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THE STATUS OF MOLECULAR ORBITAL CALCULATIONS ON PORPHYRINS AND THEIR COMPLEXES

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A. INTRODUCTION

Metal complexes of the planar tetradentate ligand porphyrin (Fig. 1) are of interest not only in themselves but also because of their relationship to biologically important molecules. Particularly significant are heme, an iron porphyrin which is the prosthetic group of hemoglobin and many cytochromes; and the chlorophylls, which are magnesium chelates of chlorins (dihydro-porphyrins, Fig. 2). Although the free base porphyrin has the disadvantage for molecular orbital calculations of being large, it has the advantages of being symmetrical and highly conjugated. Thus it is just 25 years since the first MO calculations on porphyrin were reported [1,2]. Since these necessarily crude calculations, semi-empirical MO methods have been developed and applied extensively to small and medium-sized molecules, where they have proved invaluable in correlating and interpreting properties (if not in predicting them). At the same time, the size and speed of computers have increased enough to permit the application of semi-empirical methods to sim-

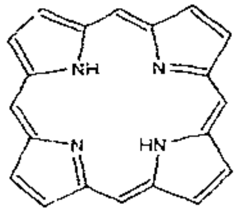

Fig. 1. Free-base porphyrin.

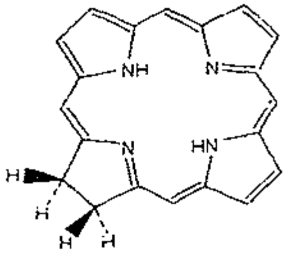

Fig. 2. Dihydroporphyrin (chlorin).

ple porphyrins and their complexes. At the time of writing, the all-valence-electron CNDO method has recently been applied to porphyrin and its dianion, to its copper(II) complex, and to two magnesium complexes [4—6]. This means that calculations of similar reliability may soon be expected for realistic analogues of chlorophylls, if not also for hemes.

In view of this stage of development, this article will review the understanding gained in the past 25 years by molecular orbital calculations on porphyrins and their complexes. Since porphyrins are highly coloured compounds, most of the calculations have been performed in order to interpret optical absorption spectra, and this emphasis will be reflected here. Consideration of excited states is also relevant to studies of energy transfer in biological processes such as photosynthesis. Most of the calculations to date have been on simple model porphyrins and their complexes. These calculations have been performed both for their own sake and also for extrapolation to the more complicated porphyrins occurring naturally. For clarity we shall discuss only the method adopted in each piece of work, and the principal results. Details of the range of porphyrins studied are given in tabular form in the Appendix.

The electronic absorption spectra of free-base porphyrins consist of four Q-bands in the region 500—600 nm, an extremely intense Soret or B-band at about 400 nm, and several other bands labelled N, L and M at shorter wavelengths (nomenclatures as in ref. 7). For metal porphyrins the spectra are similar except that only two Q-bands are seen. Recent spectra [8] of free-base octaethyl porphyrin (OEP) and of zinc OEP are shown in Figs. 3 and 4. The calculations for free-base porphyrin itself have been compared with various different experimental spectra, but to provide a common standard of reference we shall compare them all with the spectrum shown in Fig. 3.

X-ray crystallographic studies [9] have shown that in the solid state the porphyrin molecule is significantly distorted from planarity, being "ruffled" by alternate upward and downward displacements of the pyrrole rings. This distortion may persist in the free porphyrin molecule, but other molecules

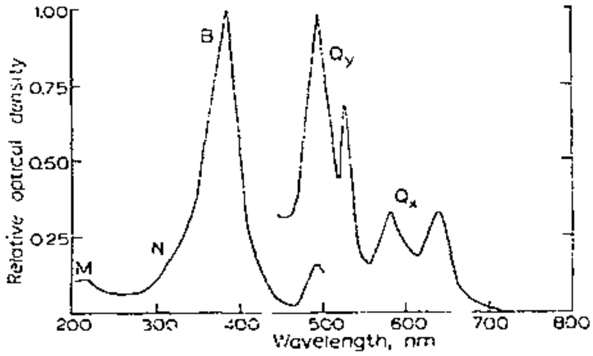

Fig. 3. Vapour-phase absorption spectrum of free-base octaethylporphyrin, after ref. 8. The intensities of the UV and visible bands are separately normalized to unity. (We are advised that the $Q_x(0,0)$ band should be somewhat weaker than the $Q_x(1,0)$ band at longer wavelengths, the comparable intensities shown being probably due to some chlorin impurity.)

found to be non-planar in the crystal [10] are known to be planar in the free state owing to the removal of the crystal forces. Accordingly, most of the MO calculations have treated the molecule as planar for simplicity (or, in the earlier calculations, for want of evidence to the contrary). In any case, a calculation [11] using the ruffled structure obtained results little different from those using the planar structure. Another structural detail concerns whether the hydrogen atoms bound to nitrogen in free-base porphyrins are bonded to opposite nitrogens (as shown in Fig. 1), giving a molecular point group of D_{2h}, or to adjacent nitrogens, giving C_{2v}. The weight of evidence [12] favours the "opposite" structure. Early X-ray work left in doubt the structure of porphyrin itself while confirming the "opposite" structure for aryl and alkyl sub-

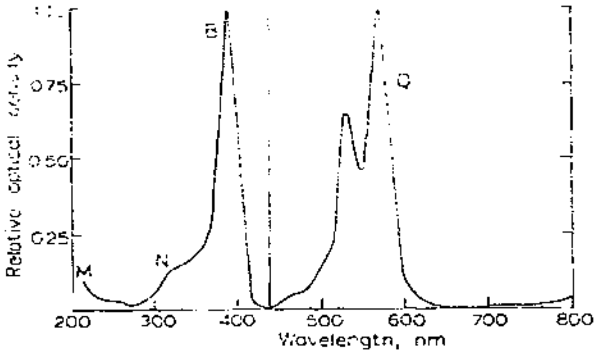

Fig. 4. Vapour-phase absorption spectrum of zinc octaethylporphyrin, after ref. 8. The intensities of the UV and visible bands are separately normalized to unity.

stituted porphyrins, but more recent work has finally confirmed the "opposite" structure for the parent compound too [13]. Most MO calculations have assumed the "opposite" structure; we note exceptions where appropriate.

Since porphyrins are such large molecules, exact or ab initio MO calculations have been out of the question. However, porphyrins have been studied using all the main empirical and semi-empirical methods (i.e. methods in which all or some of the required integrals are obtained from experimental quantities), and it proves convenient to organize this review by method of calculation. The methods fall into two classes: π-electron methods and σ-electron methods. Porphyrins are ideal subjects for π-electron methods since they are planar (with the reservations noted above) and highly conjugated. However, σ-electron methods are essential to deal with metalloporphyrins. Section B of this review deals with the π-electron methods and Section C with σ-electron methods. The results are summarized in Section D and prospects for future development are discussed. Despite the organization by method of calculation, the emphasis is on the substances rather than the details of the techniques, which have been reviewed recently [14]. For convenience of reference, the Appendix summarizes the available calculations, classified according to the porphyrin studied.

Some points about our nomenclature should be made clear at this stage. We have used "porphyrin" for all the substances we discuss, as recommended by Bonnett (ref. 13, p. 745). The parent compound illustrated in Fig. 1 is "free-base" porphyrin. This may be protonated, and the result when two protons have been added is porphyrin "dication". Conversely, two protons may be removed to give the "dianion". Complexes of divalent metals with porphyrin arise by a formal replacement of these two protons by the metal ion. In the context of metal complexes, the parent compound may therefore be thought of as the acid [11], but for consistency we do not adopt this usage.

B. π-ELECTRON METHODS

Since the porphyrins are effectively planar and highly conjugated, they are obvious candidates for π-electron MO treatments. In such treatments it is assumed that the π-electrons are free to move over the molecular skeleton independently of the σ-electrons, and that electronic spectra and other properties are principally governed by the π-electrons. The calculations are thereby greatly simplified. In particular, the size of the problem is reduced because it is governed by the symmetry of the π-electron system, D_{4h}, rather than the lower symmetry of the molecule (D_{2h} for free-base porphyrin). It should be noted that the resulting orbitals are therefore classified according to their transformation properties under D_{4h} symmetry.

(i) Free electron molecular orbital (FEMO) method

In its simplest form, this method is just an extension of the one-dimensional particle-in-a-box problem. Cyclic systems like porphyrin are treated using a particle-on-a-ring model, in which the π-electrons are considered to be confined to a ring of constant negative potential energy, with zero potential energy away from the ring. Detailed accounts of the theory are given in refs. 15 and 16. The π-electrons are fed into molecular orbitals with energies

$$E_q = q^2\hbar^2/2mr^2 \quad (q = 0, 1, 2, \ldots) \tag{1}$$

where q is the orbital ring quantum number. This equation is also conveniently written as

$$E_q = q^2h^2/2mC^2 \tag{2}$$

where C is the circumference of the ring, taken as the sum of the bond lengths making up the perimeter of the model. Energies of spectral transitions are taken as differences in the E_q.

This simplest version of the FEMO method (known as the perimeter free-electron model) was the first MO method applied to porphyrin [1,2]. The difference between carbon and nitrogen atoms was ignored, and so was the branching in the π-skeleton. Of the various possible choices of molecular perimeter, both Kuhn [1] and Simpson [2] used an eighteen-membered ring including two of the nitrogens. Kuhn reported agreement with the position of the observed spectral bands but not with their complexity. The theory actually gives four degenerate transitions beteen orbitals characterized by $q = \pm 4$ and ± 5. Simpson noted that q is essentially an angular momentum so that the excited states would have net angular momenta of ± 1 and ± 9. These combined states would then he split in energy, transitions to the former pair being allowed and to the latter forbidden, so accounting for the separation and different intensities of the Q and B bands. Simpson's energy for the degenerate transitions is given in Table 1.

Porphyrin was also treated [17] by a variant [18] of the FEMO method in which the π-electrons are treated as being confined in two cylindrical potential wells above and below the molecular plane. Again no separate account is taken of the nitrogen atoms. The results are summarized in Table 1.

TABLE 1

Energies[a] of spectral transitions in free-base porphyrin calculated by FEMO methods

Simpson [2]	Takeda and Oki [17]	Platt [19]	Nakajima and Kon [21]	Experiment [8]
16.10		16.00	15.60	16.39
			20.20	19.49
	26.40	23.00	25.60	25.97
			30.10	31.95

[a] Expressed as $E/10^3$ cm^{-1}.

Another modification of the FEMO method is the three-dimensional box model applied to porphyrin by Platt [19]. Porphyrin is represented by a circumscribed square box of side l in which two-dimensional wavefunctions are calculated, with orbital energies.

$$E = (n_x^2 + n_y^2)h^2/8ml^2 \tag{3}$$

where n_x and n_y are quantum numbers. Results are quoted in Table 1. It transpires that although no information about atomic positions is incorporated into the calculation, the net electron density given by 26 electrons in the lowest orbitals has maxima close to where the bond would be in the box. The implications for porphyrin spectra were later discussed [20] in much the same way as Simpson had done [2], in a way foreshadowing the four-orbital model [7] (see Section B(ii)).

Nakajima and Kon [21] applied a "refined" FEMO method to porphyrin and tetrahydroporphyrin, taking account of branching and heteroatoms by a combination of the FEMO and linear combination of atomic orbitals (LCAO) methods. The π-skeleton is divided into twelve parts joining the atoms where branching occurs, and each is given a separate free-electron wavefunction u_i (i = 1 to 12). The molecular wavefunctions are formed as linear combinations of the u_i, and are then treated by standard methods to give MO energies. The nitrogen atoms are simulated by deeper potential sub-boxes; their effect on the energy of a transition is incorporated as a shift calculated by first-order perturbation energy [22]. Results with these shifts are given in Table 1. The same method of incorporating the effect of the nitrogen atoms was applied to the perimeter free-electron model by Rackow [23], who used the innermost sixteen-membered ring including all four nitrogens, obtaining qualitative agreement with experiment.

Although FEMO theory gives useful results rapidly, it is a very crude approximation, which in its simplest form gives only transition energies with no specification of the symmetries or multiplicities of states. Nevertheless, the method does give physical insight into the physical origin of the spectrum. It still finds use in treating large interacting systems where no other method is feasible (cf. a recent study [24] of chlorophyll complexes).

(ii) Hückel molecular orbital (HMO) method

The HMO method is the one which has most often been applied to free-base porphyrins. It is an empirical method giving useful results without excessive computation. The molecular orbitals are expressed as linear combinations of atomic orbitals, with the advantages that they can be readily visualised and interpreted in chemical terms; they are also amenable to group-theoretical analysis, which simplifies the computation. Moreover HMO treatments yield not only transition energies but also such physically important quantities, as bond orders and charge densities. A general account of Hückel theory is given in ref. 25, from which the present notation is taken. The various treatments of porphyrins discussed here differ in the magnitude assumed for the overlap integral S and in the treatment of the empirical Coulomb and resonance integrals involving nitrogen, α_N and β_{CN}.

A general scheme for HMO calculations on large molecules including porphyrin was devised by Platt [26]. In this scheme, all αs are set equal and all βs are set equal, with $\beta_{CC} = -23\,000$ cm^{-1}, so that no account is taken of heteroatoms. The MO energies ϵ are calculated neglecting overlap, but then corrected for overlap using

$$x_{corr} = x/(1 + Sx) \qquad (4)$$

where x is $(\epsilon - \alpha)/\beta$, and the overlap integral S is taken as 0.25. The results are given in Table 2.

The standard method of modifying the empirical parameters to take account of the nitrogen atoms is by writing [25]

$$\alpha_N = \alpha_C + h_N\beta_{CC} \qquad (5)$$

$$\beta_{CN} = k_{CN}\beta_{CC} \qquad (6)$$

where h_N and k_{CN} are parameters. This scheme was used by Matlow [27] to distinguish between nitrogens with and without bonds to hydrogen. He treated not only the opposite and adjacent structures, using $h_N = 0.8$ and 1.0 for nitrogens with and without attached hydrogens, but also a hypothetical symmetrical structure with the hydrogens above and below the centre of the porphyrin plane, in which all nitrogens had $h_N = 0.9$. The adjacent structure was predicted to be most stable and the symmetrical structure least stable. Attempts were made to explain the porphyrin spectrum as that of a mixture of opposite and adjacent isomers, but this assumption is not supported by ex-

TABLE 2

Energies[a] and oscillator strengths (in brackets) of spectral transitions in free-base porphyrin calculated by HMO methods

Platt [26]	Longuet-Higgins et al. [31]	Gouterman et al. [36] (CI)	Chen [37] (CI)	Experiment [8]
9.0	14.5	16.75 (0.019)	17.24 (0.2)	16.39 19.49 (0.006)
21.3	16.5	23.98 (3.14)	24.45 (2.06)	25.97 (1.4)
21.3	23.0			

[a] Expressed as $E/10^3$ cm^{-1}.

perimental evidence, nor indeed necessary with more sophisticated theories. The effects of varying h_N between 0 and 1.5 were investigated by Kobayashi [28]. The standard method, with $h_N = 0.7$ and $k_{CN} = 1.0$, was applied by Pullman [29] to calculate charges on the carbon atoms bridging the pyrrole rings in porphyrin and chlorin. In chlorin, the charges were found to be larger on the atoms adjacent to the pyrroline (dihydropyrrole) ring, so accounting for the greater reactivity of these atoms towards electrophilic attack.

An alternative method of including the effect of the nitrogen atoms is due to Coulson and Longuet-Higgins [30] (CL). The change of Coulomb integral $\delta\alpha_N$ from carbon to nitrogen is treated as a perturbation, giving the first-order perturbation energy for the rth MO as

$$\delta\epsilon_r = \sum_i c_{ir}^2 \delta\alpha_i \tag{7}$$

where the sum runs over all nitrogen atoms and c_{ir} is the coefficient of the atomic orbital i in the MO. Longuet-Higgins et al. [31] applied this CL method to porphyrin and tetrahydroporphyrin, using Platt's scheme [26] and $\delta\alpha_N/\beta_{CC} = 1$. Their results are shown in Table 2, where it can be seen that the main effect of including the nitrogen atoms is to raise the Q-band transition energy from 9000 cm^{-1} to 14500 cm^{-1}, much closer to the experimental values. The CL method was applied by Barnard and Jackman [32] to porphyrin and its hydrogenated forms, using various values of $\delta\alpha_N$, but the results were employed mainly to make structural inferences about bacteriochlorophyll. Calculations on various hydrogenated porphyrins were also reported by Seely [33], who used the CL method with $\delta\alpha_N/\beta_{CC} = 1$.

These various HMO treatments gave transition energies in reasonable agreement with experiment, but none of them explained why the Soret or B-bands are two orders of magnitude more intense than the Q-bands. In an attempt to explain the intensities and to account for the success of the free-electron treatments, Gouterman introduced the four-orbital model [7,34]. The orbitals concerned are the highest occupied a_{1u} and a_{2u} orbitals and the lowest unoccupied pair of e_g orbitals. It was suggested that the a_{1u} and a_{2u} levels were almost degenerate. The excited configurations resulting from one-electron transitions from either level to the e_g levels would then also be nearly degenerate, and so would mix strongly to give states resembling those predicted from angular momentum considerations in the FEMO method [2,20]. Gouterman showed that this model could rationalize the changes in spectra among different porphyrins; he also applied it, less convincingly, to triplet—triplet absorption spectra [35].

A quantitative HMO treatment of the four-orbital model was given by Gouterman et al. [36]. They forced near degeneracy of the a_{1u} and a_{2u} levels by the parametrization

$$\alpha_N = \alpha_C + 2\beta_{CC}$$

$$\beta_{CN} = 0.5\beta_{CC}$$

The mixing of the nearly degenerate excited configurations was then treated by configuration interaction (CI), that is, by constructing the excited state wavefunction as a linear combination of the four configurations resulting from one-electron transitions among the four orbitals. It was found that the strong interaction of the $(a_{1u}e_g)$ and $(a_{2u}e_g)$ configurations did cause the higher-energy transition (B-band) to increase in intensity at the expense of the lower-energy one (Q-band). As can be seen from Table 2, the experimental transition energies and intensities are quite well reproduced. Unfortunately, this choice of parameters gives a C—N bond order of 0.218, corresponding to too long a C—N bond. This defect arises because the parameters imply that the nitrogen atoms contribute little to the conjugation path, which is thus effectively the outermost 20-membered ring.

A different parametrization was tried by Chen [37], viz.

$$\alpha_N = \alpha_C + 0.5\beta_{CC}$$

$$\alpha_{CN} = 0.9\beta_{CC}$$

This amounts to assuming that the conjugation path is the innermost 16-membered ring. This was further emphasized by taking the value of β_{CC} between a carbon atom on the path and one off it as 60% of that between similar carbon atoms. The results preserve a realistic geometry, but as can be seen from Table 2 the intensity of the Q-band is then an order of magnitude too large.

The main experimental observations on porphyrins can thus be rationalized semi-quantitatively using Hückel theory, notably in its most sophisticated form, the four-orbital model with limited CI. This is a substantial achievement. At the same time, the success of the HMO treatments depends on a choice of parameters which, being empirical, cannot themselves be rationalized independently. Since this feature is inherent in empirical treatments, any more fundamental understanding of porphyrins must come from semi-empirical or non-empirical methods. The remaining π-electron treatment to be described here is thus a semi-empirical one.

(iii) Pariser—Parr—Pople (PPP) method

This is a semi-empirical self-consistent-field (SCF) method. In such methods, each electron is assumed to move in an orbital subject to the nuclear potential and the average potential due to the other electrons. In exact (ab initio) SCF treatments, the MO's are true eigenfunctions of the Hartree—Fock Hamiltonian operator F (see, for example, ref. 38). Completion of such a treatment requires the evaluation of two-centre electron repulsion integrals

$$\langle\mu\nu|\sigma\rho\rangle = \iint \phi_\mu(1)\phi_\nu(1)R_{12}^{-1}\phi_\sigma(2)\phi_\rho(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{8}$$

where $\phi_\mu(1)$ is an atomic orbital based on atom μ occupied by electron 1. For

n atomic orbitals, there are thus some n^4 integrals, making an exact treatment very lengthy for porphyrins. Semi-empirical methods seek to reduce the number of integrals to be evaluated by neglecting some and estimating others.

The method introduced by Pariser and Parr [39] and Pople [40] depends on the zero differential overlap (ZDO) approximation, in which integrals involving a product of orbitals on different atoms are taken as zero. As a result, all overlap integrals are zero, and the only non-zero repulsion integrals are those of the form $\langle\mu\mu|\nu\nu\rangle \equiv \gamma_{\mu\nu}$. The other required integrals become

$$U_{\mu\mu} = \int \phi_\mu(-\tfrac{1}{2}\nabla^2 + V_\mathrm{M})\phi_\mu \mathrm{d}\tau \tag{9}$$

$$\beta_{\mu\nu} = \int \phi_\mu(-\tfrac{1}{2}\nabla^2 + V_\mathrm{M} + V_\mathrm{N})\phi_\nu \mathrm{d}\tau \tag{10}$$

where the orbitals μ and ν are centred on atoms M and N with nuclear potential V. The integrals are determined empirically, for example by fitting atomic spectroscopic data (see refs. 38 and 40).

The PPP method was applied to free-base porphyrin by Kobayashi [42], who used the results to provide a value of $h_\mathrm{N} = 1.0$ for Hückel calculations. He also undertook PPP calculations with and without CI (number of configurations not stated) [43]. The $\gamma_{\mu\nu}$ were evaluated using Mataga and Nishimoto's method [44]:

$$\gamma_{\mu\nu} = 1/[R + 2/(\gamma_{\mu\mu} + \gamma_{\nu\nu})] \tag{11}$$

the $\gamma_{\mu\mu}$ being obtained from Pariser's approximation as $I_\mu - A_\mu$, where I and A are the ionization potential and electron affinity of the atomic valence state, and the $U_{\mu\mu}$ being taken as $-I_\mu$. The calculated singlet energies are shown in Table 3; they agree reasonably well with the measured absorption spectrum.

Weiss et al. [45] studied both free-base D_{2h} porphyrin with a different parameter U_NN for pyrrole and pyridine-like nitrogens, and a D_{4h} model with equivalent nitrogens, referred to as "metal porphin". The $\gamma_{\mu\nu}$ were obtained by Mataga and Nishimoto's method, while the $\beta_{\mu\nu}$ were calculated by scaling the value for benzene in the ratio of the overlaps between two Slater p_z orbitals at the actual distance and at the benzene distance. Two sets of values for the $U_{\mu\mu}$ and $\gamma_{\mu\mu}$ were used. Transition energies were calculated without CI, with CI on the four-orbital model, and then with 52 singly-excited configurations. The successive improvements are shown in Table 3. These calculations showed that the four-orbital model was substantially correct, for it was found that, whichever set of parameters was used, the $(a_{1u}e_g)$ and $(a_{2u}e_g)$ configurations were indeed nearly degenerate before CI. Moreover, these configurations made up over 97% of the states giving rise to the Q-bands. The separation between the B-bands and Q-bands remained too large, and the intensity ratio B:Q was now rather too large, probably because the Q-band intensity depends critically on its interaction with the B-band. Triplet states were also investigated. The lowest triplet state was found to be 92% pure, and little

TABLE 3

Energies^{a} and oscillator strengths (in brackets) of spectral transitions in free-base porphyrin calculated by PPP methods

Kobayashi [43]^{e}		Weiss et al. [45]^{e}			Sundbom [80]	Experimental [8]
1^{b}	$?^{b,c}$	1^{b}	4^{b}	52^{b}	all^{b}	
					$13.6x^{d}$ (0.002)	Q_x : 16.39
	14.4		16.9 (0.004)	16.2 (0.004)	$16.3y^{d}$ (0.012)	Q_y : 19.49 (Q : 0.006)
19.7		22.7				
21.0		23.4				
					$26.4x^{d}$ (0.53)	B : 25.97 (1.4)
	24.7		29.0 (6.86)	28.7 (5.86)	$30.9y^{d}$ (1.8)	
					$35.2x^{d}$ (2.5)	N : 31.95
25.9	26.2	36.8_5		34.6 (0.90)	$35.7y^{d}$ (0.6)	
					$40.2x^{d}$ (1.0)	L : 37.74
26.1	27.3	36.9_5		37.8 (0.30)	$42.4y^{d}$ (0.5)	

[a] Expressed as $E/10^3$ cm^{-1}.

[b] Number of singly-excited configurations mixed to construct excited states; 1 corresponds to no CI.

[c] Number not stated (but greater than 1).

[d] Polarization.

[e] D_{4h} symmetry used rather than D_{2h}.

changed when represented by 58 instead of 16 singly and doubly excited configurations. The second triplet, represented by 31 configurations, was of very mixed parentage. This accounts for the relative failure of the four-orbital model in explaining the triplet-triplet absorption spectrum [35], which these later calculations explain very satisfactorily. Similar calculations by Caughey et al. [46], using 29 configurations, were employed to interpret a series of spectra, especially near-UV bands.

Knop and Knop [47] included all 143 singly excited configurations, but still obtained too large a separation between the B- and Q-bands. They concluded that in free-base porphyrin conjugation was stronger over the eighteen-membered ring incorporating the nitrogens without attached hydrogens than over the corresponding ring incorporating the other nitrogens, whereas in "metal porphyrin" with equivalent nitrogens the conjugation was much the same in the inner sixteen-membered ring over the nitrogens as in the outer twenty-membered ring avoiding the nitrogens. These conclusions substantiate the use of the eighteen-membered ring in the earliest FEMO calculations [1,2]. Honeybourne [48] reported calculations with 81 configurations using the variable beta method [49], in which the $\beta_{\mu\nu}$ depend on the calculated bond orders. The results, which were much the same as in previous work, were applied to a study of porphyrin-like molecules, and later extended to calculate reactivity indices and spin distribution [50]. Electron densities and reactivity had also been studied earlier [51] for porphyrin and some reduced porphyrins.

The PPP method was also used [52] to study the effect of the systematic changes in the ring geometry in complexes with metals of different ionic radii. It was found that the energies of singlet excited states depended little on the changes in the ring, both with the four-orbital model and with more extensive CI. The triplet energies, however, decreased systematically with increasing ionic radius; only the four-orbital model was used for these calculations. These findings agreed well with absorption and phosphorescence spectra except for a constant shift in the energies.

As we have seen, a major concern of MO calculations on porphyrins has been to explain the great difference in intensity between the B- and Q-bands, which has proved difficult, partly owing to the sensitivity of the Q-band intensity to the amount of CI. The calculations described so far obtained intensities from matrix elements of the dipole length operator. However, the intensities can equally well be obtained from matrix elements of the momentum or dipole gradient operator. The results are identical if the wavefunctions are exact, but not otherwise. In an approximate MO treatment one can therefore ask which method gives better agreement with experiment. Following work which showed that the dipole gradient method was better than the dipole length method for various conjugated hydrocarbons [53], Hush and Williams [54] applied the dipole gradient method to porphyrins. Both free-base and a "metal porphyrin" were investigated for the four-orbital model and by CI including 16 configurations, using the variable beta method. The positions of the bands generally accorded with those of Weiss et al. [45], but it was found that the gradient operator did indeed give a much better intensity for the Soret B-band in both porphyrin systems. The intensity calculated for the Q-band remained unsatisfactory, and it was concluded that improved results would entail the use of vibronic wavefunctions. Similar results were obtained by McHugh et al. [55] in a study using more extensive CI. This work showed that the gradient operator correctly gave the y-polarized component of the Q-band as more intense than the x-polarized component, a result obtained previously [45] with the length operator only by including $\beta_{\mu\nu}$ between non-nearest neighbours. The results were used to interpret the spectrum in some detail, and were extended to calculate orbital angular momenta which were in reasonable agreement with those deduced from magnetic measurements.

One π-electron method very different from the PPP method is nevertheless conveniently mentioned here because, like the PPP method, it takes account of electron repulsion. This is the projected electron density method of Försterling et al. [56]. In this method, all π-electron orbitals are assumed to have the same functional form perpendicular to the molecular plane, reducing the problem to one in two dimensions. Electron-pair repulsion is treated electrostatically, the other electrons being taken to constitute a medium of dielectric constant 2.5. Absorption spectra were calculated directly by time-dependent perturbation theory, with the approximation that transitions were allowed to only two states. The calculated spectrum of porphyrin, with arbitrarily chosen damping constants, was in good qualitative agreement with experiment, but overestimated both the separation between the B- and Q-bands and the Q-band intensity.

The PPP method can be seen to have put the successful predictions of Hückel theory on a sounder theoretical footing. In particular, it is confirmed that the Q- and B-bands arise from transitions to states which are essentially the sum and difference of the lowest energy excited configurations. Extensive CI, coupled with modified effective Hamiltonians and the use of the dipole gradient operator, has proved capable of reproducing all the main features of the spectrum down to the relative intensities of sub-bands. Nevertheless, being a π-electron method, the PPP treatment can only give information about $\pi \rightarrow \pi^*$ transitions. It cannot tell us about the $n \rightarrow \pi^*$ transitions expected for nitrogen-containing molecules, nor about the effects of σ-bonding to metals (though $n \rightarrow \pi^*$ transitions have not been observed — for reasons which will appear later — and different metals have relatively small effects on absorption spectra). So once again, a more thorough understanding of porphyrins demands the application of more all-embracing theory, this time taking σ-electrons into account.

C. σ-ELECTRON METHODS

(i) Modified Hückel treatments

The first attempts to treat σ-electrons used Hückel theory modified to include only the σ-bonding between the nitrogens and a central metal atom. The extended Hückel method including all valence electrons is discussed in the next subsection. Extensions of Hückel theory to σ-electron systems usually follow the scheme introduced by Wolfsberg and Helmholtz for calculations on oxyanions [57]. Overlap integrals $S_{\mu\nu}$ are calculated theoretically using Slater orbitals, and "resonance integrals" $\beta_{\mu\nu}$ are estimated from the equation [57,58]

$$\beta_{\mu\nu} = \tfrac{1}{2}kS_{\mu\nu}(\beta_{\mu\mu} + \beta_{\nu\nu}) \qquad (12)$$

Here the $\beta_{\mu\mu}$ are "Coulomb integrals", obtained from valence-state ionization potentials, and k is an empirically determined parameter close to 2.

Calculations of this type were reported by Pullman et al. [59] and by Spanjaard and Berthier [60], who studied iron porphyrins using $3d$, $4s$ and $4p$ orbitals on iron, $2p\sigma$ and $2p\pi$ orbitals on nitrogen, and $2p\pi$ orbitals on carbon. The results showed that the molecular orbitals giving rise to the optical spectra were predominantly on the porphyrin ligand, as expected from the similarity of free-base and metal porphyrin spectra. Calculations for a divinyl porphyrin gave a smaller energy gap between the highest occupied and lowest empty MO than for the unsubstituted porphyrin; this finding accords with the shift to longer wavelengths in going from cytochrome c, with an alkyl-substituted porphyrin, to cytochrome b with the divinyl-substituted protoporphyrin. These calculations were extended by Ohno et al. [61] to include the effects of nitrogen atoms, charges and dipoles placed above and below the ring; they also allowed the parameter values to depend on the calculated charges. Results for iron(II) porphyrin were acceptable, but it proved impossible to obtain a consistent description of iron(III) porphyrin.

Further calculations on iron(II) porphyrin with axial nitrogen ligands were reported by Millie and Veillard [62]. Here Coulomb integrals were obtained by a modification [63] of the PPP method relating them to spectroscopic term values. The results again confirmed how little the higher occupied and lower unoccupied orbitals of porphyrin are affected by complex formation.

(ii) Extended Hückel (EH) method

This method, due to Hoffmann [64], is essentially that described in the previous subsection, but with all valence electrons included and with resonance integrals retained between all atoms instead of just nearest neighbours. The deficiencies of HMO theory were already clear when EH theory was developed, and doubts were expressed as to the likely usefulness of the method. Nevertheless, EH theory is less purely empirical than HMO theory, and offered the hope of a systematic, if qualitative, treatment of σ-bonded systems which could guide and stimulate experiment. For metal porphyrins, the EH method was particularly attractive because of the desire to include σ-electrons without inordinate amounts of computation.

Exhaustive EH calculations on metal porphyrins were carried out by Zerner and Gouterman [11,65—68]. The "Coulomb integrals" were calculated self-consistently from atomic orbital ionization potentials in the neutral and singly-charged atom averaged according to the calculated net charge. The "resonance integrals" were calculated from the improved version of eqn. (12)

$$\beta_{\mu\nu} = \tfrac{1}{2}S_{\mu\nu}(\beta_{\mu\mu} + \beta_{\nu\nu})[\kappa + (1-\kappa)\delta_{\mu\nu}] \tag{13}$$

where the value of the parameter κ, taken to be the same for both σ- and π-electrons, was determined by comparison with PPP π—π^* transition energies. Use of the EH method allowed calculations to be performed using the actual non-planar porphyrin geometry found by X-ray crystallography (for nickel etioporphyrin [70]). As noted in the Introduction, the non-planarity had negligible effect. The spectroscopically important π-orbitals of the planar structure were modified into MO's in which 99% of the electron density was still in π-AO's, with energy shifts not exceeding 0.1 eV and no changes of energy order among the MO's.

The first set of EH calculations [11] dealt with porphyrin complexes of the first transition series from manganese to zinc. It proved possible to rationalize the observed magnetic behaviour of the complexes in terms of the assignment of electrons to the erstwhile d-orbitals, provided account was taken of the likely effect of ligands coordinated in the axial positions. In manganese(II) and iron(II) porphyrins, the d-orbitals had similar energies to the highest occupied (a_{2u}) porphyrin π-orbital, in keeping with the complicated behaviour of these porphyrins. The net charges on the metals were calculated to vary from +0.11 on Mn to +0.40 on Zn. It was confirmed that the metal atoms were only weakly coupled to the porphyrin π-system, but the small variations in spectrum from metal to metal were not reproduced. Some transitions other than $\pi \rightarrow \pi^*$ were also discussed. Further calculations [65] treated iron porphyrins with water, carbon monoxide and oxygen ligands in a variety of geometries, and this work was extended [70] to include nitrogen as a ligand as well as iron(III) complexes with hydroxyl, fluoride, chloride and cyanide ion. Suggestions that nitrogen could bond were shown to be unlikely, and it was also calculated that the oxygen molecule could bond parallel to the porphyrin ring but not perpendicular (axially). The spin states of the complexes were found to depend on the geometry assumed.

After this largely interpretive work, EH calculations were performed for predictive purposes. For vanadyl (VO^{2+}) porphyrin [60], the assumption that the vanadium atom was in the porphyrin plane led to strong mixing of the metal orbitals with the porphyrin ones, implying an unusual spectrum unlike that observed experimentally. An out-of-plane structure gave weak mixing and a more normal spectrum. Calculations for the unknown vanadium(II) porphyrin indicated that it should be stable, though readily oxidizable to vanadyl porphyrin. As the only first transition series metal forming neither a porphyrin nor a phthalocyanine complex was scandium, calculations were also performed [67] for $ScOH^{2+}$ porphyrin. In this case, the strong mixing between metal and porphyrin orbitals found for vanadyl porphyrin persisted even with the scandium well above the porphyrin plane. This implied an unusual spectrum, but the complex was predicted to be stable though possibly liable to photodissociate.

EH theory was also applied to porphyrin complexes with non-transition metals. For the alkaline earth metals beryllium, calcium and magnesium, as well as for a hypothetical $(BeCl)_2^{2+}$ porphyrin with both beryllium atoms in the porphyrin plane, the porphyrin π-structure was found to be preserved once more, though there was the possibility of extra transitions in the spectra [68]. The degree of covalent binding in the calcium and magnesium porphyrins was less than for most of the transition metals, and comparable with that calculated [11] for zinc. Calculations were also performed [71] for porphyrin complexes with divalent and tetravalent group IV elements. It was deduced that the Ge^{II} complex was planar, with the two extra electrons on the ring, while the Sn^{II} and Pb^{II} complexes were non-planar, with the extra electrons on the metal. A charge-transfer band in the spectrum was predicted, in apparent accord with experimental data. Charge-transfer bands were also found to be induced by hydroxyl and chloride ligands on the tetravalent elements.

The free-base porphyrin molecule has also been studied by the EH method. Mathur et al. [72] calculated $\pi \to \pi^*$ transitions farther into the ultra-violet, using eqn. (12) for the $\beta_{\mu\nu}$, with the rather high value of $k = 2.52$, chosen to fit the Q-band energy. The results correlated with the observed spectra [8,73]. Schaffer and Gouterman [74] studied the spectral effects both of distortion of the carbon—nitrogen skeleton from D_{4h} to D_{2h} symmetry and of placing the hydrogens symmetrically between adjacent nitrogens. They concluded that observed environmental effects on the Q_x—Q_y band splitting (change of solvent, change from solution to vapour, etc.) could be attributed to skeletal distortions.

Reservations about the use of EH theory have been expressed by several authors (e.g., Dewar [75]), but its shortcomings were well known to Gouterman and co-workers when they applied it to porphyrins (e.g., see ref. 11). However, as they remark in several papers, EH theory, used judiciously, does permit clear and qualitatively correct predictions to be made. For instance, EH calculations have shown that there may be marked spectral differences in complexes with the metal atom in or out of the porphyrin plane, so permitting structural inferences to be made from spectra. The usefulness of EH theory in providing MO's for other purposes is illustrated by applications to interpreting the luminescence of porphyrin complexes [76—78]. Recent work [111] has treated hemoglobin and coboglobin and their oxygen, carbon monoxide and nitric oxide adducts, using calculations of Mössbauer and ESR parameters to distinguish between possible configurations.

(iii) Modified PPP treatments

This subsection deals with calculations by a Swedish group which has extended the PPP method to include metal atoms and σ lone pairs on nitrogen [79]. Sundbom [80] investigated porphyrin and its dianion and dication using a set of parameters obtained by the group specifically for nitrogen-containing molecules [81]; all singly-excited configurations were incorporated. Recognising the possibility of hydrogen bonding between the pyrrole and pyridine-like nitrogens, she studied both a D_{2h} model for the free base with pyrrolic and pyridinic nitrogen parameters and a D_{4h} model with equivalent parameters, corresponding to strong hydrogen bonding. The experimental spectrum could be fitted by a model with an intermediate degree of hydrogen bonding, about two-thirds of that in the D_{4h} model. The lowest $n \to \pi^*$ transition was calculated to be weak and in the Soret region, which explained why it had not been observed. With this treatment, the Q_y-band was correctly predicted to be more intense than the Q_x-band even though the dipole length method was used. The results are compared with π-electron PPP treatments in Table 3.

Later, Roos and Sundbom [82] studied copper(II) porphyrin, using a method and parameters due to Roos [83—85]. The nitrogen σ lone pairs were included as before, together with $3d$, $4s$ and $4p$ orbitals on copper, but to obtain a correct multiplet structure for copper, one-centre exchange integrals had to be calculated outside the ZDO approximation. All singly-excited configurations were used to form excited states. In the ground state, the copper configuration was found to be approximately $3d^9 4s^{0.5} 4p^{0.5}$, with a net charge +0.8. This value accords with ESR data [86,87] suggesting that the odd electron resides mainly on the metal, and is as usual considerably larger [11] than the EH value +0.28, in which electronic repulsion is not explicitly accounted for. In the excited states, the porphyrin $\pi \to \pi^*$ transitions were found to survive essentially unchanged, but some of the metal-only $d \to d$ transitions were found to mix strongly with charge-transfer transitions between the metal and the porphyrin ring. The excited state energies and MO's were used to calculate ESR g-values and hyperfine coupling constants in good agreement with the experimental results [86,87].

The value of this work was realistically assessed by Roos and Sundbom themselves [82]. It emphasizes the need for CI to reproduce the mixed character of some excited states, and should be useful for spectral assignments by giving the correct order of energy levels, if not their absolute positions.

(iv) Complete neglect of differential overlap (CNDO) method

The CNDO method is an all-valence-electron SCF MO method introduced by Pople, Santry and Segal [88—91]. It consists of applying the ZDO approximation to the Hartree—Fock SCF equations, together with certain constraints to ensure that the results are independent of the choice of coordinate axes. (This problem did not arise in the PPP method because the π-atomic orbitals have a natural choice of axis, perpendicular to the molecular plane.) Detailed accounts of the theory and its parametrization are given in refs. 41 and 92. There are in fact various CNDO treatments, each with different possible ways of obtaining the parameters. The treatment [90] most often applied to ground-state properties is CNDO/2.

The first application of CNDO theory to porphyrin appears to have been not to the free base itself but to copper(II) porphyrin [4]. This treatment used an extension of CNDO/2 to complexes containing atoms of the first transition series [93]. The results were used principally to interpret ESR parameters, and the calculated orbital energies were not quoted. It was found that there was considerable covalent bonding between the copper d_{xz} and d_{yz} orbitals and the ring, but that this changed substantially for small changes in the Cu—N distance.

The CNDO/2 method was applied to porphyrin itself and to its dianion and its magnesium and aquo-magnesium complexes by Maggiora [5]. In the aquo-magnesium complex of tetraphenylporphyrin, the metal is known [94] to lie out of the porphyrin plane, but the position of the water protons is not known; the calculations showed that the protons must lie on the far side of the metal from the ring. The structure of the magnesium complex is not known, but the calculations confirmed the expectation that the metal should lie out of the porphyrin plane as in the aquo-complex. In Table 4, the energies and symmetries of the three highest occupied MO's are compared with the modified PPP results of Sundbom [80] and the EH results of Zerner and Gouterman [11,68]. According to Koopmans' theorem [95], the ionization potential is the negative of the energy of the highest occupied MO; as can be seen, the results of Maggiora [5] and Sundbom [80] bracket the experimental [96] value 7.42 eV. The principal disagreement between the various treatments lies in the symmetries of the successive MO's, but the order given by the CNDO treatment seems to be consistent [5] with ESR data on cation radicals.

It is known that the CNDO/2 method, though adequate for ground-state calculations to predict conformations etc. is unreliable for excited-state calculations and hence for spectral assignments and predictions. A method more suitable for calculations of spectra is the CNDO/S method developed by Del Bene and Jaffé [97]. This was subsequently improved [98] to give better energies, and to permit the intensities of $n \to \pi^*$ and $\sigma \to \pi^*$ transitions to be calcu-

TABLE 4

Symmetries and energies[a] of highest occupied MO's in free-base porphyrin and magnesium porphyrin calculated by σ-electron methods (after Maggiora [5])

Free-base porphyrin (D_{2h})

Sundbom [80]		Zerner and Gouterman [11]		Maggiora [5]	
b_{1u}	−6.58	b_{1u}	−11.66	a_u	−8.34
a_u	−6.67	a_u	−12.00	b_{1u}	−8.59
b_{2g}	−8.50			b_{3g}	−11.79

Magnesium porphyrin (C_{4v})

Zerner and Gouterman [68]		Maggiora [5]	
b_1	−10.65	a_2	−8.37
a_1	−11.15	a_1	−8.82
a_2	−11.55	b_1	−12.14

[a] Expressed as E/eV.

lated by a partial relaxation of the ZDO approximation, which in its strict form makes such intensities zero. The improved method was applied to porphyrin and its dianion by Maggiora and Weimann [6]. Configuration interaction was carried out among the 80 lowest singly-excited configurations. The results were found to be generally as good as or better than those of preceding work [80,46]: the predicted spectra, though subject to the usual overestimated Q-B separation, again gave the Q_y intensity as greater than the Q_x when the dipole length operator was used. Differences arose mainly in the L- and M-band region, where the calculated intensities were mostly smaller than calculated by Sundbom [80]. For the dianion, one $n \rightarrow \pi^*$ band was predicted in the L-band region, in contrast to the two predicted by Sundbom [80], one in the B-band region and the other in the M-band region; unfortunately, experimental resolution of these predictions will prove difficult owing to the nearby intense $\pi \rightarrow \pi^*$ transitions.

Exactly the same method has been applied to the triplet states of porphyrin [99]. The lowest triplet energies are shown in Table 5, together with those calculated by Kobayashi [43] using the PPP method. The PPP levels are much more widely spaced than the CNDO levels (the E_u levels split into B_{1u} and B_{2u} levels as the assumed D_{4h} symmetry is reduced to D_{2h}), but the CNDO calculation still obtains one level substantially lower than that indicated by the phosphorescence [100]. The triplet-triplet absorption spectrum has not been investigated in detail, owing to the need [45] to include doubly-excited configurations, but the positions of the transitions are in general accord with the experimental results [101], whether the lowest or second-lowest triplet is used as the lower state.

TABLE 5

Energies[a] of triplet states of free-base porphyrin

Kobayashi [43][b]		Chantrell et al. [99][c]		Phosphorescence [100]
0.79	(E_u)	1.02	(B_{3u})	
		1.41	(B_{1u})	
1.60	(E_u)	1.61	(B_{3u})	1.57[d]
		1.71	(B_{1u})	
2.61	(E_u)	2.79	(A_g)	
		2.79	(B_{2g})	
2.91	(E_u)	2.80	(B_{1u})	
		2.98	(B_{2g})	

[a] Expressed as E/eV.
[b] PPP method with CI; D_{4h} symmetry assumed.
[c] CNDO/S method with CI (80 singly-excited configurations).
[d] Tetraphenylporphyrin.

Progress towards a CNDO treatment of chlorophylls has continued in recent work on free-base chlorin and bacteriochlorin and their dianions [108]. The CNDO/S method was used to calculate absorption spectra as before [6]. There was found to be no systematic relationship between the calculated and experimental transition energies, although the energy differences appeared small enough to allow experimental spectra to be analysed with fair confidence. In the free bases, the hydrogens on the pyrrolic nitrogens are opposite one another, but may be on the reduced or both on unreduced pyrrole rings. CNDO/2 calculations indicated that the configuration with both hydrogens on unreduced rings was more stable in each case; this was confirmed by the CNDO/S spectral calculations for bacteriochlorin, but for chlorin the weight of evidence favoured the other configuration. The CNDO/2 calculations should be the more reliable in this case, but did give a smaller energy difference between the two configurations for chlorin than for bacteriochlorin. Examination of configuration mixing showed that, while the Q states could still be adequately described in terms of the four-orbital model, the B states involved substantial interaction with other configurations, to an extent markedly dependent on the position of the protons on nitrogen. Calculations by the CNDO/2 method have also been completed on magnesium complexes of these and other reduced porphyrins [109].

The value of CNDO calculations on porphyrins has yet to be explored thoroughly, partly because the computing demands of the method remain rather severe (the CNDO/S calculations for the free-base singlet and triplet states [99] took some ten minutes on an ICL 1906A/CDC 7600 computer). The method also has different variants for different purposes. However, it seems likely that by careful comparison with calculations on similar smaller molecules, CNDO calculations will give results at a uniform level of approximation. In particular one might hope to obtain a reliable treatment of the effect of substituents on spectra. For example, recent CNDO/S calculations on 2,4-divinylporphyrin show that the vinyl groups leave the Q-bands' position unchanged but make the B-bands extend to the lower energies (cf. the discussion in Section C(i)).

D. RETROSPECT AND PROSPECT

The strengths and weaknesses of the various methods have been discussed in detail in the appropriate subsection. The variety of porphyrins which has been studied is indicated by the Appendix, where the methods applied to each substance are noted. By way of conclusion, we make some more general remarks.

As we have seen, the size of the porphyrin molecule has restricted MO calculations on porphyrins to those small enough to be tackled by the relevant generation of computers, and this has meant the use of methods one or two steps less sophisticated than those possible for smaller molecules. However, this restriction has not been without advantages. By the time it becomes technically feasible to apply a particular method to porphyrins, the method's strengths and weaknesses have become apparent from studies on smaller molecules. In effect, only mature theories are applied to porphyrins. This fact may account for the extent to which each more sophisticated method has confirmed the general conclusions of its predecessors. So for example the physical understanding of free-base porphyrin spectra given by the free-electron methods has not charged substantially through the successive development of the qualitative four-orbital model, the HMO treatment of the four-orbital model with CI, the PPP treatments with extensive CI, and the CNDO/S treatment.

However, this is not to say that the steady increase in sophistication has not been worthwhile. The successive treatments have greatly increased our detailed knowledge of the electronic structure of porphyrins, and also its reliability. We have progressed from asking why all porphyrin spectra are much the same to asking why porphyrin spectra differ. The differences are small, but small differences in molecules can often lead to significant changes in biological properties. Since the biologically-active porphyrins and related compounds contain metal atoms, the development of MO treatments for σ electrons has been essential. The extended Hückel method has proved very useful in interrelating properties of metal porphyrins, and in treating conformational and ligand effects. However, this method gives a distorted picture of the interaction of the metal with the ring, owing to its neglect of electron correlation, so that to understand fully the importance of the metal atom it has been necessary to apply SCF treatments, which do include some allowance for correlation.

This brings us to the modified PPP method and the all-valence electron CNDO method, which are the most sophisticated so far applied to porphyrins. The strengths and weaknesses of the CNDO method are now well appreciated from studies on smaller molecules. It has only recently been extended to treat transition-metal compounds, but its application to metal porphyrins seems now to be a problem mainly of computing. Larger CNDO programs may also be expected to yield information on substituted and less symmetrical free-base porphyrins, and, in the foreseeable future, on realistic analogues of chlorophyll.

These are developments of theories already applied to porphyrins. A more sophisticated theory which is being applied to porphyrins is the method of molecular fragments [102]. In this method, the molecule is divided into fragments like CH_2, NH_2, etc. Orbitals for each fragment are next calculated by exact numerical solution of the Hartree—Fock SCF equations, usually with a small basis set of atomic orbitals. Molecular orbitals for the whole molecule are then constructed from the fragment orbitals. Results have been published for molecules as large as naphthalene and the tetrapeptide of glycine [103]. The method has now also been applied to free-base and magnesium porphyrin [110], with results essentially in agreement with the CNDO/2 calculations.

Another development which may be expected is more extensive use of available MO calculations to estimate spectroscopic properties. The Q-band in porphyrin spectra is clearly resolved into 0—0 and 0—1 vibronic sub-bands, and the weakness of this band indicates the need to consider vibronic borrowing of intensity and hence vibronic wavefunctions [104]. Similar considerations apply to porphyrin luminescence [76—78], where spin—orbit coupling must also be treated. There is scope for further work on ESR parameters, Zeeman splittings and Jahn—Teller distortion [105]. In effect, we are reaching a stage where we have an adequate knowledge of the energies of porphyrin excited states and can go on to use MO calculations in investigating properties other than the energy.

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APPENDIX: SUMMARY OF CALCULATIONS

Free-base porphyrin itself has been studied by all the methods discussed in the text. Here we summarize the available MO calculations on other porphyrins. We use the symbol PH_2 for free-base porphyrin, so that a complex with a divalent metal M is written as MP. Other abbreviations are as in the text.

Compound	Method	References
(i) Free-base porphyrins		
Porphyrin dianion (P^{2-})	Modified PPP + CI	80
	CNDO/2	5
	CNDO/S + CI	6
Porphyrin dication (PH_4^{2+})	Modified PPP + CI	80
Dihydroporphyrin (chlorin)	HMO	27,28,29,32,33
	HMO + CI	36
	PPP	51
	PPP + CI	45,55
	CNDO/S + CI	108
Tetrahydroporphyrin	FEMO	21
	HMO	26,31,32,33
	HMO + CI	36
	PPP	51
	PPP + CI	45,55
	CNDO/S + CI	108

Compound	Method	References
Hexahydroporphyrin	HMO	33
	HMO + CI	36
	PPP + CI	45
Octahydroporphyrin	HMO	33
	HMO + CI	36
meso-Tetraphenylporphyrin (TPP)	FEMO	17
	HMO	106
Etioporphyrin	FEMO	17
2-Vinyl-6-formyl-7,8-dihydroporphyrin	HMO	29
2,4-Divinylporphyrin	CNDO/S + CI	99
(ii) Metalloporphyrins		
BeP	EHT	68
Be_2Cl_2P	EHT	68
MgP	EHT	68
	CNDO/2	5
$MgP(H_2O)$	CNDO/2	5
CaP	EHT	68
Sc(OH)P	EHT	67
VP	EHT	66
VOP	EHT	66
MnP	EHT	11
$Fe^{II}P$	Modified HMO	60,61,62
	EHT	11,65
$Fe^{II}P(H_2O)$	EHT	65,70
$Fe^{II}P(CO)$	EHT	65,70
$Fe^{II}P(N_2)$	EHT	70
$Fe^{II}P(O_2)(H_2O)$	EHT	65
Fe^{II}divinylporphyrin (protoporphyrin)	Modified HMO	60
$Fe^{III}P$	Modified HMO	60
$[Fe^{III}P]OH$	EHT	70
$[Fe^{III}P]F$	EHT	70
$[Fe^{III}P]Cl$	EHT	70
$[Fe^{III}P]CN$	EHT	70

Compound	Method	References
CoP	EHT	11
NiP	EHT	11
CuP	EHT Modified PPP + CI CNDO	11 82 4
ZnP	EHT	11
ZnTPP	FEMO	107
$Si^{IV}(OH)_2P$	EHT	71
$Ge^{II}P$	EHT	71
$Ge^{IV}(OH)_2P$	EHT	71
$Ge^{IV}Cl_2P$	EHT	71
$Sn^{II}P$	EHT	71
$Sn^{IV}Cl_2P$	EHT	71
$Pb^{II}P$	EHT	71

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