d orbitals are low in energy and similar to those of Zn.

In Ni and Co the b_{1g} is unoccupied and lies above the empty porphyrin e_g (π). Unlike Zn and Cu it is mostly metal $d_{x^2-y^2}$. The other d orbitals are almost pure and lie within 0.05 eV of one another in the gap between the highest filled porphyrin a_{2u} (π), and empty porphyrin e_g (π). Ni and Co have a nearly identical effect on the porphyrin π system, in agreement with experiment.

For Fe (II) and Mn (II) the $d_{x^2-y^2}$ orbital lies above the empty porphyrin e_g (π). The other d orbitals are split considerably more than in Co and Ni and are close in energy to the a_{2u} (π). This calculated finding may relate to the strong observed attraction of Fe (II) and Mn (II) porphyrins for additional ligands. Additional ligands raise the d_{z^2} well above the a_{2u} (π) and remove these accidental degeneracies. Ferric porphyrins, where the d_{z^2} is raised by the repulsion of the negative counter ion, do not have so strong an attraction for ligands [*39*].

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* For example, one can attempt a bond order bond length correlation, see LONGUET-HIGGINS, H. C., and L. SALEM: Proc. Roy. Soc. **A 251**, 172 (1959); **A 255**, 435 (1960).

Table 7. *Top Filled Orbitals*[a]

A. Ligand Field Orbitals

	b_{1g}			
	$3d_{x^2-y^2}$	N ($2s$)	N ($2p\sigma$)	All Others
Mn	−0.8279, 0.5455	−0.1242, 0.0264	0.3654, 0.3788	−, 0.0493
Fe	−0.8236, 0.5531	−0.1237, 0.0268	0.3568, 0.3700	−, 0.0501
Co	−0.8577, 0.6051	−0.1322, 0.0296	0.3401, 0.3284	−, 0.0369
Ni	−0.8373, 0.5882	−0.1306, 0.0300	0.3383, 0.3392	−, 0.0426
Cu	−0.6158, 0.2962	−0.1434, 0.0408	0.4076, 0.5584	−, 0.1046
Zn	−0.2346, 0.0283	−0.1349, 0.0392	0.4456, 0.7176	−, 0.2149

	a_{1g}				
	$3d_{z^2}$	$4s$	N ($2s$)	N ($2p\sigma$)	All Others
Mn	−0.9524, 0.8908	−0.2417, 0.0620	−0.0049, 0.0000	0.0926, 0.0308	−, 0.0164
Fe	−0.9569, 0.8991	−0.2174, 0.0529	−0.0096, 0.0004	0.0945, 0.0328	−, 0.0148
Co	−0.9757, 0.9420	−0.1959, 0.0401	−0.0030, 0.0000	0.0578, 0.0112	−, 0.0067
Ni	−0.9787, 0.9491	−0.1781, 0.0341	−0.0037, 0.0000	0.0543, 0.0104	−, 0.0064

	e_{gx} ($d\pi$)		
	$3d_{xz}$	N ($2p\pi$)	All Others
Mn	0.9247, 0.8224	−0.1370, 0.0340	−, 0.1236
Fe	0.9376, 0.8692	−0.1222, 0.0270	−, 0.1038
Co	0.9450, 0.8862	−0.0767, 0.0100	−, 0.1038
Ni	0.9514, 0.8981	−0.0927, 0.0152	−, 0.0867

	b_{2g}		
	$3d_{xy}$	N ($2p_x$)	All Others
Mn	0.9838, 0.9592	−0.0478, 0.0072	−, 0.0336
Fe	0.9866, 0.9663	−0.0432, 0.0056	−, 0.0281
Co	0.9879, 0.9692	−0.0395, 0.0044	−, 0.0264
Ni	0.9886, 0.9716	−0.0391, 0.0044	−, 0.0240

B. Porphyrin Orbitals

	a_{2u} (π)		e_g (π)	
	$4p_z$	All Others	$3d\pi$	All Others
Mn	−0.1161, 0.0262	−, 0.9738	−0.1558, 0.0204	−, 0.9796
Fe	−0.1382, 0.0344	−, 0.9656	−0.1488, 0.0187	−, 0.9813
Co	−0.1654, 0.0475	−, 0.9525	−0.2066, 0.0374	−, 0.9626
Ni	−0.1520, 0.0434	−, 0.9566	−0.1647, 0.0235	−, 0.9765
Cu	−0.1555, 0.0450	−, 0.9550	−0.0659, 0.0031	−, 0.9969
Zn	−0.2177, 0.0697	−, 0.9303	−0.0242, 0.0003	−, 0.0007

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[a] The first number is the orbital coefficient; the second is the electronic population. For Nitrogen coefficient is for one atom; population is for all four nitrogens.

c) Electron Transitions

Tab. 8 shows the π electron energy differences and compares them with the calculated SCMO-PPP π electron transitions. The energies are the averages of the singlet and triplet and correspond to eq. (8). In comparing the calculated ΔE with experiment, we average ΔE ($a_{2u} \to e_g$) and ΔE ($a_{1u} \to e_g$). This procedure is based on a proper treatment of two electron terms which shows that these transitions are thoroughly mixed; that is, that the two resulting nearly degenerate E_u excited states mix completely through configuration interaction. The experimental average is not accurately known because of the absence of data on the second triplet [*3*]. We assume, for Tab. 7, that this triplet is 0.1 eV above the first triplet*. Since the interaction parameter $\varkappa$ was chosen to fit ΔE, good results are expected for the extended Hückel model. The point to note is that variations among the transition elements are small, as is observed experimentally.

The delicate frequency trends of the visible band with transition metal pointed out by GOUTERMAN [*17*] are not directly reproduced by this model. Although this may be caused by the fact that the entire shift is less than 0.075 eV, and the electronic gaps have not converged to this accuracy under the self consistent charge treatment, it is much more likely a shortcoming of the crude model.

Table 8. *Electronic Energy Gaps*

	This Work	SCMO-PPP	Experiment
ΔE ($a_{2u} \to e_g$)[a]	2.01 eV	2.15 eV	
ΔE ($a_{1u} \to e_g$)	2.35 eV	2.23 eV	
ΔE	2.18 eV	2.19 eV	2.19 eV
q^2 ($a_{2u} \to e_g$)	9.61 Å^2	11.06 Å^2	
q^2 ($a_{1u} \to e_g$)	10.10 Å^2	11.23 Å^2	
Total q^2	19.81 Å	22.29 Å^2	5.16 Å^2

[a] ΔE defined in eq. (8), and in text.

It might be argued that spectra should be obtained in this model from the subtraction of the total energies of two separate calculations; that is, the ground configuration, and one in which an electron is removed from a top filled orbital and placed in a low lying empty one. At present this is too time consuming a calculation. A preliminary investigation of this method, calibrating to fit spectroscopic data as before, indicates a much larger value of the interaction parameter $\varkappa$. In these calculations the one electron MO energies are much closer to those given by the SCMO-PPP method.

Tab. 8 shows a comparison of the calculated transition dipole strength q^2, with those of the SCMO-PPP method and experiment. Both calculated numbers are 3 — 4 times too large. This is a common ailment of MO theory, and has been shown to be greatly ameliorated by the inclusion of doubly excited configurations in a configuration interaction refinement [*5*].

d) Non planarity

A calculation on Ni porphin has been performed using the non-planar etioporphyrin coordinates in Tab. 1. There appears to be no significant differences even though the z coordinates vary by over $\frac{1}{2}$ Å. The filled π orbitals of the planar compound lie slightly above their counterparts in the non-planar calculation; the empty lie below. The difference between the two never exceeds 0.1 eV. The average energy gap between the highest filled a_{2u} (π) and a_{1u} (π) and first empty e_g (π) for the etio compound is blue shifted in the etio by some 0.04 eV. The MO's lie in the same order for both; that is, there are no energy order reversals.

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* Suggested from the SCMO-PPP calculations of Ref. [*41*].

The π character of MO's in the planar system is essentially preserved in the non planar calculation. For example, each highest filled a_{1u} (π) electron has 0.994 electrons in π symmetry AO's; each highest filled a_{2u} (π) has 0.990 electrons in π symmetry AO's; for the lowest empty e_g (π), 0.988 electrons lie in π type AO.

The total orbital and atomic populations for the two systems, Tab. 9, demonstrate no significant differences.

Table 9. Ni *Porphyrin*
Electronic Population

	Total		π Only	
	Planar	Non-Planar	Planar	Non-Planar
H (1)	0.4394	0.9414		
H (4)	0.9190	0.9190		
C (2)	4.0493	4.0490	$2p_z$ 1.0052	1.0056
C (3)	3.9781	3.9787	$2p_z$ 1.0599	1.0550
C (5)	4.0343	4.0328	$2p_z$ 0.9592	0.9629
N	5.1882	5.1840	$2p_z$ 1.3965	1.4015
Ni	9.6985	9.7041	$3d_{xz}$ 1.9480	1.9512
			$4p_z$ 0.1605	0.1565

That the non planarity of porphyrin systems does not much affect the results of these calculations is further demonstrated by a calculation of a non planar diacid with the central protons lying 0.5 Å from the molecular plane and 1.0 Å from the porphyrin nitrogens giving the molecule S_4 symmetry.

Other Results

a) Electronic Populations

Although not directly measurable experimentally, the distribution of electronic charge is interesting. Without self consistent charge the metal porphyrin calculations make no sense; the charge on the metal is often too great to be physical, and the position of the ligand orbitals is contrary to experience. A demonstration of the type of charge moderation caused by the self consistent charge procedure is shown in Tab. 10 for the case of acid porphin. Interesting is the rever-

Table 10. *Acid Porphin: Effect of Self-Consistant Charge*

	Before SCC		After SCC	
	Total	π Only	Total	π Only
H (1)	0.9139	–	0.9343	–
C (2)	4.1360	1.0234	4.0293	0.9899
C (3)	3.6511	0.8955	3.9391	1.0342
H (4)	0.9022	–	0.9105	–
C (5)	4.1860	1.0473	4.0085	0.9509
C (6)	3.6511	0.8955	3.9391	1.0342
C (7)	4.1360	1.0234	4.0293	0.9899
H (8)	0.9139	–	0.9343	–
N (9)	5.3459	1.6150	5.0634	1.5010
Acid-H	0.6638	–	0.7121	–

sal in all of these calculations of the order of the highest filled π orbitals from a_{1u} to a_{2u}, to agree with the SCMO-PPP calculations.

Tab. 11, 12, 13 give electron populations after self consistent charge. From these calculations it is seen that the metals do not exist in a $+2$ state. The order in decreasing charge is Zn > Co > Ni > Cu. This order is reminiscent of the order of electrochemical half cell potentials, $M \rightarrow M^{+2} + 2e$, which we may use for some indication of the electronegativity of the transition metal series. The calculated charges of Mn and Fe porphins do not fall in this order, but can readily be made to do so by adding a water molecule to the fifth and sixth coordinate positions of the central metal.

Table 11. *Total Electron Populations*

	Zn	Cu	Ni	Co	Fe	Mn	Acid
H (1)	0.9451	0.9413	0.9394	0.9422	0.9400	0.9384	0.9343
H (4)	0.9224	0.9213	0.9191	0.9224	0.9209	0.9209	0.9105
C (2)	4.0543	4.0476	4.0493	4.0507	4.0488	4.0440	4.0293
C (3)	3.9813	3.9795	3.9781	3.9808	3.9794	3.9750	3.9391
C (5)	4.0315	4.0299	4.0343	4.0341	4.0330	4.0312	4.0085
N	5.1850	5.1823	5.1882	5.1817	5.1662	5.1607	5.0634
Total Porphin	112.4007	112.2807	112.3012	112.3412	112.2253	112.1106	111.1512
Net Porphin	−0.4007	−0.2807	−0.3012	−0.3412	−0.2253	−0.1106	+0.8488
Acid Proton							0.7121

Table 12. *Metal Electron Populations*

	$3d$	$4s$	$4p$	Total	Net
Zn	9.9880	0.6639	0.9472	11.5991	+0.4009
Cu	9.6642	0.4876	0.5673	10.7191	+0.2809
Ni	8.6828	0.4653	0.5505	9.6986	+0.3014
Co	7.6370	0.4221	0.5994	8.6585	+0.3415
Fe	6.9946	0.3542	0.4256	7.7744	+0.2256
Mn	6.1815	0.4096	0.2980	6.8891	+0.1109

Table 13. *π Electron Populations*

	Zn	Cu	Ni	Co	Fe	Mn	Acid	SCF (metal)[b]
C (2)	1.0099	1.0058	1.0052	1.0084	1.0055	0.9980	0.9899	1.0188
C (3)	1.0568	1.0584	1.0599	1.0629	1.0542	1.0484	1.0342	0.9378
C (5)	0.9614	0.9583	0.9592	0.9613	0.9623	0.9625	0.9509	0.9877
N	1.3360	1.3783	1.3965	1.3882	1.3723	1.3648	1.5010	1.5990
$3d_{xz}$[a]	1.9991	1.9917	1.9480	1.9182	1.5224	1.1098	–	–
$4p_z$	0.2782	0.1572	0.1605	0.1954	0.1388	0.1004	–	–

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[a] Population of one of the degenerate d_π.

[b] Ref. [*41*]

Tab. 12 shows the detailed distribution of charge around the metal. It is seen that there is roughly one additional electron in the metal d orbitals beyond the classical ligand field d^{n-2} configuration, with the exception, of course, of Zn. It is also apparent that the electronic population of the $4s$ orbital is about the same as the three $4p$'s. The electronic population on the metal is thus more nearly $d^{n-1}\,s^{\cdot 5} p^{\cdot 5}$ (almost neutral) than d^{n-2} ($+$ 2).

Tab. 12 shows a comparison between total and π electron charge distribution calculated by the extended Hückel model and the charges calculated by SCMO-PPP theory. The net charge of the extended Hückel theory increases in the order C (3) < C (5) < C (2), while the π only is C (5) < C (2) < C (3). For the SCMO-PPP calculation the π order is C (3) < C (5) < C (2). This agreement between *total* charges of extended Hückel model and *π only* charges of SCMO-PPP theory has been found with all the other nitrogen heterocyclics that we have calculated. For pyrrole and pyrrole like structures the π electron distribution of the extended Hückel model is in agreement with that inferred from electrophilic substitution [*34*]. These results suggest a greater role of σ core polarizations in π systems than is normally considered in "σ electron only" theories [*11*].

The average net charge on the nitrogens of Zn, Cu, Ni and Co porphin is about —0.18. For the Fe (II) and Mn (II) compounds it is somewhat less, —0.16; the acid, —0.06. The π electron density, 1.5 from classical consideration of 2-pyrrole and 2-pyridine type nitrogens becomes 1.36 for the metals and 1.50 for the acid. The SCMO-PPP calculations give 1.60, assuming the σ electrons are unpolarized.

The central hydrogens of the acid compound are +0.29. This is to be compared with a pyrrole hydrogen with +0.21 and phthalimide with +0.25. Phthalimide readily forms metallic salts, pyrrole only with some difficulty.

b) Low lying electronic states

An examination of Fig. 2 suggests the presence of low lying electronic states. As previously discussed, the single orbital energy differences ($w_j - w_i$) may not be a good guide for locating other than $\pi \rightarrow \pi^*$ transitions because in our present treatment only one $\varkappa$ value is used and two electron terms are neglected. Nonetheless, an examination of nitrogen heterocyclics using this model with one $\varkappa$ seems to reproduce the actual low lying electronic states with some accuracy. It is thus interesting to catalogue the electronic levels in porphyrin predicted to lie between the lowest $\pi \rightarrow \pi^*$ excited state and the ground state. This catalogue raises a number of questions which we hope to take up in future work.

In Zn the transition

$$b_{1g}\,(\sigma) \rightarrow e_g\,(\pi)$$

is predicted to lie in the IR region. This transition is, of course, forbidden, but it might effect emission properties. In Cu there are two such transitions,

$$b_{1g}\,(d) \rightarrow e_g\,(\pi)$$
$$a_{2u}\,(\pi) \rightarrow b_{1g}\,(d)\,.$$

We expect, however, the latter process to be at considerably higher energy than indicated in Fig. 2 because of d-d repulsion. Both transitions are forbidden. Again we know of no experimental evidence for these transitions.

Ni has the possibility of any number of metal-to-porphyrin charge transfer transitions. These bands may lie at lower energy than indicated by single orbital energy gaps as *d*-*d* repulsion is lost. Co has these bands plus the possibility of

$$a_{2u}\,(\pi) \rightarrow a_{1g}\,(d)\,.$$

This transition is allowed (z polarized), but because of the local character of the $a_{1g}\,(d)$ must be weak. Again, as with Cu, the transition energy will be larger than the energy gap in Fig. 2. This transition may account for the lack of emission in Co mesoporphyrin [*3*]. There is also the possibility in Co that the hole in the d shell might occupy any of the four nearly degenerate orbitals giving rise to low lying states $^2A_{1g}$, ^2E_g, and $^2B_{2g}$.

In Fe and Mn the situation is more complex. In Fe the two d holes give rise to two ^3E_g's and two $^3B_{2g}$'s. For the predicted ground state ^3E_g of ferrous, there are two allowed transitions

$$a_{2u}\,(\pi) \rightarrow a_{1g}\,(d)$$
$$a_{2u}\,(\pi) \rightarrow e_g\,(d)\,.$$

This latter has the same polarization as the porphyrin π absorptions and might be expected to borrow intensity from them. The IR bands observed in many iron porphyrins may be due to such transitions [*15*].

The situation in Mn is very similar to that in Fe. The 3 holes in the nearly degenerate d orbitals give rise to $^4B_{2g}$, $^4A_{1g}$ and ^4E_g. The predicted ground state is $^4B_{2g}$. For both the Fe and Mn compounds in their ground states there exist also the possibility of the allowed

$$a_{1u}\,(\pi) \rightarrow e_g\,(d)$$

charge transfer. This transition, though identical in symmetry to $a_{2u}\,(\pi) \rightarrow e_g\,(d)$, will have little intensity of its own because the $a_{1u}\,(\pi)$ has no density on the nitrogens.

c) Electrolytic Reduction

Tab. 14 shows half wave potentials for various metal tetraphenylporphyrins as determined by FELTON and LINSCHITZ [*47*]. They also found a difference between the first waves of tetraphenylporphyrin (TPP) and etioporphyrin-I as

Table 14. *Half Wave Potentials of Tetraphenylporphyrins*[a]

Cmpd.	First Reduction	Second Reduction	Difference
Mg	1.35	1.80	0.45
Zn	1.31	1.72	0.41
Cu	1.20	1.64	0.48
Ni	1.18	1.75	0.57
Co	0.82	1.87	1.05
H_2	1.05	1.47	0.42

[a] Ref. [*12*]

follows: 1. H_2TPP-H_2Etio, 0.29 V, 2. ZnTPP-Zn Etio, 0.29 V, 3. CuTPP-CuEtio, 0.26 V, 4. CoTPP-CoEtio I, 0.22 V. FELTON [*12*] originally assigned the two waves to one and two electron reductions of the porphyrin ring, as do HUSH and CLACK [*7*], on the basis of the polarographic data itself plus some information gained from electrolytic and metal reduction. However, he suggested that in the Co case it might be the metal that is reduced. This possibility arose not only because of the large difference between the CoTPP half-wave potentials given in Tab. 14 but also because of peculiarities shown on electrolytic and metal reduction.

The present calculations clearly would assign extra electrons to e_g (π) orbitals for Zn, Ni, and H_2 porphyrins. For Cu porphin there is some ambiguity, as the added electron may be added to either the b_{1g} $(d_{x^2-y^2})$ orbital or the e_g (π). We assign this additional electron to the e_g (π) because of the closeness in energy of these two orbitals, and the relatively large *d-d* repulsion energy effected by pairing b_{1g} electrons. This assignment is consistent with a calculation which shows that if the b_{1g} orbital is doubly occupied, the self consistent charge procedure raises its energy above that of the e_g (π). Finally in Co, Fig. 2 strongly suggests that the added electron goes into a_{1g} (d_{z^2}).

The order of reduction potential Ni $<$ Cu $<$ Zn $<$ Mg can also be understood from our calculations. Since the electron goes into the porphin moiety, we would expect increasing half wave potential to be correlated with increasing negative charge in the ring. This order of increasing negative ring charge is given by our calculations*. That the free base is lower than all of these can be understood from the fact that the empty e_g orbitals are split and the lower orbital which has the same energy as does the e_g in the metal calculations, has nodes at the two more negative nitrogen atoms. The added electron sees an almost neutral ring.

d) Stability

It is interesting to note that the resultant metal charges from these calculations, Mg $>$ Zn $>$ Co $>$ Ni $>$ Cu are the reverse order of the Mellar-Moley order [*24*] of stability for metal complexes. Thus we find that the order of increased observed stability corresponds to a calculated decrease in the ionic character of the metal-porphyrin bond. PHILLIPS [*29*], however, has deduced from metal and acid replacement reactions and from spectroscopic information that the order should be Ni $>$ Co $>$ Cu $>$ Zn $>$ Mg, the most serious anomaly being the position of Cu. PHILLIPS does go on to remark, however, that Co, Zn and Mg can add two ligands, while Cu and Ni resist even one [*25*]. BEREZIN [*4*], from a study of acid replacement in metal phthalocyanines, notes this anomaly and suggests the order of stability Cu $>$ Ni $>$ Co $>$ Zn in agreement with the Mellar-Moley order and our results.

Conclusions

Previous authors have shown that the extended Hückel model can provide useful insights into various experimental problems. We have refined the model and carried out a set of calculations on metal porphins. These calculations provide a clear insight into the relation of the metal orbitals to those of the ring that will be subject to verification through EPR and spectroscopic studies. The calculated ionic properties of the metal and ring correlate successfully to chemical stabilities and to reduction potentials. The model should thus provide a quideline and challenge to future theoretical and experimental work.

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* The net charge on the Mg ring is -0.5717 to be compared with the ring charges presented in Tab. 11.

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