

A Comparison of Molecular Orbital and Crystal Field Calculations of Ferric Heme Compounds

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In this paper molecular orbital and crystal field calculations of some properties of five coordinated ferric heme proteins are compared. In particular, choosing hemin as an example, we have compared the following quantities: single orbital energies, electron repulsion energies, term energies, electron population of the Fe *d* orbitals, net atomic charges and the electric field gradient at the Fe nucleus calculated from the two models. Smaller term energy intervals between low lying sextet, doublet and quartet states, and an electric field gradient of opposite sign and three times the magnitude appear to be predicted from the MO calculation. These and other results are discussed in some detail.

In dieser Arbeit werden MO- und Kristallfeldrechnungen einiger Eigenschaften von fünfzählig koordinierten Fe-Häm-Proteinen verglichen. Insbesondere haben wir am Beispiel des Hämins folgende Größen verglichen: Energien von einem einzigen Orbital, Elektronenabstoßungsenergien, Energieterme, Elektronenbesetzung der Eisen-*d*-Orbitale, atomare Nettoladungen und den elektrischen Feldgradient am Eisenkern, der auf Grund zweier Modelle berechnet wurde. Kleinere Energietermintervalle zwischen den niedrig liegenden Sextett-, Dublett- und Quartettzuständen sowie ein elektrischer Feldgradient mit entgegengesetzten Vorzeichen und dreifachem Betrag scheinen durch die MO-Rechnung vorausgesagt zu werden. Diese und andere Resultate werden eingehender diskutiert.

Comparaison de calculs d'orbitales moléculaires et de champ cristallin pour quelques propriétés de protéines à hème ferrique pentacoordiné. En particulier, l'hémine étant prise comme exemple, nous avons comparé les quantités suivantes: énergies orbitales, énergies de répulsion électronique, termes énergétiques, population électronique des orbitales *d* de Fe, charges atomiques nettes et gradient du champ électrique au noyau Fe, calculés selon les deux modèles. Les calculs en orbitales moléculaires prédisent des termes d'intervalle d'énergie plus faibles entre les plus bas états sextet, doublet et quartet, ainsi qu'un gradient du champ électrique trois fois trop grand et de signe opposé. Ces résultats et certains autres sont discutés en détail.

1. Introduction¹

There now exists both molecular orbital (MO) [1] and crystal field (CF) calculations [2] for very similar high spin, isolated, five coordinated ferric heme compounds. In this paper we wish to discuss the differences and similarities in the MO and CF calculations for these compounds. In both methods a basis set of one electron functions is chosen, a molecular symmetry is assumed, and one electron energies are calculated. Total states are formed from certain chosen configuration and estimates of electron repulsion and total state energies made. While having these features in common, the way in which each is done is quite different in each case. It is these differences and similarities we wish to discuss and also to compare the electric field gradient calculated for one compound by both

¹ The MO calculation is actually for the porphine Cl but known hemin structure parameters are used in it.

methods. In most comparisons made, hemin was chosen as a sample compound since it is one for which both an MO¹ and CF calculation exist, and for which there is a good deal of experimental data.

2. One Electron Orbital Properties: Energies and States

A. The Crystal Field Approach

In the strong crystal field approximation which we have made for the ferric heme compounds, the crystal field perturbation which describes the total effect of bonding of the Fe to its ligand atoms, is presumed to be greater than the electrostatic repulsion between the 3d valence electrons. Thus we consider the effect of bonding directly on the single electron orbitals. We take as a basis set the 5 degenerate 3d atomic orbitals of the free ferric ion. We must also choose a reasonable local symmetry of ligand atoms. For the isolated heme compounds we have used D_4 axial symmetry. The choice of symmetry then allows us to write a formal crystal field potential. The symmetry of the potential determines the way in which the five 3d orbital energies split, while the coefficients of the terms in the potential determine the extent of this splitting, i.e., the single orbital energy intervals. In D_4 symmetry the d orbitals split into four distinct energy levels associated with $a_1(d_{z^2})$, $b_1(d_{x^2-y^2})$, $b_2(d_{xy})$ and $e(d_{xz}, d_{yz})$ orbitals. We have previously shown that the energy intervals between these orbitals can be directly expressed in terms of the formal crystal field parameters [2]. The relationship of the crystal field parameters to single orbital energy differences is shown in Fig. 1. As can be seen from this figure, the 3 crystal field parameters which relate directly to the energy intervals are Δ , u and δ' . These quantities can also be expressed as various com-

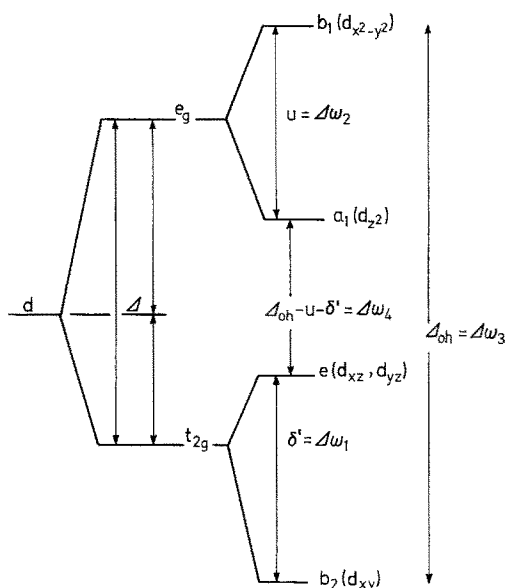


Fig. 1. Orbital energy differences in terms of crystal field parameters

binations of the 3 coefficients A_4^0 , A_2^0 , and A_4^4 appearing in the perturbing potential of D_4 symmetry. Thus the three parameters Δ , u and δ' are a direct link to the single orbital energy intervals on the one hand and to the formal coefficients in the electrostatic potential on the other. In our crystal field calculations of the ferric heme compounds these parameters are treated as a measure of the general bonding perturbation of the ligand atoms and are varied in a self consistent way corresponding to the actual physical-chemical variations occurring in the series of related compounds. However, in order to best link such parameter variations with the actual changes occurring through such a series, we have rearranged these parameters somewhat and use 3 different but related parameters Δ_{oh} , u' and C' ; defined as follows in terms of the energy interval parameters:

$$\Delta_{\text{oh}} = \Delta + 7/6 C' = \varepsilon(b_1) - \varepsilon(b_2) = \Delta \omega_3 = \Delta \varepsilon(\sigma \pi), \quad (1a)$$

$$u = u' + C' = \varepsilon(b_1) - \varepsilon(a_1) = \Delta \omega_2 = \Delta \varepsilon(\sigma), \quad (1b)$$

$$\delta' = -3/4 u' + C' = \varepsilon(e) - \varepsilon(b_2) = \Delta \omega_1 = \Delta \varepsilon(\pi). \quad (1c)$$

The advantage of using Δ_{oh} , u' and C' ; rather than Δ , u and δ' is that the former are a rearrangement of the 3 crystal field coefficients. The resultant expression which then links them to a formal point-charge electrostatic model for the bonding perturbation has more direct physical significance. These formal expressions are as follows:

$$\Delta_{\text{oh}} = (5/3) (q/R^5) \langle r^4 \rangle, \quad (2a)$$

$$u' = (8/7) (q/R^3 - p/Z^3) \langle r^2 \rangle, \quad (2b)$$

$$C' = (10/21) (q/R^5 - p/Z^5) \langle r^4 \rangle, \quad (2c)$$

where

- q is the point charge of the in-plane ligand,
- p is the point charge of the axial ligand,
- R is the Fe-N distance,
- Z is the Fe-axial ligand distance.

With the parameters in this form, and treating the right hand side of these equations symbolically so that they represent the total effect of in-plane and axial bonding, i.e., not taking the point charge literally, these expressions then become guidelines for determining reasonable parameter variations in a series of similar compounds with known physical-chemical variations. For example, terms in q and R are translated as in-plane bonding interactions while terms in p and Z are translated as axial bonding interactions.

With imposed conditions for self-consistent variations of parameters then, values of Δ_{oh} , u' and C' were obtained which accounted for the observed [3] zero field splittings of a series of 10 heme compounds [2] and also accounted for the observed quadrupole splitting in five of them [4]. Using Eqs. (1b) and (1c), single energy intervals $\Delta \omega_1$ and $\Delta \omega_2$ can be calculated from these parameter values.

In CF theory then a configuration is the specification of the orbitals for the 5 Fe d electrons and a configuration energy is the sum of the filled orbital energies, relative to the lowest orbital. For the heme compounds the configuration with one electron in each orbital is chosen as a zero of energy. All other configuration energies are measured relative to it by electron promotion and demotion.

B. The MO Approach to Single Orbital Properties: Energies and States

In the molecular orbital calculation which we have mentioned [1], an attempt is made to obtain one electron molecular orbitals and energies directly. To do this an extended Hückel calculation is made with a one-electron, effective Wolfsberg-Helmholz potential. The details of this calculation are presented elsewhere [1, 5]. We present here only a short summary as a prelude to a comparison of the results obtained with those from the crystal field calculation. An extensive basis set was used consisting of the valence atomic orbitals of every atom in the Fe-porphyrin molecule, in contrast to the simple 5 Fe d orbital basis sets of CF theory. Slater atomic orbitals were used for each basic function. To make an initial calculation of one electron energies and orbitals, for a given iron-porphyrin compound, the geometry of the molecule was assumed to be either C_{2v} or D_4 , internuclear distances were fixed, a configuration specified and neutral atoms assumed. With such initial conditions one electron matrix elements between pairs of atomic orbitals were calculated, and the Hamiltonian matrix diagonalized to give molecular orbitals which are linear combinations of atomic orbitals and a set of orbital energies. The charge on each atom was also calculated. In this calculation, the matrix elements between pairs of atomic orbitals are very sensitive to the net charge on the atoms involved. This is because these matrix elements were calculated from atomic valence state ionization potentials of each orbital, an overlap integral and an "interaction parameter". The atomic state ionization potentials are very sensitive to the net charge on the atom involved. Therefore this extended Hückel model was used with what is called a self-consistent charge procedure. After an initial calculation for a specific configuration and neutral atoms, the charge distribution calculated as a result of the diagonalization was used to change the values of the one-electron matrix elements and the matrix was again diagonalized.

This process of energy matrix diagonalization, charge distribution calculation, altering of matrix elements and rediagonalization was continued iteratively until for two successive diagonalizations, the charge distribution remained unchanged to within a stated tolerance, for example, 0.01 electrons/atom. The choice of configuration also affected the way in which the one electron matrix elements changed in the interactions. Specifying a configuration involves a guess as to the final energy ordering of the molecular orbitals. For all compounds it was assumed that the highest filled orbitals would be the ones with predominantly metal d atomic orbital components. If a very poor original choice was made, that is, if, in the configuration chosen, low lying molecular orbitals are left empty or 1/2 filled or relatively high energy orbitals are filled or 1/2 filled, then the iterative procedure does not converge. For the four ferric compounds studied the Cl, F and OH derivatives were presumed to have a configuration which could lead to a sextet ground state. That is, a single electron was placed in each of the 5 molecular orbitals which were primarily iron d orbitals. In the energy ordered MO's obtained after convergence this meant skipping a porphyrin $e_g(\pi)$ orbital which was between the $a_1(d_{z^2})$ and $b_1(d_{x^2-y^2})$ orbitals and only 1/2 filling a porphyrin $a_{2u}(\pi)$ orbital. These inconsistencies were not large enough to prevent convergence of one electron energies and functions for these assumed configurations. Thus in a sense

Table 1. *Orbital energy intervals^a in a series of ferric porphine compounds MO results*

Axial ligand	$\Delta\omega_1(\delta')$	$\Delta\omega_2(u)$	$\Delta\omega_3(\Delta_{\text{oh}})$
F ⁻	2025	13510	21600
Cl ⁻	2700	10800	20900
OH ⁻	4500	10130	22300
CN ⁻	600	5060	18600

^a All energies are in units of cm^{-1}

$$\Delta\omega_1 = \Delta(e - b_2), \Delta\omega_2 = \Delta(a_1 - b_1), \Delta\omega_3 = \Delta(b_1 - b_2).$$

this configuration for these compounds was forced upon the calculation and not predicted from it. The resulting molecular orbital energies, functions, electron populations and net atomic charges are all affected by this choice. For the CN⁻ derivative, the configuration chosen for the last five electrons was ($b_2^2 e_x^2 e_y$) leading to an unique 2E_g state. For this configuration, no molecular orbitals had to be skipped and hence it is more consistent with the one electron energy ordering calculated. Table 1 gives the molecular orbital energy differences obtained for the 5, primarily d orbitals, for the 4 ferric heme compounds. These numbers were generated from tables and figures given in Ref. [1]. In this table, the energy intervals are labelled $\Delta\omega_i$, $i = 1 - 3$ following Fig. 1 which identifies these intervals and shows how each is related to the crystal field parameters. These molecular orbitals are the delocalized analogues of the 5 pure d atomic orbitals used as a basis set for the perturbing potential in the crystal field approach. We see that MO results predict a smaller splitting of all the d orbital energies for the low spin CN⁻ derivative, i.e., the energy intervals:

$$\Delta\omega_3 = d_{x^2-y^2} - d_{xy}, \quad (3a)$$

$$\Delta\omega_2 = d_{x^2-y^2} - d_{z^2} \quad (3b)$$

and

$$\Delta\omega_1 = d_{xz,yz} - d_{xy}, \quad (3c)$$

are all smaller than for the high spin compounds. Since only the axial ligand is changed, these diminutions must be directly related to increased strength of binding along the Z axis. While one can immediately see that the energy of the d_{z^2} orbital would increase greatly thus diminishing $\Delta\omega_2$ the other orbital energy effects are too subtle for qualitative insight. It is difficult for example to imagine why the overall energy interval ($d_{x^2-y^2} - d_{xy}$) should diminish under such circumstances.

C. A Comparison of Single Orbital Energies, Electron Distributions and Net Atomic Charges in Hemin

The crystal field parameters obtained for hemin which explained both the observed zero field splitting and quadrupole splitting were $\Delta_{\text{oh}} = 29,850 \text{ cm}^{-1}$, $C' = 6200 \text{ cm}^{-1}$, and $u' = 2000 - 4000 \text{ cm}^{-1}$. The range of values of u' correspond to a possible range of values of nuclear quadrupole moment, $Q = 0.2 - 0.4$ Barns [6, 7].

To see if these crystal field parameters correspond at all to single orbital energies calculated by the molecular orbital method, values of the C' and u'

crystal field parameters were calculated directly from the molecular orbital energies of the Cl derivative of porphyrin. This compound is very similar to hemin, whose geometric parameters were used in the calculation.

From Table 1 for the Cl⁻ derivative, $\Delta\omega_1 = 2700 \text{ cm}^{-1}$ and $\Delta\omega_2 = 10,880 \text{ cm}^{-1}$. Using these two values in Eqs. (1 b) and (1 c) to solve for u' and C' , we obtain a MO value of $C' = 6175$ and $u' = 4630 \text{ cm}^{-1}$. The agreement between the two values of C' obtained from the two methods is very good, indeed far better than one should expect for such disparate methods of estimating one electron integrals. Since the MO method attempts a more *ab initio* calculation of single MO energies, we can take this agreement as a sign, that the crystal field formalism does not do too badly in approximating the effect of bonding on valence electron energies. The value of u' obtained from the MO calculation is close to the high end of the range of values of u' calculated for different values of Q from the crystal field expression. If we think of the MO calculation as supplying an independent estimate of the value of u' , we could then conclude that it favors a value of Q on the low side of the accepted range; i.e., $Q \leq 0.2$ Barns.

We proceed now to a discussion of the difference in the electron population in the d orbitals from the two calculations. For a pure d orbital basis set, the configuration which produces the 6A_1 ground state has one electron in each of the 5 d orbitals. If these five 3 d orbitals are allowed to form molecular orbitals, as they are in the molecular orbital calculation, the net electron population in these d orbitals will change. The 5 electrons that were each originally in pure d orbital states are now in molecular orbitals which are primarily localized on the Fe but which have some ligand and porphyrin atomic orbital character. Thus some d electron density is lost by such delocalization, leading to an effective (back) donation of d electrons from the metal to the surrounding atoms. In a so-called ligand field calculation, where only these molecular orbitals are considered, the d electron density will then be less than for the corresponding crystal field calculation. However, there are molecular orbital partners of these primarily d -orbital states which have mainly porphyrin or ligand character but which have small amounts of d orbital mixed with them. These orbitals then represent delocalizations of the original porphyrin or ligand orbitals thus providing additional electron density to the Fe d orbitals by a (forward) donation of electrons primarily from the N atoms and axial ligand to the metal. Table 2 gives the crystal field, the ligand field and the full molecular orbital electron populations of the various metal orbitals for hemin. The CF population is simply obtained from the configuration, the ligand field population shows the effect of delocalization of the d orbitals by MO formation. The MO population shows the effect of both back and forward donation. For the high spin configuration, CF results place one electron in each d orbital. Ligand field orbitals, i.e., back donation by MO formation depletes each of these orbitals, back donation being the smallest for the d_{xy} orbital and exceeding 50% for the d_{z^2} and $d_{x^2-y^2}$ orbitals which are pointing right at the axial ligand and porphyrin nitrogens respectively. From the total MO results, we see that for the d_{xy} orbital forward donation approximately equals back donation so that the electron population is about 1 in that orbital. However for the other 4 orbitals, forward donation exceeds back donation and the total electron population in each of these orbitals exceeds 1. There is, in addition, some electron population

Table 2. Comparison of electron population of Fe orbitals in hemin in three approximations^a

Orbital	(CF) ^b	(LF) ^c	(MO) ^d
b_{2g}	1	0.96	1.034
e_g	1	0.65	1.332
e_g	1	0.65	1.332
a_{1g}	1	0.48	1.478
b_{1g}	1	0.46	1.518
p_x	0	0	0.164
p_y	0	0	0.164
p_z	0	0	0.304
4s	0	0	0.408

^a Constructed from data in Ref. [1].

^b CF = Crystal Field Theory; high spin configuration $(b_{2g})(e_g(x))(e_g(y))(a_{1g})(b_{1g})$. All pure d orbitals.

^c LF = Ligand Field Theory, high spin configuration. Each orbital is delocalized and is LCAO of pure d + ligand a.o. This column shows the effect of "back donation".

^d MO = Molecular Orbital Calculation; configuration specifies *all* filled and 1/2 filled orbitals. The populations include back donation of e by metal + forward donation of e to metal.

due to forward donation of both the 4s and 4p orbitals of Fe. These are also given in Table 2. We shall use the electron populations given in this table later on to calculate the electric field gradient in hemin from a molecular orbital view point.

From the MO results, the net charge on the Fe atom is +0.265, on the porphyrin N is -0.182 and on the Cl⁻ -0.190. The crystal field calculation while implicitly assuming a +3 charge on the Fe because it is assumed to have a $3d^5$ valence electron configuration, does not invoke charges on any of the atoms as such. This is because we do not use the literal interpretation of the crystal field parameters, but rather link them to one-electron energy intervals. We use their link to crystal field potential coefficients only loosely to represent total bonding interactions. However Eqs. (2a)–(2c) for the parameters do provide expressions for calculation of parameters from point charges q and p on the N and Cl placed at certain distances R and Z from the Fe. It would not however be valid to use the charges obtained from the MO calculation to calculate values of parameters to be used in a CF calculation. This is because these net charges already reflect delocalization effects and are not a measure of the total interaction of the Fe and its neighbors if we wish to translate the interaction formally to a totally electrostatic one. The use of the "delocalized" atomic charges in the CF calculation would then tend to grossly underestimate the value of parameters which are supposed to include the total effect of bonding. To see that this is the case for hemin, we have calculated a value of u' from expression (2b) using the values of R and Z used in the MO calculation and obtained from the X-ray analysis of hemin and a value of $\langle r^2 \rangle$, from a SCF calculation of ferric ion. When we do this the expression (2b) for u' becomes:

$$u'(\text{cm}^{-1}) = 5.34 \times 10^4(0.116q - 0.047p). \quad (4)$$

If we now use the MO calculated values of $q = 0.182$ and $p = 0.190$ we obtain a value of $u' = 750 \text{ cm}^{-1}$. If however we use a consistent picture of replacing all

interaction by a pseudo-classical electrostatic interaction and allow the N and Cl to have unit point charges we obtain a value for $u' = 3700 \text{ cm}^{-1}$ a value substantially in agreement with that obtained for u' by fitting it to both zero field splitting and quadrupole splitting data. Thus the crystal field model is consistent with a localized model, both from the point of view of using only Fe atomic orbitals and from the formal picture it presents of the net charge on each atom. The link between the MO and CF model, is not then to use delocalized atomic charges obtained from the MO calculation to calculate CF parameters but to allow both theories to independently and consistently calculate single orbital energy intervals and to compare these for corresponding orbitals. We have done this for hemin and show that in this case the agreement in the two energy intervals, $\Delta\omega_1$ and $\Delta\omega_2$, is quite good. The magnitude of the overall energy splitting of these orbitals, as seen in Fig. 1, is given by the parameter $\Delta\omega_{\text{oh}}$ which corresponds to the energy interval $\Delta\omega_3$. For hemin, the MO value is $20,800 \text{ cm}^{-1}$ compared to $29,600$ from the CF results. The large discrepancy obtained for the splitting of the e_g and t_{2g} orbitals is linked to the difference in estimating electron repulsion energies in the two calculations.

3. Total State Energies

A. The Crystal Field Approach

Total states can be formed from any given configuration. For example in O_h symmetry there are five possible configurations $t_{2g}^n e_g^{5-n}$ each with a different configuration (one electron) energy. These five configurations lead to 43 multiplets labelled by spin and symmetry eg ${}^6A_1, {}^4T_1, {}^2T_2$, etc. which correspond to 100 doubly degenerate states. Griffith [9] has formed these 43 multiplets appropriate to O_h symmetry and calculated the electron repulsion energy matrix elements $\langle N | e^2/r_{ij} | M \rangle$ for all pairs of states with the same spin-symmetry label. These matrix elements are given in terms of the so-called Racah Parameters, A , B , and C and it is this interaction which separates multiplets belonging to the same configuration. The diagonal elements of such matrices give then the first order electrostatic repulsion energy between different multiplets. Thus the crystal field formalism not only provides a very straightforward way of expressing one electron configuration energies in terms of crystal field parameters. It also allows the calculation of two-electron repulsion energies for the total states formed from each configuration in at least a formally straightforward manner. The ground state is chosen as the 6A_1 state. The electrostatic energy of all other states relative to it can be expressed in terms of only two Racah parameters B and C . The configuration which gives rise to the 6A_1 state, the $t_{2g}^3 e_g^2$ configuration, is assumed to correspond arbitrarily to zero configuration energy. Other configuration energies obtained by promoting and demoting electrons, are given relative to this configuration. Multiplets appropriate to D_4 symmetry can be formed as linear combinations of O_h multiplets and the configuration can also be expressed in terms of D_4 basis states. In our calculations we have kept only those excited multiplets which are reasonably near the 6A_1 ground state in strongly perturbed environments. These are particularly the first excited quartet state a 4T_1 state and the doublet state 2T_2 arising from an unique t_{2g}^5 configuration.

Table 3. Crystal field and electrostatic energies of total electronic states in D_4 symmetry

$ Sh\rangle_{\text{oh}}$	$ Sh\rangle D_4$	D_4 Configuration	Term energy
6A_1	6A_1	$(e)^2 (b_2) (a_1) (b_1)$	0
4T_1	4A_2	$(e)^2 (b_2)^2 (a_1)$	$10B + 6C - \Delta_{\text{oh}}$
4T_1	4E_2	$-1/2(e)^3 (b_2) (a_1)$ $+ \sqrt{3}/2(e)^3 (b_2) (b_1)$	$10B + 6C - \Delta_{\text{oh}} + 7/4 C'$
2T_2	2E_2	$(e)^3 (b_2)^2$	$15B + 10C - 2\Delta_{\text{oh}} + 2C' + u'/4$
2T_2	2B_2	$(e)^4 (b_2)$	$15B + 10C - 2\Delta_{\text{oh}} + 3C' - u'/2$

The symmetry behavior of these states when an axial distortion is imposed on the octahedral environment and the D_4 configurations which give rise to these D_4 states are given in Table 3. In this table is also given the total energies of these states including single orbital configuration energies and electron repulsion energies to first order. It is these states and energies which we take as a starting point to calculate properties of the ferric ion complex which can be reasonably associated with the localized electron distribution about the ferric ion. For such calculations we add spin-orbit coupling among these states to all orders for our final picture of the perturbed ferric ion states and energies.

In all of our crystal field calculations, there are then 6 parameters involved, 3 crystal field parameters to characterize configuration energies, two Racah parameters to characterize electron repulsion energies and a spin-orbit coupling parameter to characterize the strength of such interactions among the total states. As can be seen from the energies in Table 3, the larger the value of B and C chosen the greater the separation between the sextet, doublet, and quartet states which interact. Thus the larger will be the overall crystal field perturbation, measured by the value of Δ_{oh} , needed to obtain the same magnitude of interaction. The observed zero field splittings of the 6A_1 states is due to its interaction with excited quartet and doublet states. The value of Δ_{oh} which accounts for this splitting, while unique for a given value of B and C , depends on the actual values chosen for these parameters. For all crystal field calculations we have arbitrarily fixed the value of $B = 1100 \text{ cm}^{-1}$ and of C to equal 3750 cm^{-1} , which are their maximum free ion values. It is with these values of B and C that we obtain a value for $\Delta_{\text{oh}} = 29,850 \text{ cm}^{-1}$.

B. MO Approach

In the MO calculation, only one configuration was used to calculate single orbital energies for each compound. The relative energy of other configurations was set equal to the difference in orbital energies of occupied orbitals in the two configurations. Since one electron energy intervals in this model depend on the configuration, this assumption is an approximate one. It was further assumed in the MO calculation that a configuration energy is the average energy of all terms arising from that configuration, weighted by the orbital degenerate only; i.e., energy differences $\omega(j) - \omega(i) = \bar{E}_A - \bar{E}_B$ where A and B are configurations related by the transfer of an electron from molecular orbital j to molecular orbital i ; and \bar{E}_A and \bar{E}_B are the average energies of all terms arising from the configurations A and B respectively. Individual term energies are then determined by adding in the

exchange integrals that cause the term energy to differ from this average. Formally then the difference $\bar{E}_B - \bar{E}_A \cong \omega(j) - \omega(i)$ includes all the one and two electron terms which all the terms arising from a given configuration have in common. This difference is however approximated by the difference of one electron orbital energy. The result of this formulation is that the following expressions are obtained for the following term energy differences:

$${}^6A_1(A) - {}^2E_g(B) = (\omega_e - \omega_a) + (\omega_d - \omega_b) - 3/5 \sum K_{ij}, \quad (5)$$

$${}^4A_2(C) - {}^2E_g(B) = (\omega_d - \omega_b) - 2/3 \sum K_{lm}, \quad (6)$$

$${}^6A_1(A) - {}^4A_2(C) = (\omega_e - \omega_a) - 3/4 \sum K_{ij} + 2/3 \sum K_{lm}. \quad (7)$$

A , B and C label configurations

$$A = (b_2 e_x e_y a_1 b_1),$$

$$B = (b_2^2 e_y^2 e_x),$$

$$C = (b_2^2 e_y e_x a_1),$$

and the orbital labels are:

$$|a\rangle = |b_2\rangle = |d_{xy}\rangle,$$

$$|b\rangle = |e_y\rangle = |d_{yz}\rangle,$$

$$|c\rangle = |e_x\rangle = |d_{xz}\rangle,$$

$$|d\rangle = |a_1\rangle = |d_{z^2}\rangle,$$

$$|e\rangle = |b_1\rangle = |d_{x^2-y^2}\rangle.$$

The sum over exchange integrals is

$$\sum K_{ij} = K_{ab} + K_{ac} + K_{ad} + K_{ae} + K_{bc} + K_{bd} + K_{be} + K_{cd} + K_{ce} + K_{de}.$$

Each integral can be written in terms of the Slater Condon integrals, F , resulting from an expansion of $1/r_{ij}$.

$$K_{ab} = ac = bc = be = ce = 3F_2 + 20F_4,$$

$$K_{cd} = bd = F_2 + 30F_4,$$

$$K_{ac} = 35F_4,$$

$$K_{de} = da = 4F_2 + 30F_4,$$

adding these together, Eq. (5) becomes

$${}^6A_1(A) - {}^2E_g(B) = (\omega_e - \omega_a) + (\omega_d - \omega_b) - (15F_2 + 135F_4) \quad (5')$$

similarly Eq. (6) becomes

$${}^4A_2(C) - {}^2E_g(B) = (\omega_d - \omega_b) - [10F_2/3 + 160F_4/3] \quad (6')$$

and

$${}^6A_1 - {}^4A_2 = (\omega_c - \omega_a) - [35F_2/3 + 245F_4/3]. \quad (7')$$

C. Comparison of Term Energy Intervals

From Table 3 we see that the total states 6A_1 , 4A_2 , and 2E_2 considered in the crystal field calculation arise from the same configurations as do the molecular orbital states. The only difference is again that the 5 orbitals involved in the MO results are somewhat delocalized molecular orbitals. From Table 3 we can write the CF state energy differences:

$${}^6A_1 - {}^2E_g = 2\Delta_{\text{oh}} - 2C' - u'/4 - (15B + 10C), \quad (8)$$

$${}^4A_2 - {}^2E_g = \Delta_{\text{oh}} - 2C' - u'/4 - (5B + 4C), \quad (9)$$

$${}^6A_1 - {}^4A_2 = \Delta_{\text{oh}} - (10B + 6C). \quad (10)$$

The single orbital energy intervals given in Eqs. (1 a) to (1 c) can be rearranged to yield the following orbital energy intervals in terms of crystal field parameters: from (1 a):

$$\varepsilon(b_2) - \varepsilon(b_1) = \omega_e - \omega_a = \Delta_{\text{oh}}, \quad (11)$$

from (1 a) - (1 b) - (1 c):

$$\varepsilon(a_1) - \varepsilon(e) = \omega_a - \omega_b = \Delta_{\text{oh}} - u'/4 - 2C'. \quad (12)$$

Also:

$$B = F_2 - 5F_4, \quad (13)$$

$$C = 35F_4. \quad (14)$$

Substituting expressions (11)–(14) into Eqs. (5'), (6'), and (7') we obtain:

$${}^6A_1 - {}^2E_g = 2\Delta_{\text{oh}} - 2C' - u'/4 - (15B + 6C), \quad (5'')$$

$${}^4A_2 - {}^2E_g = \Delta_{\text{oh}} - 2C'' - u'/4 - (10B/3 + 2C), \quad (6'')$$

$${}^6A_1 - {}^4A_2 = \Delta_{\text{oh}} - (35B/3 + 4C). \quad (7'')$$

Comparing the two sets of state energy intervals obtained by the two methods, i.e., Eqs. (8)–(10) with Eqs. (5'')–(7'') we see that while the one electron configuration energies have the same form, the expression for electron repulsion energies as a function of B and C obtained by each method is different. Thus even for the same values of B and C , and for the same values of one electron energies, different state energies would be obtained from each calculation. In addition, the integrals F_2 and F_4 and hence values of B and C are quite sensitive to the net charge on the atom. The values of B and C used in the CF calculations were for ferric ion with a net charge of +3. In the molecular orbital calculations the net charge on the iron in hemin is +0.265. Therefore on a charge basis alone the value for F_2 and F_4 which is used in the MO calculations is greatly reduced. This reduction is not due to direct covalent effects, since the exchange integrals are evaluated assuming that the molecular orbitals are pure atomic d orbitals. The effect of MO formation does of course enter indirectly into the charge reduction. The MO values of B and C used for the +0.265 iron were then $C = 2900$ and $B = 800 \text{ cm}^{-1}$ both less than the CF values. Correspondingly, the MO value of Δ_{oh} was 8000 cm^{-1} less than the CF value, while values of u' and C' were comparable. We now have a complete set of five parameters for hemin from each of the calculations. We can use these values to calculate state energy differences for the two models. From the

Table 4. Summary of differences between MO and CF calculations for hemin

Quantity	MO	CF
B	800	1100
C	2900	3750
Δ_{oh}	20900	29850
C'	6175	6200
u'	4630	3600
$\Delta E(6-2)$	1800	7400
$\Delta E(6-4)$	630	3600
$q(efg)$	(-4.29×10^{15})	$+1.35 \times 10^{15}$
Q	(0.067)	(0.2)

crystal field results using $B = 1100 \text{ cm}^{-1}$, $C = 3750 \text{ cm}^{-1}$, $\Delta_{\text{oh}} = 29,850 \text{ cm}^{-1}$, $C' = 6200 \text{ cm}^{-1}$, $u' = 4000 \text{ cm}^{-1}$ we obtain

$${}^2E_g - {}^6A_1 = 7400 \text{ cm}^{-1}$$

and

$${}^4A_2 - {}^6A_1 = 3650 \text{ cm}^{-1}.$$

For the MO results: using $B = 800 \text{ cm}^{-1}$, $C = 2900 \text{ cm}^{-1}$, $\Delta_{\text{oh}} = 20,900 \text{ cm}^{-1}$, $C' = 6175 \text{ cm}^{-1}$, and $u' = 4630 \text{ cm}^{-1}$ we obtain

$${}^2E_g - {}^6A_1 \cong 1800 \text{ cm}^{-1}$$

and

$${}^4A_2 - {}^6A_1 = 630 \text{ cm}^{-1}.$$

These results are summarized in Table 4.

We see then that the molecular orbital calculation for hemin predicts much lower lying 4A_2 and 2E_g states than does the crystal field calculation. The two calculations give quite comparable values of the one electron energy intervals due to an axial distortion. They differ considerably in their estimate of the total one electron energy interval in a cubic environment Δ_{oh} and also in the numerical estimate of the electrostatic energy differences between multiplets. The result of these two differences is that the MO calculations predict smaller term separations than do the crystal field calculations. For the case of hemin the excited state energies are high enough that in either case they are out of the range of thermal contribution to such properties as the magnetic moments or the electric field gradients. However, if the energy separations were as small as predicted by the MO results, the amount of spin-orbit coupling among the states would increase. We have used a value of the spin orbit coupling parameter of 420 cm^{-1} for the calculation of the extent of spin mixing among the sextet, doublet and quartet states. It is this spin-mixing which is the main cause of the zero field splitting of the Kramers doublets of ground sextet state. Our crystal field parameters, for given values of B and C and therefore our term energy intervals were adjusted to give that amount of spin-mixing which corresponds to the measured zero field splittings in hemin. Therefore the term energies obtained from the crystal field calculation, linked as they are to the amount of spin-mixing in the ground state functions and the corresponding values of zero field splitting, are probably more

reliable than the term energy intervals obtained from the molecular orbital calculations. An alternate suggestion is that the spin-orbit coupling parameter is also reduced in the MO formalism. To be consistent with the use of pure d atomic orbitals and a net effective charge on the Fe of +0.265 we can use the neutral atom value for Fe which is 390 cm^{-1} . This small reduction in the spin-orbit coupling strength will not diminish the interaction appreciably. Therefore the MO results with their smaller term energy intervals for hemin would predict a very much larger zerofield splitting than the 13.6 cm^{-1} that is observed for this compound. There would also be a good deal more of spin-mixing of doublet and quartet states into the ground state function. This would be manifest in a reduction of the magnetic moment, increase in the electric field gradient and decrease in the g values observed in the electron spin resonance of the ground sextet state. None of these effects of substantial spin-mixing are observed for the hemin, thus the larger term energies calculated from the crystal field results seem more accurate.

It is not surprising that the crystal field calculation does a better job of estimating the term energy from states arising from pure d orbital configurations. The entire formalism and use of parameters is geared to such a calculation. Molecular orbital calculations describe the individual electron distributions in a more realistic way and should allow the assignment of porphyrin transitions in the electronic spectra.

D. Criterion for Low Spin Ground State

From the CF term energies given in Table 3, it may seem that the 2E_2 state becomes the ground state in D_4 symmetry if:

$$2\Delta_{\text{oh}} \geq 15B + 10C + 2C' + u'/4.$$

From the MO term energy interval given in Eq. (5'') this criterion is:

$$2\Delta_{\text{oh}} \geq 15B + 6C + 2C' + u'/4.$$

Comparing these two expressions, we see that the MO value of Δ_{oh} needed for a doublet ground state is smaller than the CF values. The difference between the MO and CF estimates of the minimum Δ_{oh} is the quantity $2C$. Thus the MO results predict a low spin ground state at a value of Δ_{oh} about 6000 cm^{-1} less than the CF result, if the same values of B , C , C' , and u' are used in each case. This is a rather large discrepancy and is due to the different ways of estimating electron repulsion energies in the two methods.

Using the MO parameters $C' \cong u' \cong 2500\text{ cm}^{-1}$ calculated from Table 1 for the low spin CN^- compound and the value of $B = 800\text{ cm}^{-1}$ and $C = 2900\text{ cm}^{-1}$, we obtain a minimum value of Δ_{oh} needed for a doublet ground state of $17,500\text{ cm}^{-1}$. The calculated MO value of Δ_{oh} for CN^- exceeds this and is therefore consistent with the choice of a low spin configuration for this compound.

From Table 1, it may be seen that the high spin compounds have values of Δ_{oh} which exceed $17,500\text{ cm}^{-1}$. However, they also have larger tetragonal splittings of both the t_{2g} and e_g states. The larger this splitting, i.e., the larger the value of u' and C' , the larger the minimum value of the overall splitting needed for a doublet ground state. Substituting the values of $C' = 6175$ and $u' = 4830$ already calculated

for the Cl^- compound into the above expression, we find $\Delta_{\text{oh}} \geq 21,450 \text{ cm}^{-1}$ is needed for a low spin state. The MO value for the Cl compound is less than that. Hence the MO configuration and single orbital energies are also consistent for a high spin compound.

With the higher value of B and C we have previously used in CF calculation, the numerical discrepancy in the Δ_{oh} criterion for the low spin ground state becomes even greater. However, the value of B and C we use is an upper limit and could very well be reduced to the MO value. What remains is the 6000 cm^{-1} discrepancy in the prediction of the two methods even when the same value of parameters is used. If localized “ $d-d$ ” electronic transitions could be observed spectroscopically in some of these isolated heme compounds, it might be possible to determine Δ_{oh} experimentally and thereby check the minimum values of Δ_{oh} predicted for low spin compounds by the two methods.

4. Electric Field Gradient Calculations

We have previously indicated the crystal field model used to calculate electric field gradients at the Fe nucleus [2, 4]. In this model the assumption is made that the total gradient is the sum of two contributions: a lattice contribution due to the arrangement of nearest neighbors and a valence contribution due to the average contribution of all non-spherically symmetric states within thermal range of the ground states. For hemin and most of the other high spin isolated heme derivatives, the amount of spin-mixing in the spherically symmetric sextet ground state is small. Excited states are far away and also spherically symmetric. Therefore it turns out that the valence contribution to the electric field gradient in these compounds is completely negligible compared to the lattice contribution. In axial symmetry, this axial contribution is proportional to the value of u' in the compounds. The observed quadrupole splitting in such a case is then: $\Delta E_Q = C'qQ$. To explain the observed values of the quadrupole splittings for five of the ten compounds in the series of high spin isolated heme compounds studied with a constant value of Q , the excited nuclear state quadrupole moment, the following relationship was obtained for hemin: $u' = C'/8.59Q$, where C' , the other tetragonal crystal field parameter is determined from the zero field splitting to have a value of 6200 cm^{-1} . The value of Q most quoted from previous results is in the range $0.2-0.4$ [6, 7, 8]. Therefore the uncertainty in u' is a factor of 2 and so also is that in the predicted electric field gradient. For $Q = 0.2$ Barns, $u' = 3615 \text{ cm}^{-1}$ and the electric field gradient is $1.35 \times 10^{15} \text{ esu/cm}^3$ including the Sternheimer anti-shielding factor. This is an approximate maximum value of q predicted from crystal field theory. Let us see how this compares with a calculation of the electric field gradient from MO theory.

To calculate the electric field gradient in a molecular orbital framework, we have made the following model and assumptions. We assume that the electric field gradient is due only to an electron distribution centered on the Fe nucleus. We, therefore, include the electron population of all Fe orbitals and none others. However, we allow the full molecular orbital electron population in these orbitals, the combined effect of forward and back donation in MO delocalization. We then express the total electric field gradient as the sum over single orbital electric field

gradients weighted by the electron population of that orbital:

$$q_{\text{total}} = \sum_i Z_i q_i \quad (15)$$

where the sum is over all occupied Fe orbitals

$$Z_i = \text{electron population of the } i^{\text{th}} \text{ orbital } \phi_i, \quad (16)$$

$$q_i = \langle \phi_i | q | \phi_i \rangle, \phi = p, d$$

and

$$q = \langle V_{zz}/e \rangle = -1/r^3 (3 \cos^2 \Theta - 1) = (-4\sqrt{\pi}/5) Y_2^0/r^3, \quad (17)$$

$$q_i = c_i \langle \phi | Y_2^0 | \phi_i \rangle$$

where

c_i is proportional to the radial integral $\langle r^{-3} \rangle$ for orbital ϕ_i .

To obtain values for q_i the products of the d and p orbitals were expressed as sums of spherical harmonic functions. These expressions are given in Table 5. In these products, only the term in d_0 gives a non-vanishing expectation value of the V_{zz} operator. Table 6 gives the non-zero values of q_i , and values of z_i for all the contributing Fe orbitals. Using the values in this table, and the relationships given in Eqs. (15) and (17) we obtain the result that

$$q = -0.260 \langle r^{-3} \rangle. \quad (18)$$

With $\langle r^{-3} \rangle$ in atomic units and using other conversion factors we obtain

$$q \left(\frac{\text{esu}}{\text{cm}^3} \right) = -3.24 \times 10^{15} (0.260) \langle r^{-3} \rangle_{\text{AU}}. \quad (19)$$

Table 5. Products of orbitals as sums of spherical harmonics

Orbital	S_0	d_0	g_0	$(d_2 + d_{-2})$	$(g_2 + g_{-2})$	$(g_4 + g_{-4})$
$\langle d_{xy} d_{xy} \rangle$	$1/2\sqrt{\pi}$	$\frac{-5}{7\sqrt{\pi}}$	$\frac{1}{14\sqrt{\pi}}$			$\frac{-\sqrt{5}}{2\sqrt{14\pi}}$
$\langle d_{xy} d_{xz} \rangle$	$1/2\sqrt{\pi}$	$\frac{5}{14\sqrt{\pi}}$	$\frac{-2}{7\sqrt{\pi}}$	$\frac{-\sqrt{30}}{28\sqrt{\pi}}$	$\frac{-10\sqrt{2}}{28\sqrt{5\pi}}$	
$\langle d_{yz} d_{yz} \rangle$	$1/2\sqrt{\pi}$	$\frac{5}{14\sqrt{\pi}}$	$\frac{-2}{7\sqrt{\pi}}$	$\frac{\sqrt{30}}{28\sqrt{\pi}}$	$\frac{10\sqrt{2}}{28\sqrt{5\pi}}$	
$\langle d_{z^2} d_{z^2} \rangle$	$1/2\sqrt{\pi}$	$\frac{5}{7\sqrt{\pi}}$	$\frac{3}{7\sqrt{\pi}}$			
$\langle d_{x^2-y^2} d_{x^2-y^2} \rangle$	$1/2\sqrt{\pi}$	$\frac{-\sqrt{5}}{7\sqrt{\pi}}$	$\frac{1}{14\sqrt{\pi}}$			$\frac{\sqrt{5}}{2\sqrt{14\pi}}$
$\langle p_z p_z \rangle$	$1/2\sqrt{\pi}$	$\frac{1}{\sqrt{5\pi}}$				
$\langle p_x p_x \rangle$	$1/2\sqrt{\pi}$	$\frac{-1}{2\sqrt{5\pi}}$		$\frac{\sqrt{3}}{10\sqrt{\pi}}$		
$\langle p_y p_y^* \rangle$		$\frac{-1}{2\sqrt{5\pi}}$		$\frac{-\sqrt{3}}{\sqrt{10\pi}}$		

Table 6. Single orbital contributions to electric field gradient^a

Orbital	Z_i^a	$q_i/\langle r^{-3} \rangle^a$
d_{xy}	1.034	4/7
d_{xz}	1.332	-2/7
d_{yz}	1.332	-2/7
$d_{x^2-y^2}$	1.478	-4/7
d_{z^2}	1.518	+4/7
p_z	0.304	-4/5
p_x	0.164	+2/5
p_y	0.164	+2/5

^a Z_i = electron population of orbital i

$$q_i = C_i \langle \phi_i | Y_2^0 | \phi_i \rangle.$$

Using an estimate of $\langle r^{-3} \rangle_{\text{AU}} = 5.1$ from an SCF treatment of the Fe atom we obtain $q = -4.29 \times 10^{15}$ esu/cm [8].

Comparing this value of the electric field gradient with the maximum value obtained from the crystal field approach we see that it is about three times as great and of opposite sign. From experimental results, the crystal field calculation predicts the correct sign. (If the magnitude of the q calculated from the MO model were correct, then in order to account for the observed quadrupole splitting of 0.78 mm/sec, a value of $Q = 0.06$ Barns would be predicted. This is considerably smaller than any value heretofore suggested for any iron compounds.) We could reduce the value of q by reducing the value of the radial integral chosen. However there is no present argument or calculation justifying this and we would still be left with the sign discrepancy. Thus it appears that at least for hemin, the calculation of the electric field gradient from a crystal field model is better than from a MO model.

5. Summary

In this paper we have compared the molecular orbital and crystal field calculations for five coordinated ferric heme compounds. In particular, choosing hemin as an example, we have compared the following quantities: single orbital energies, electron repulsion energies, term energies, electron population in the ferric ion orbitals, net atomic charges, and finally the electric field gradients calculated from the two models. Table 4 summarized the results of these comparisons. The net effect of a much lower electron repulsion energy and a somewhat lower bonding perturbation from the MO calculation, makes the term energy intervals calculated from the MO treatment much less than that from the crystal field. Since the state energy intervals are obtained in the CF model by adjusting spin-orbit interaction among these states so that agreement with the observed zero field splitting of the sextet term is obtained, it would appear that these energy intervals are more realistic than the MO estimates. Thus localized iron electron transitions (so called $d-d$ transition) in the spectra of ferric heme compounds should be more accurately predicted by a CF model. However these are the only transitions such a model can predict and the MO approach must be used for porphyrin and charge transfer transitions, being much better for the former than the latter.

The electric field gradient calculated from the MO model is three times as great and of opposite sign from the CF model. By comparison with experiments, the CF model predicts the correct sign, a positive one².

It is hoped that in this comparative study of MO and CF calculations, some of the virtues and disadvantages of each model, have emerged and will be of some help in determining the future use and appropriateness of these two models for specific applications.

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² The $I_z = \pm 3/2$ state is at a higher energy than the $I_z = \pm 1/2$ state when quadrupole split.