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Simple Molecular Orbital Calculations on the Electronic Structure of Iron-Porphyrin Complexes*

By

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The simple Hückel method was first applied to the electronic structure of the iron-porphyrin complexes by Pullman et al. [12]. In this paper, their work is extended to include (a) the effect of a dipole or a point charge placed at the sixth coordination position, and (b) the effect of a nitrogen atom placed at the fifth coordination position. A set of new parameter values is used, whose estimation is made by directing special attention to their dependence on the charge distribution among the atoms.

The resulting charge distribution for ferro-porphyrin seems to be reasonable. The fact that the position of the Soret peak is insensitive to the sixth ligand can be understood from the resulting orbital energy levels.

The difficulty of finding a reasonable charge distribution for ferri-porphyrin is discussed.

Die einfache Hückelsche Methode ist auf die Elektronenstruktur der Eisen-Porphyrin-Komplexe zuerst von Pullman et al. [12] angewandt worden. In der folgenden Arbeit wird ihr Verfahren auf (a) die Wirkung eines Dipols oder einer Punktladung an der sechsten Koordinationsstelle und (b) die eines Stickstoffatoms an der fünften erweitert. Ein Satz neuer Parameterwerte wird verwandt, bei deren Bestimmung besonders auf ihre Abhängigkeit von der Ladungsverteilung geachtet wird.

Die erhaltene Ladungsverteilung für Ferroporphyrin erscheint vernünftig. Die Unempfindlichkeit der Lage der Soret-Bande gegen den sechsten Liganden ist aus den erhaltenen Energieniveaus zu verstehen.

Die Schwierigkeit, eine vernünftige Ladungsverteilung für Ferriporphyrin zu finden, wird diskutiert.

La simple méthode de Hückel a été appliquée à la structure électronique des complexes fer-porphyrine pour la première fois par Pullman et al. [12]. Dans l'article suivant, leur travail est étendu afin d'inclure (a) l'effet d'un dipôle ou d'une charge ponctuelle sur la sixième position coordinative, et (b) l'effet d'un atome de nitrogène sur la cinquième position. Un jeu de nouvelles valeurs des paramètres est usé qu'on détermine en tenant compte spécialement de leur dépendance de la distribution des charges atomiques.

La distribution de charge obtenue pour la ferroporphyrine semble être raisonnable. Le fait que la position de la bande Soret est insensitive contre le sixième ligand, peut être compris à l'aide des énergies des orbitales calculées.

La difficulté de trouver une distribution de charge raisonnable pour la ferriporphyrine est discutée.

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1. Introduction

One of the most interesting chemical properties of *Fe*-porphyrin complexes is the existence of "high-spin" and "low-spin" states. For example, the number of unpaired spins in HbH_2O and HiH_2O is 4 and 5 respectively, while that in HbO_2 and $HiOH^-$ is 0 and 1 respectively.

Another interesting feature is their spectra. All these complexes show an extremely strong band, called the Soret band, at 390 — 430 mμ. The position of the peak does not change very much for HbH_2O, HbO_2 and even for metal-free porphins.

The complexes are known to play very important roles in oxidative and reductive reactions in biological systems. It has been pointed out that this redox power is closely related to the orbital energies of the highest occupied and the lowest unoccupied molecular orbitals [*11*].

It is very difficult to give a theoretical interpretation of these phenomena from first principles. And it is even more difficult to explain the oxygen-uptake power of haemoglobin. However, it is clear that one of the most fundamental pieces of knowledge about this molecule is its electronic structure.

We use the simple Hückel method in this work not because it is adequate for our purposes, but because it is simple enough to be easily applied to complicated systems such as the iron-porphyrin complexes.

The simple Hückel method was first applied to the iron-porphyrin complexes by PULLMAN, SPANJAARD and BERTHIER [*12*, *13*]. Their calculations are extended in this work to include (a) the effect of a dipole or a point charge placed at the sixth coordination position, and (b) the effect of a nitrogen atom placed at the fifth coordination position. We also introduce new parameter values, whose estimation is made by directing special attention to their dependence on the charge distribution among the atoms.

In PULLMAN and others' work [*12*, *13*] it was assumed that in the high-spin complexes the 3 *d* electrons of the iron atom do not participate in the bonding between *Fe* and the porphin ring, while in the low-spin complexes, they do. The calculated molecular orbital energies differed considerably for these two types of complexes. The work, therefore, suggested that when a complex changes its spin state, there are drastic changes both in the character and in the energy of the molecular orbitals involving the 3 *d* orbitals. This may well be true, but the specific assumption mentioned above is rather artificial. Here we lift this assumption. Changes in molecular orbitals will be brought about through the dependence of the parameters on the charge distributions which are different for the high- and low-spin state.

2. The Model

All the peripheral substituents of the porphyrin ring are neglected so that the system under consideration contains 20 *C*'s, 4 *N*'s, and one *Fe* in the molecular plane (cf. Fig. 1), and one *N* under the *Fe* atom — this will be denoted hereafter N'. The assumed distances between the atoms are the following: $Fe - N$ 1.80 Å, $N - C'$ 1.38 Å, $C' - C$ and $C' - C''$ 1.40 Å, $Fe - N'$ 2.10 Å. The bond angle $< C'NC'$ of 108° is also assumed. These figures are fairly close to the observed ones for nickel ethioporphyrin [*1*] and myoglobin [*5*].

The ligand at the sixth coordination position apparently determines the spin state of the system. We replace this ligand by a dipole or a point charge and investigate its effect. A dipole with its axis perpendicular to the molecular plane or a point charge is thus placed above the *Fe* atom at the distance of 2.06 Å. The system has the symmetry C_{4v}.

The system is so large that only the bonds between *Fe* and four surrounding *N*'s are considered for the σ part; also the possible π bonding between *Fe* and *N'* is neglected. With all these simplifications, there are 42 electrons (one each from *C*, three each from *N*, 8 from *Fe* and 2 from *N'*) for the ferrous complex and 41 electrons for the ferric complex. To describe them, we use the following 38 atomic orbitals: one 2 $p\pi$ of each *C*, one 2 $p\pi$ and one sp^2 hybridized σ of each *N*, five 3 *d*, one 4 *s* and three 4 *p* of *Fe* and one sp^2 hybridized orbital of *N'* pointing to *Fe*.

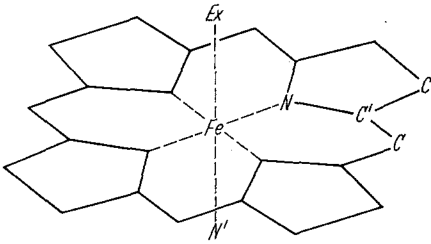

Fig. 1. The skeleton of iron-porphyrin. Ex indicates the position of a dipole or a point charge

3. Method of Calculation

Our model has the symmetry of C_{4v} but if we disregard the point charge or dipole at the sixth coordination position and the *N'* atom at the fifth coordination position, the symmetry is D_{4h}. It is more convenient to name some of the molecular orbitals after the irreducible representations of the group D_{4h}. The names of the irreducible representations of the groups D_{4h} and C_{4v} and the relation between them can be seen in Tab. 1.

Table 1. *Irreducible representations of the groups D_{4h} and C_{4v}*

D_{4h}	$\underbrace{A_{1g}\ A_{2u}}$	$\underbrace{B_{1g}\ B_{2u}}$	$\underbrace{A_{2g}\ A_{1u}}$	$\underbrace{B_{2g}\ B_{1u}}$	$\underbrace{E_g\ E_u}$
C_{4v}	A_1	B_1	A_2	B_2	E

Putting aside the orbital of *N'*, we form linear combinations of the 37 atomic orbitals available. The linear combinations form bases for the irreducible representations of D_{4h}. These are called symmetry orbitals and explicit forms are given in Appendix I. The irreducible representations which appear and the number of linearly independent functions belonging to these follow: A_{1u} (2), A_{2u} (5), B_{1u} (3), B_{2u} (3), E_g (7), A_{1g} (3), B_{1g} (2), B_{2g} (1) and E_u (2).

When the atom *N'* and/or a point charge or a point dipole are considered, we have A_1 (9) instead of A_{1g} (3) and A_{2u} (5) and an sp^2 hybrid of *N'* pointing to the *Fe* atom. Off-diagonal elements between B_{1g} and B_{2u}, B_{2g} and B_{1u}, E_g and E_u will be zero under the approximations employed in the present calculations. (This will be explained in the next section.) Even in the general case we shall keep the symmetry notation of D_{4h} except for A_{1g} and A_{2u}.

Thus we have expressed the symmetry orbitals in terms of atomic orbitals. In order to know how much these symmetry orbitals mix to give molecular orbitals, we have to set up and solve the secular equations.

Integrals which appear in the secular equations can be reduced to those involving atomic orbitals. In the simple Hückel theory, they are the Coulomb integrals α, the resonance integrals β and the overlap integrals S. They are defined as

$$\alpha_p = \int \chi_p^* (1)\, \boldsymbol{H}_{eff} (1)\, \chi_p (1)\, d\tau_1, \tag{3.1}$$

$$\beta_{pq} = \int \chi_p^* (1)\, \boldsymbol{H}_{eff} (1)\, \chi_q (1)\, d\tau_1, \tag{3.2}$$

$$S_{pq} = \int \chi_p^* (1)\, \chi_q (1)\, d\tau_1, \tag{3.3}$$

where χ_p and χ_q are the atomic orbitals. The total Hamiltonian is assumed to be a sum of one-electron effective Hamiltonians $\boldsymbol{H}_{eff}$:

$$\boldsymbol{H} = \sum_i \boldsymbol{H}_{eff} (i). \tag{3.4}$$

The one-electron effective Hamiltonian $\boldsymbol{H}_{eff}\,(i)$ may be considered to have the following form:

$$\boldsymbol{H}_{eff} (i) = -\frac{1}{2} \Delta_i + \sum_a \boldsymbol{v}_a (i), \tag{3.5}$$

where $\boldsymbol{v}_a$ is the effective potential due to atom a.

The Coulomb integral α_p for an atomic orbital χ_p centred on the atom a can be split into two parts, α_p' and α_p'':

$$\alpha_p = \int \chi_p^* \left(-\frac{1}{2} \Delta + \boldsymbol{v}_a \right) \chi_p \, d\tau + \sum_{b \neq a} \int \chi_p^* \, \boldsymbol{v}_b \, \chi_p \, d\tau = \alpha_p' + \alpha_p'' . \tag{3.6}$$

The first term α_p' may be equated to a suitable valence-state ionization potential for occupied atomic orbitals (e.g. 2 $p\pi$ of C, N and 3 d of Fe^{++}) or to an electron affinity for empty atomic orbitals (e.g. 4 s and 4 p of Fe^{++}). The second term α_p'' is neglected unless atom b has an appreciable formal charge. When the atom b does have a formal charge, Z_b, the term is evaluated by assuming that a point charge, Z_b, is situated at the nucleus b.

The resonance integrals β_{pq} are estimated by a slightly modified Wolfsberg-Helmholz approximation [*15*], namely

$$\beta_{pq} = S_{pq} \left(K \frac{\alpha_p' + \alpha_q'}{2} + \frac{\alpha_p'' + \alpha_q''}{2} \right) , \tag{3.7}$$

where $K = 2$ for π bonds and 1.67 for σ bonds. The basis of this approximation is not quite clear but it is certainly most convenient in reducing the number of unknown parameters. The modification we made consists in separating off the electrostatic part α_p'' from α_p'. This is made in order to fulfill the requirement that the resulting orbital-energy differences should not change, if we change the zero point of the energy by adding a constant potential to the Hamiltonian.

The values of the overlap integrals can be evaluated without too much difficulty, at least in principle.

It should be noted that all the parameters α, β and S depend on the formal charge which the atoms carry. This necessitates the use of the method of trial and error which goes as follows. We first assume a charge distribution and determine the parameters. Then we obtain the molecular orbitals and orbital energies, and thus we are led to a plausible electron configuration. Analyzing the wave function of this electron configuration, we obtain a resulting charge distribution. If this is close to the starting charge distribution, we can stop there. If the resulting electron distribution differs from the starting one, we have to start again assuming a more appropriate charge distribution. This is a requirement of self-consistency in charge distribution which seems to be quite important in dealing with very hetero-polar systems like metal-porphyrine complexes.

The potentials due to a point charge (charge Ze) and a dipole (moment μ with the axis on the z axis) placed at the distance R from the origin can be expressed, respectively, in the polar coordinates as follows:

$$\boldsymbol{V} = \sum_{k=0}^{\infty} P_k (\cos\vartheta) \frac{Ze}{R} \begin{cases} (r/R)^k, & r < R, \\ (R/r)^{k+1}, & r > R, \end{cases} \tag{3.8}$$

$$\boldsymbol{V} = \sum_{k=0}^{\infty} P_k (\cos\vartheta) \frac{\mu}{R^2} \begin{cases} -(k+1)\,(r/R)^k, & r < R, \\ k\,(R/r)^{k+1}, & r > R. \end{cases} \tag{3.9}$$

In calculating matrix elements of these potentials with respect to the s-, p- and d-type atomic orbitals, the integrals can be carried out over the angular parts easily and the resulting expressions are listed in Appendix II.

4. Values of the Parameters for Ferrous Complexes

As was explained in the previous section, our parameter values depend on the charge distribution we assume.

The choice of parameters by Spanjaard and Berthier [*13*] indicated that they started from a model in which all the atoms are neutral. The resulting formal-charge distributions were $Fe^{3.5+}$ porphin $^{3.5-}$ and $Fe^{1.5+}$ porphin $^{1.5-}$ for low- and high-spin ferrous complexes respectively. In view of these results, we start with a model in which the formal-charge distribution is $Fe^{2.0+}$ $N^{0.5-}$, all carbon atoms being considered as neutral.

4.1. Valence-state ionization potential and electron affinity

The first term α_p' of the parameter α [cf. (3.6)] is equated to a suitable valence-state ionization potential for occupied atomic orbitals or to an electron affinity for unoccupied atomic orbitals. The values of these used in the present calculation are collected in Tab. 2.

4.2. Contribution to α from the other atoms carrying a formal charge

The second term α_p'' is estimated by assuming the point charges Ze ($Z = +2$ for Fe, and -0.5 for each of four N) are located on the nuclei. For C, for example, we have

$$\alpha_C'' = 2 \int \frac{|2\,p\,\pi_C(\mathfrak{r})|^2}{|\mathfrak{r} - \mathfrak{R}_{Fe}|}\,d\tau - \int \frac{|2\,p\,\pi_C(\mathfrak{r})|^2}{|\mathfrak{r} - \mathfrak{R}_N|}\,d\tau - \int \frac{|2\,p\,\pi_C(\mathfrak{r})|^2}{|\mathfrak{r} - \mathfrak{R}'_N|}\,d\tau \tag{4.1}$$

where $\mathfrak{R}_N$ and $\mathfrak{R}'_N$ are the position vectors of the nitrogen nuclei nearer and farther to the C atom under consideration, respectively. Each term in the right hand side of (4.1) is a so-called nuclear attraction integral.

For the atomic orbitals used in estimating these integrals, for example $2\,p\,\pi_C$ in (4.1), we take the Slater orbitals. The orbital exponents δ are assumed as follows:

$$\begin{aligned} \delta\,(N) &= 1.95, \\ \delta\,(C) &= 1.625, \\ \delta\,(Fe\,3\,d) &= 2.08, \\ \delta\,(Fe\,4\,s) &= \delta\,(Fe\,4\,p) = 1.01. \end{aligned} \tag{4.2}$$

Table 2. *Valence-state ionization potentials and electron affinities* (*in* eV)

Ionization potential I			Electron affinity A		
Atom	Orbital	I	Atom	Orbital	A
C	$2\,p\pi$	11.42 *	Fe^{2+}	$4\,s$	16.18***
N'	$2\,p\pi$	14.26 **	Fe^{2+}	$4\,p$	11.41***
N'	σ	18.67 **			
$N^{0.5-}$	$2\,p\pi$	7.79 **			
$N^{0.5-}$	σ	12.08 **			
Fe^{2+}	$3\,d$	30.65***			

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* The valence state is assumed to be the tetra-valent sp^3 state. The value is taken from the paper by H. O. Pritchard and H. A. Skinner, Chem. Rev. 55, 745 (1955).

** For nitrogen, the valence state is assumed to be a mixture of $V_3\, s^2\, p^3$ with factor 1/3 and $V_3\, sp^4$ with factor 2/3. In estimating I for the sp^2 hybridized σ, I of $2\,s$ for $V_3\, s^2\, p^3$ is assumed to be the same as that for $V_3\, sp^4$. Numerical values are taken from Pritchard and Skinner's paper.

For $N^{0.5-}$, an additional assumption is necessary. It is observed that the ionization potential of $2\,p$ electrons for N^-, N and N^+ is a linear function of the ionicity of the atom. Thus it is assumed that

$$I(N^{0.5-}) = \frac{1}{2}\,[I\,(N) + I\,(N^-)].$$

*** $I\,(Fe^{2+}\,3\,d) = E\,(3\,d^5) - E\,(3\,d^6)$,
$A\,(Fe^{2+}\,4\,s) = E\,(3\,d^6) - E\,(3\,d^6\,4\,s)$,
$A\,(Fe^{2+}\,4\,p) = E\,(3\,d^6) - E\,(3\,d^6\,4\,p)$.

Atomic term values are found in the book by C. E. Moore: "Atomic Energy Levels", National Bureau of Standards, Vol. II (1952).

For N and C, the values of the nuclear attraction integrals are obtained by interpolation of the table by Kotani et al. [*6*]. To calculate the nuclear attraction integrals which involve Fe atomic orbitals, the formulae given in Appendix II are used, where the values of the incomplete Γ function are interpolated from Pearson's table [*9*].

4.3. *Values of Coulomb integrals* α

The values of α_p', α_p'' as well as $\alpha_p = \alpha_p' + \alpha_p''$ are listed in Tab. 3.

Table 3. *The parameter* α *for the model* $Fe^{2+}\,N^{0.5-}$ (*in* eV)

Atom	Orbital	α'	α''	$\alpha = \alpha' + \alpha''$
$N^{0.5-}$	π	-7.79	-7.92	-15.71
$N^{0.5-}$	σ	-12.08	-11.72	-23.80
C'	π	-11.42	0.91	-10.51
C''	π	-11.42	0.44	-10.98
C	π	-11.42	0.28	-11.14
Fe^{2+}	$3\,d$	-30.65	15.80	-14.85
Fe^{2+}	$4\,s$	-16.18	13.12	-3.06
Fe^{2+}	$4\,p$	-11.41	13.12	1.71
N'		-18.67	-4.99	-23.66

4.4. *Overlap integrals*

The values of the overlap integrals (except those involving the N' orbital) were calculated by Spanjaard and Berthier [*13*] using Slater orbitals. Those involving the N' orbital, we have calculated using the same AO's.

We adopt SPANJAARD and BERTHIER's values for the overlap integrals between C and C, and C and N. However, their values for the overlap integrals between Fe and N are modified by multiplying them by the constant factor 0.75. This factor is the ratio a/b. a is the overlap integral between the Fe^{2+} Hartree-Fock $3\,d\sigma$ [14] and the N sp^2 hybridized Slater orbital evaluated along the internuclear axis. b is the same integral between the Fe Slater $3\,d\sigma$ orbital and the N sp^2 hybridized Slater orbital. This procedure is introduced to obtain approximate overlap integrals between Fe^{2+} and N, but is certainly a very crude one. However, it is hoped that the results of the calculations are not so sensitive to the values of theoverlap integrals. The values used are given in Tab. 4.

Table 4. *Values of overlap integrals*

$(C\,2\,p\pi \mid C\,2\,p\pi)$	0.2444
$(C\,2\,p\pi \mid N\,2\,p\pi)$	0.1930
$(Fe\,3\,d\pi \mid N\,2\,p\pi)$	0.1040
$(Fe\,4\,p\pi \mid N\,2\,p\pi)$	0.1297
$(Fe\,3\,d_{z^2} \mid N\,2\,p\sigma)$	-0.1133
$(Fe\,3\,d_{x^2-y^2} \mid N\,2\,p\sigma)$	0.1963
$(Fe\,4\,s \mid N\,2\,p\sigma)$	0.2129
$(Fe\,4\,p\sigma \mid N\,2\,p\sigma)$	0.2939
$(Fe\,3\,d_{z^2} \mid N')$	0.1560
$(Fe\,4\,s \mid N')$	0.2025
$(Fe\,4\,p \mid N')$	0.2976

4.5. *Resonance integrals*

Resonance integrals between non-neighbours are neglected. Those between neighbours are calculated from Coulomb and overlap integrals by using the formula (3.7).

4.6. *Effects of a point charge or a dipole*

The cases in which a dipole of either 0.5 or 1.0 a. u., or a point charge of 1.0 a. u. is placed at the sixth coordination position are investigated.

The effects of these static fields on the Coulomb integrals (α'') are calculated by the formulae given in Appendix II. The resonance integrals are changed accordingly [cf. (3.7)]. However, direct contributions of the static fields to the resonance integrals are neglected.

In the non-oxygenated condition of haemoglobin, the water molecule is attached at the sixth coordination position, while in the oxygenated condition, the oxygen molecule is attached there.

The permanent dipole of the water molecule is known to be 0.728 a.u. (=1.85 Debye) by experiment. Induced dipoles of the water and oxygen molecules placed at a distance of 2.01 Å from Fe are estimated to be 0.54 and 0.55 a.u., respectively. In this estimation, we must, of course, take into account the effect from the negative formal charge of 0.5 on each nitrogen atom.

Assume that we can neglect the polarization of the surroundings although this is very doubtful. Then the main part of the electrostatic interaction between the haem and the oxygen (or water) molecule may be represented by placing a dipole of 0.5 (1.0) a.u. at the sixth coordination position.

5. Results and Discussion for Free Porphin and Ferrous Porphyrin

5.1. *Orbital energy and atomic population analysis*

Orbital energies are tabulated in Tab. 5, and the significant energy levels are illustrated in Fig. 2. Because a comparison of the absolute energies of cases having different external fields has little meaning, the orbital energy differences are recorded with respect to the $1\,a_{1u}$ orbital, as shown in the figure.

For free porphin, we choose a model in which the two protons inside the porphin ring are completely screened by σ electrons. The four nitrogens contribute

6 π-electrons to the system. 26 π-electrons occupy the lowest 13 molecular orbitals as follows:

$$(1\,a_{2u})^2\,(1\,e_g)^4\,(1\,b_{2u})^2\,(1\,b_{1u})^2\,(2\,e_g)^4\,(2\,a_{2u})^2\,(2\,b_{2u})^2\,(3\,e_g)^4\,(1\,a_{1u})^2\,(3\,a_{2u})^2.$$

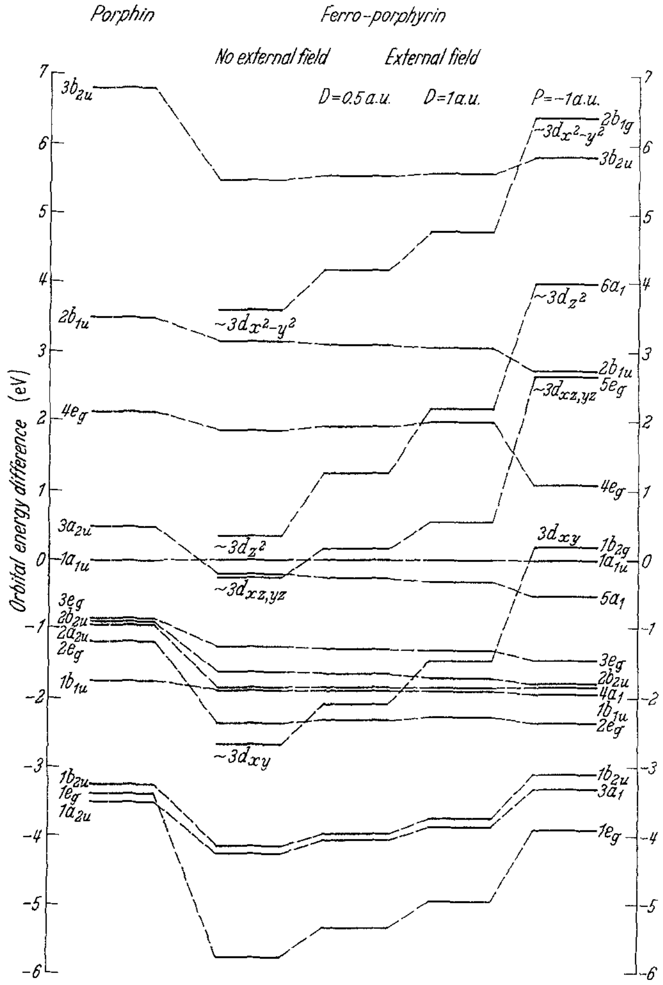

Fig. 2. Energy levels of porphin and ferro-porphyrin

If we apply MULLIKEN's population analysis [7] to the wave function representing this electronic configuration, we obtain the following charge distribution:

$$N^{1.60}\ C^{0.95}\ C'^{0.95}\ C''^{1.03}.$$

The charge distribution suggests that the nitrogen atoms attract electrons from the carbon atoms but the degree is very small, and the whole molecule is almost homo-polar.

For ferrous porphyrin, the degree of mixing of the iron orbitals in the molecular orbitals is of some interest. In Tab. 6, the atomic populations are given for the molecular orbitals which have more than 10% *Fe* 3 *d* population.

Table 5. *Orbital energies* (*in* eV)

Porphin		Iron-porphyrin							
		No external field		$D = 0.5$ a.u.		$D = 1.0$ a.u.		$P = -1.0$ a.u.	
		$9\,a_1$	7.27	$9\,a_1$	7.73	$9\,a_1$	8.22	$9\,a_1$	14.76
		$2\,e_u$	5.17	$2\,e_u$	5.54	$2\,e_u$	5.90	$2\,e_u$	10.62
		$8\,a_1$	2.49	$8\,a_1$	2.93	$8\,a_1$	3.37	$8\,a_1$	8.88
		$3\,b_{1u}$	0.11	$3\,b_{1u}$	0.25	$3\,b_{1u}$	0.39	$3\,b_{1u}$	3.75
		$7\,e_g$	-0.21	$7\,e_g$	-0.05	$7\,e_g$	0.11	$7\,e_g$	3.57
$3\,b_{1u}$	-0.50	$7\,a_1$	-1.51	$7\,a_1$	-1.30	$7\,a_1$	-1.09	$7\,a_1$	2.66
$6\,e_g$	-0.59	$2\,a_{1u}$	-3.37	$2\,a_{1u}$	-3.25	$2\,a_{1u}$	-3.12	$2\,a_{1u}$	0.10
$4\,a_{2u}$	-0.71	$6\,e_g$	-4.62	$6\,e_g$	-4.44	$6\,e_g$	-4.25	$6\,e_g$	-0.71
$2\,a_{1u}$	-3.95	$3\,b_{2u}$	-6.63	$3\,b_{2u}$	-6.43	$3\,b_{2u}$	-6.22	$2\,b_{1g}$	-1.94
$5\,e_g$	-4.89	$2\,b_{1g}$	-8.48	$2\,b_{1g}$	-7.76	$2\,b_{1g}$	-7.04	$3\,b_{2u}$	-2.52
$3\,b_{2u}$	-6.14	$2\,b_{1u}$	-8.97	$2\,b_{1u}$	-8.86	$2\,b_{1u}$	-8.74	$6\,a_1$	-4.35
$2\,b_{1u}$	-9.39	$5\,e_g$	-10.29	$5\,e_g$	-10.07	$6\,a_1$	-9.60	$2\,b_{1u}$	-5.61
$4\,e_g$	-10.79	$6\,a_1$	-11.80	$6\,a_1$	-10.70	$5\,e_g$	-9.80	$5\,e_g$	-5.67
$3\,a_{2u}$	-12.47	$1\,a_{1u}$	-12.14	$4\,e_g$	-11.83	$4\,e_g$	-11.27	$4\,e_g$	-7.26
$1\,a_{1u}$	-12.92	$5\,a_1$	-12.36	$1\,a_{1u}$	-11.98	$1\,a_{1u}$	-11.81	$1\,b_{2g}$	-8.14
$3\,e_g$	-13.82	$4\,e_g$	-12.40	$5\,a_1$	-12.23	$5\,a_1$	-12.10	$1\,a_{1u}$	-8.35
$2\,b_{2u}$	-13.84	$3\,e_g$	-13.39	$3\,e_g$	-13.25	$3\,e_g$	-13.11	$5\,a_1$	-8.79
$2\,a_{2u}$	-13.86	$2\,b_{2u}$	-13.76	$2\,b_{2u}$	-13.63	$1\,b_{2g}$	-13.28	$3\,e_g$	-9.80
$2\,e_g$	-14.12	$4\,a_1$	-14.02	$4\,a_1$	-13.85	$2\,b_{2u}$	-13.49	$2\,b_{2u}$	-10.20
$1\,b_{1u}$	-14.66	$1\,b_{1u}$	-14.05	$1\,b_{1u}$	-13.89	$4\,a_1$	-13.68	$4\,a_1$	-10.22
$1\,b_{2u}$	-16.16	$2\,e_g$	-14.50	$1\,b_{2g}$	-14.07	$1\,b_{1u}$	-13.73	$1\,b_{1u}$	-10.30
$1\,e_g$	-16.30	$1\,b_{2g}$	-14.85	$2\,e_g$	-14.28	$2\,e_g$	-14.08	$2\,e_g$	-10.69
$1\,a_{2u}$	-16.40	$1\,b_{2u}$	-16.30	$1\,b_{2u}$	-15.93	$1\,b_{2u}$	-15.56	$1\,b_{2u}$	-11.44
$(1\,e_u)$	-18.75	$3\,a_1$	-16.37	$3\,a_1$	-16.02	$3\,a_1$	-15.67	$3\,a_1$	-11.67
$(1\,a_{1g})$		$1\,e_g$	-17.91	$1\,e_g$	-17.31	$1\,e_g$	-16.75	$1\,e_g$	-12.23
$(1\,b_{1g})$		$2\,a_1$	-23.73	$2\,a_1$	-23.42	$2\,a_1$	-23.09	$1\,e_u$	-18.28
		$1\,e_u$	-23.97	$1\,e_u$	-23.56	$1\,e_u$	-23.14	$2\,a_1$	-18.41
		$1\,a_1$	-24.54	$1\,a_1$	-24.09	$1\,a_1$	-23.68	$1\,b_{1g}$	-19.09
		$1\,b_{1g}$	-24.95	$1\,b_{1g}$	-24.47	$1\,b_{1g}$	-24.00	$1\,a_1$	-20.34

The molecular orbitals which have the largest contribution of *Fe* 3 *d* atomic orbitals are

$$2\,b_{1g} \sim 3\,d_{x^2-y^2},$$
$$6\,a_1 \sim 3\,d_{z^2},$$
$$4\,e_g \sim 3\,d_{xz},\ 3\,d_{yz},$$

and

$$1\,b_{2g} \sim 3\,d_{xy}.$$

They are indicated so in Fig. 2. There is one exception. In the case of the point charge field, 5 e_g instead of 4 e_g has the largest 3 d_{xz}, 3 d_{yz} character.

The order of the orbital energies ε of these orbitals, namely

$$\varepsilon\,(1\,b_{2g}) < \varepsilon\,(4\,e_g) < \varepsilon\,(6\,a_1) < \varepsilon\,(2\,b_{1g}),$$

is in agreement with the order indicated by electron spin resonance experiment on ferrite complexes [*2*]. However, the calculated difference between these levels is much too big in comparison with the values obtained by analysis of observed g tensor of ferrihaemoglobin azide [*4*]. For example, the calculated value of $\varepsilon\,(4\,e_g) - \varepsilon\,(1\,b_{2g})$ is 2.5 eV while GRIFFITH's estimate is only about 0.2 eV.

It is apparent in Figure 2 that the orbital energies of the four orbitals of strong *Fe* character are more sensitive to the external field strength than the energy of the other molecular orbitals. This is quite natural since the *Fe* atom is the nearest to the source of the external field. However, both the energy differences between these levels and the percentage of *Fe* AO's in the orbitals do not change very much when the dipole is increased from 0 to 1 a.u. (about 2.5 Debye) or even for the case when a point charge increases from 0 to 1 a.u.

Table 6. *Atomic population for some molecular orbitals*

MO \ Atom	*Fe* (3 *d*)	*Fe* (4 *s*, 4 *p*)	4 *N* σ	4 *N* π	4 *C*	8 *C′*	8 *C″*	*N′*
(I) No external field								
$2\,b_{1g}$	0.821	—	0.179	—	—	—	—	—
$6\,a_1$	0.848	0.029	0.069	0.000	0.001	0.000	0.000	0.053
$4\,e_g$	0.429	—	—	0.247	0.001	0.090	0.233	—
$2\,e_g$	0.114	—	—	0.004	0.177	0.334	0.371	—
$1\,b_{2g}$	1.000	—	—	—	—	—	—	—
$1\,e_g$	0.375	—	—	0.579	0.001	0.044	0.001	—
$1\,a_1$	0.127	—0.008	0.573	0.000	0.000	0.000	0.000	0.307
$1\,b_{1g}$	0.179	—	0.821	—	—	—	—	—
(II) Dipolar field of 0.5 a.u.								
$2\,b_{1g}$	0.830	—	0.170	—	—	—	—	—
$6\,a_1$	0.862	0.032	0.060	0.000	0.000	0.000	0.000	0.045
$4\,e_g$	0.462	—	—	0.190	0.001	0.144	0.203	—
$1\,b_{2g}$	1.000	—	—	—	—	—	—	—
$1\,e_g$	0.321	—	—	0.616	0.002	0.058	0.003	—
$1\,a_1$	0.111	—0.007	0.477	0.000	0.000	0.000	0.000	0.420
$1\,b_{1g}$	0.170	—	0.830	—	—	—	—	—
(III) Dipolar field of 1.0 a.u.								
$2\,b_{1g}$	0.838	—	0.162	—	—	—	—	—
$6\,a_1$	0.873	0.035	0.052	0.000	0.000	0.000	0.000	0.039
$5\,e_g$	0.174	—	—	0.121	0.285	0.153	0.266	—
$4\,e_g$	0.442	—	—	0.120	0.013	0.213	0.211	—
$1\,b_{2g}$	1.000	—	—	—	—	—	—	—
$1\,e_g$	0.272	—	—	0.646	0.004	0.074	0.005	—
$1\,b_{1g}$	0.162	—	0.838	—	—	—	—	—
(IV) Point charge of —1.0 a.u.								
$2\,b_{1g}$	0.844	—	0.156	—	—	—	—	—
$6\,a_1$	0.890	0.033	0.049	0.000	0.000	0.000	0.000	0.028
$5\,e_g$	0.522	—	—	0.156	0.154	0.035	0.133	—
$4\,e_g$	0.165	—	—	0.004	0.136	0.362	0.334	—
$1\,b_{2g}$	1.000	—	—	—	—	—	—	—
$1\,e_g$	0.177	—	—	0.627	0.016	0.141	0.038	—
$1\,b_{1g}$	0.156	—	0.844	—	—	—	—	—

5.2. *Electronic configuration and charge distribution of the low-spin state*

For the low-spin state of ferro-porphyrin (with $S = 0$), the electrons occupy the lowest 21 molecular orbitals as follows:

$$(1\,b_{1g})^2\,(1\,a_1)^2\,(1\,e_u)^4\,(2\,a_1)^2\,(1\,e_g)^4\,(3\,a_1)^2\,(1\,b_{2u})^2$$
$$(2\,e_g)^4\,(1\,b_{2g})^2\,(1\,b_{1u})^2\,(4\,a_1)^2\,(2\,b_{2u})^2\,(3\,e_g)^4\,(5\,a_1)^2$$
$$(1\,a_{1u})^2\,(4\,e_g)^4.$$

This configuration yields, by the population analysis [7], the charge distributions which are given in Tab. 7. These, except for the point charge case, are reasonably close to our starting assumption about the formal charge, namely $Fe^{2.0+}\,N^{0.5-}$. In the case of the point charge of -1 a.u., its effect is so big that electrons are repelled from the central *Fe* atom to the peripheral carbon atoms, and the formal charge on the *Fe* atom is as great as $+4.0$. As no stable ferrous complex with a negative ion at the sixth coordination position is known, an effort to make the calculation consistent in the charge distribution is not attempted.

Table 7. *Charge distribution of ferro-porphyrin in the low-spin state. The values in parentheses are the formal charges*

	No external field	$D = 0.5$ a.u.	$D = 1.0$ a.u.	$P = -1.0$ a.u.
C''	1.03 (– 0.03)	1.05 (– 0.05)	1.07 (– 0.07)	1.20 (– 0.20)
C'	0.88 (0.12)	0.89 (0.11)	0.92 (0.08)	0.94 (0.06)
C	1.01 (– 0.01)	1.02 (– 0.02)	1.05 (– 0.05)	1.22 (– 0.22)
N	3.66 (– 0.66)	3.64 (– 0.64)	3.61 (– 0.61)	3.53 (– 0.53)
Fe	6.16 (1.84)	5.93 (2.07)	5.54 (2.46)	3.97 (4.03)
N'	1.91 (0.09)	1.92 (0.08)	1.94 (0.06)	1.97 (0.03)

5.3. Electronic configuration of the high-spin state

For the high spin state (with $S = 2$), we must have four singly-occupied orbitals. The sum of orbital energies is higher than that in the low-spin state, and the first stabilizing factor we can think of is the exchange interaction. Then the singly-occupied orbitals should be fairly localized around the *Fe* atom. The following configuration suggests itself

$$\ldots\,(1\,a_{1u})^2\,(4\,e_g)^2\,(6\,a_1)\,(2\,b_{1g}).\,^{\star}$$

The charge distributions obtained from the above configuration are given in Tab. 8. The computed charge distribution is not as close to the starting charge distribution as it was in the case of the low-spin state. We should repeat the calculation starting from a new charge distribution something like $Fe^{1.2+}\,N^{0.5-}\,C'^{0.1+}$. Then we could obtain new orbitals and their orbital energies and see how much they are different from those in the low-spin case. We have not repeated the calculation, however, because the dependence of the molecular orbitals and their energies on the spin-state is caused also by electron-electron interaction which is not explicitly taken into account in the Hückel method.

The orbital energy differences (cf. Tab. 5) $\varepsilon\,(6\,a_1) + \varepsilon\,(2\,b_{1g}) - 2\,\varepsilon\,(4\,e_g)$ are 4.5 eV, 5.2 eV and 5.9 eV for $D = 0$, 0.5, 1.0 a.u., respectively. It seems not

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[⋆] For the case of the point charge,

$$\ldots\,(1\,a_{1u})^2\,(5\,e_g)^2\,(6\,a_1)\,(2\,b_{1g})$$

would be the configuration, but we shall not discuss it because of its inconsistency in charge distribution with the starting model.

unreasonable to suppose that 4.5 — 6 eV could be gained from the electron interaction energy in going from the low-spin to the high-spin state. To settle this point, as well as to obtain better molecular orbitals, it is necessary to apply a method, such as PARISER-PARR-POPLE's [*8*, *10*], in which the Coulomb repulsion between electrons is explicitly taken into account.

It may be worth mentioning that the orbital energy difference $\varepsilon(6a_1) + \varepsilon(2b_{1g}) - 2\varepsilon(4e_g)$ is bigger when the dipolar field strength D is greater. As there is no big change in the iron AO percentages of the three molecular orbitals $6a_1$, $2b_{1g}$, and $4e_g$ when D increases from 0 to 1 a.u. (see Tab. 6), there should not be much change in the electron interaction energy. It looks, therefore, like the high-spin state being more unstable when the dipolar field is greater. However, ferrohaemoglobin (with the water molecule as the sixth ligand) is known to be in the high-spin state while oxygenated haemoglobin (with the oxygen molecule, which has only an induced dipole*, as the ligand) is in the low-spin state. Thus the computed result contradicts the experimentally known fact. This might suggest that there is a weak chemical bond between O_2 and haem and that the interaction is not essentially electrostatic.

Table 8. *Charge distribution of ferro-porphyrin in the high-spin state. The values in parentheses are the formal charges*

	No external field	$D = 0.5$ a.u.	$D = 1.0$ a.u.
C''	0.97 (0.03)	1.00 (0.00)	1.02 (– 0.02)
C'	0.86 (0.14)	0.86 (0.14)	0.86 (0.14)
C	1.01 (– 0.01)	1.02 (– 0.02)	1.04 (– 0.04)
N	3.60 (– 0.60)	3.60 (– 0.60)	3.60 (– 0.60)
Fe	7.00 (1.00)	6.73 (1.27)	6.40 (1.60)
N'	1.96 (0.04)	1.97 (0.03)	1.98 (0.02)

5.4. Spectrum

Iron-porphyrin complexes show either one or two bands of moderate intensity in their visible spectra in the region 6300 Å (~ 2.0 eV) to 5000 Å (~ 2.5 eV) and an extremely strong band, called the Soret band, at about 4000 Å (~ 3.0 eV). Thus HbO_2, HbH_2O and even metal-free porphyrin have Soret peaks around 4000 Å.

The simple Hückel method employed here is known to be not reliable in discussing spectra. Nevertheless we try to see what we can say about the spectra from the results of the present calculations.

We assume that the Soret band for metal-free porphin is assigned to the transitions from the ground state to two excited configurations as follows: in one an electron is excited from $3a_{2u}$ to $4e_g$, in the other from $1a_{1u}$ to $4e_g$ [*3*]. For iron-porphyrin, then, it is natural to assign the Soret band to the transitions $5a_1 \rightarrow 5e_g$ and $1a_{1u} \rightarrow 5e_g$, since $5a_1$, $1a_{1u}$ and $5e_g$ correspond to $3a_{2u}$, $1a_{1u}$ and $4e_g$ in porphin, respectively (cf. Fig. 2).

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* The effect of a quadrupole is examined and found to be very small for a reasonable range of the strength of the quadrupole field.

The differences between the orbital energies of these two configurations $\varepsilon\,(5\,e_g) - \varepsilon\,(1\,a_{1u})$ and $\varepsilon\,(5\,e_g) - \varepsilon\,(5\,a_1)$ are listed in Tab. 9. This table shows that these orbital energy differences are insensitive to the dipolar field strength. There is a suggestion that the inter-configuration matrix element is roughly constant for all porphins [3]. If we assume this, Tab. 9 indicates that the peak of the Soret band is insensitive to the external field or the ligand at the sixth coordination position, in accordance with the experimental observation.

Table 9. $\varepsilon\,(5\,e_g) - \varepsilon\,(1\,a_{1u})$ *and* $\varepsilon\,(5\,e_g) - \varepsilon\,(5\,a_1)$ (*in* eV)

	Iron-porphyrin			Porphin	
	No external field	$D = 0.5$ a.u.	$D = 1.0$ a.u.		
$\varepsilon\,(5\,e_g) - \varepsilon\,(1\,a_{1u})$	1.85	1.91	2.01	$\varepsilon\,(4\,e_g) - \varepsilon\,(1\,a_{1u})$	2.13
$\varepsilon\,(5\,e_g) - \varepsilon\,(5\,a_1)$	2.07	2.16	2.19	$\varepsilon\,(4\,e_g) - \varepsilon\,(3\,a_{2u})$	1.68

The inter-configuration mixing matrix element of 0.42 eV was used by GOUTERMAN [3]. This value and the calculated orbital energy differences give the peak of the Soret band at about 2.5 eV ($\sim$ 4960 Å), which is too big by 0.5 eV. However, the agreement is as good as we could expect in the simple Hückel method*.

6. A Difficulty with Ferric Iron-Porphyrin

As was shown in Tab. 7, we obtained a charge distribution which is reasonably close to the starting model $Fe^{2+}\,N^{0.5-}$ for the ferrous iron-porphyrin in the low-spin state.

We have failed to obtain this consistency for the ferric iron-porphyrin. By starting from the model $Fe^{3+}\,N^{0.5-}$, all the orbitals with strong *Fe* 3 *d* character turn out to have much too low energies. The resulting formal charge on *Fe* is nearly zero. By starting from the model $Fe^{2+}\,N^{0.25-}$ instead, the orbitals of strong iron character still come out much too low.

If we regard the ferric complex as the ferrous complex minus an electron in the highest occupied orbital, we arrive at the following model:

$$N'^{0.1+}\;Fe^{2.5+}\;N^{0.6-}\;C'^{0.1+}\ \text{(an electron missing from } 4\,e_g).$$

If we speculate about the ferric complexes in the high-spin state, the above models lead to a picture in which unpaired electrons are fairly delocalized. Then the problem immediately arises; what is the stabilizing factor for the high-spin state, as the exchange interaction should be small ?

On the other hand, if we assume the unpaired electrons are localized around the *Fe* atom, we have to explain why an electron can be taken away only from the *Fe* atom (without disturbing the balance between the *Fe* atom and the porphin ring), when the ferrous complex is oxidized.

It would be extremely nice if we could find out the distribution of these unpaired electrons in the complex from some experiment, such as a double resonance experiment.

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* As the system is large and all the molecular orbitals involved in the transitions are spread over the porphin ring, we need not worry too much about a singlet-triplet splitting. The exchange integrals between these orbitals should be fairly small.

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Appendix I

Symmetry Orbitals

The co-ordinate system and the numbering of atoms in the molecular plane are shown in Fig. 3.

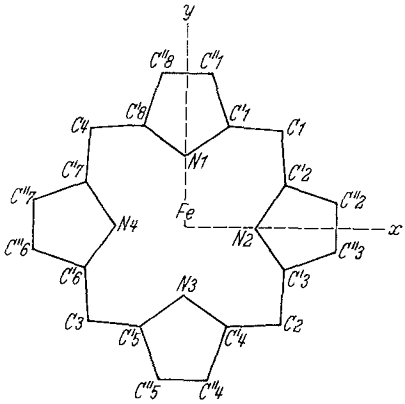

Fig. 3. The co-ordinate system and numbering of atoms

(I) *Orbitals of the π-character*

A_{1u}	C' $2\,p\pi$	$1-2+3-4+5-6+7-8$
	C'' $2\,p\pi$	$1-2+3-4+5-6+7-8$
A_{2u}	Fe $4\,pz$	
	N $2\,p\pi$	$1+2+3+4$
	C $2\,p\pi$	$1+2+3+4$
	C' $2\,p\pi$	$1+2+3+4+5+6+7+8$
	C'' $2\,p\pi$	$1+2+3+4+5+6+7+8$
B_{1u}	C $2\,p\pi$	$1-2+3-4$
	C' $2\,p\pi$	$1+2-3-4+5+6-7-8$
	C'' $2\,p\pi$	$1+2-3-4+5+6-7-8$
B_{2u}	N $2\,p\pi$	$1-2+3-4$
	C' $2\,p\pi$	$1-2-3+4+5-6-7+8$
	C'' $2\,p\pi$	$1-2-3+4+5-6-7+8$
E_g	Fe $3\,d_{xz}$, $(3\,d_{yz})$	
	N $2\,p\pi$	$2-4$, $(1-3)$
	C $2\,p\pi$	$1+2-3-4$, $(1-2-3+4)$
	C' $2\,p\pi$	$2+3-6-7$, $(1-4-5+8)$
	C' $2\,p\pi$	$1+4-5-8$, $(2-3-6+7)$
	C'' $2\,p\pi$	$2+3-6-7$, $(1-4-5+8)$
	C'' $2\,p\pi$	$1+4-5-8$, $(2-3-6+7)$.

Here C' $2\,p\pi$ $1-2+3-4+5-6+7-8$, for example, means

$$\psi\,(A_{1u}) = K\,[\,(2\,p\pi)_{C'1} - (2\,p\pi)_{C'2} + (2\,p\pi)_{C'3} - (2\,p\pi)_{C'4} + (2\,p\pi)_{C'5} - \\ - (2\,p\pi)_{C'6} + (2\,p\pi)_{C'7} - (2\,p\pi)_{C'8}\,],$$

with a suitable normalization constant K.

(II) *Orbitals of the σ-character*

A_{1g}	Fe $3\,d_{z^2}$	
	Fe $4\,s$	
	N σ	$1+2+3+4$
B_{1g}	Fe $3\,d_{x^2-y^2}$	
	N σ	$1-2+3-4$
B_{2g}	Fe $3\,d_{xy}$	
E_u	Fe $4\,px$, $(4\,py)$	
	N σ	$2-4$, $(1-3)$

Appendix II

Matrix elements of the potentials due to a point charge and a dipole

We denote the radial part of an atomic orbital by $R_{nl}\,(r)$, and introduce the following integrals:

$$[k]_{ll'} = \frac{Ze}{R}\left(\int\limits_0^R R_{nl}\,R_{n'l'}\,(r/R)^k\,r^2\,dr + \int\limits_R^\infty R_{nl}\,R_{n'l'}\,(R/r)^{k+1}\,r^2\,dr\right) \qquad \text{(A 1)}$$

for the point charge case,

$$[k]_{ll'} = \frac{\mu}{R^2}\left(-(k+1)\int\limits_0^R R_{nl}\, R_{n'l'}\, (r/R)^k\, r^2\, dr + k\int\limits_R^\infty R_{nl}\, R_{n'l'}\, (R/r)^{k+1}\, r^2\, dr\right) \qquad \text{(A 2)}$$

for the dipole case.

By using them, the matrix elements can be expressed as follows:

$$(s \mid V \mid s) = [0]_{ss},$$

$$(z \mid V \mid z) = [0]_{pp} + \frac{2}{5}[2]_{pp},$$

$$(x \mid V \mid x) = (y \mid V \mid y) = [0]_{pp} - \frac{1}{5}[2]_{pp},$$

$$(z^2 \mid V \mid z^2) = [0]_{dd} + \frac{2}{7}[2]_{dd} + \frac{6}{21}[4]_{dd},$$

$$(x^2 - y^2 \mid V \mid x^2 - y^2) = (xy \mid V \mid xy) = [0]_{dd} - \frac{2}{7}[2]_{dd} + \frac{1}{21}[4]_{dd},$$

$$(yz \mid V \mid yz) = (zx \mid V \mid zx) = [0]_{dd} + \frac{1}{7}[2]_{dd} - \frac{4}{21}[4]_{dd},$$

$$(s \mid V \mid z^2) = \frac{1}{\sqrt{5}}[2]_{sd},$$

$$(s \mid V \mid z) = \frac{1}{\sqrt{3}}[1]_{sp},$$

$$(z \mid V \mid z^2) = \frac{2}{\sqrt{15}}[1]_{pd} + \frac{9}{7\sqrt{15}}[3]_{pd},$$

$$(x \mid V \mid zx) = (y \mid V \mid zy) = \frac{1}{\sqrt{5}}[1]_{pd} - \frac{3}{7\sqrt{5}}[3]_{pd}.$$

The integrals $[k]_{ll'}$ can be expressed in terms of elementary functions when the atomic orbitals involved are Slater functions and their principal quantum numbers are integers. When the principal quantum number is not an integer (e.g. for 4 s and 4 p), the integrals can be expressed in terms of incomplete gamma functions.

Literature

[1] Crute, M. B.: Acta cryst. **12**, 24 (1959).
[2] Gibson, J. F., D. J. E. Ingram and D. Schonland: Disc. Faraday Soc. **26**, 72 (1958).
[3] Gouterman, M.: J. chem. Physics **30**, 1139 (1959).
[4] Griffith, J. S.: Nature **180**, 30 (1957).
[5] Kendrew, J. C., R. E. Dickerson, B. E. Strandberg, R. G. Hart, D. R. Davies, D. C. Phillips and V. C. Shore: Nature **185**, 422 (1960).
[6] Kotani, M., A. Amemiya, E. Ishiguro and K. Kimura: Table of Molecular Integrals. Tokyo: Maruzen Co. 1955.
[7] Mulliken, R. S.: J. chem. Physics **23**, 1833 and 1841 (1955).
[8] Pariser, R., and R. G. Parr: J. chem. Physics **21**, 466 and 767 (1953).
[9] Pearson, K.: Tables of the Incomplete Γ-Function. Cambridge: The University Press 1957.
[10] Pople, J. A.: Trans. Faraday Soc. **49**, 1375 (1953).
[11] Pullman, B., and A. Pullman: Proc. natl. Acad. Sci. U.S.A. **44**, 1197 (1958) and Revs. mod. Physics **32**, 428 (1960).
[12] —, C. Spanjaard and G. Berthier: Proc. natl. Acad. Sci. U.S.A. **46**, 1011 (1960).
[13] Spanjaard, C., and G. Berthier: J. Chim. physique **58**, 169 (1961).
[14] Watson, R. E.: Physic. Rev. **118**, 1036 (1960).
[15] Wolfsberg, M., and L. Helmholz: J. chem. Physics **20**, 837 (1952).

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