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Calculation of Hyperfine Field and Quadrupole Splitting in Ferriprotoporphyrin IX Chloride (Hemin)*

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Extended Hückel wavefunctions for iron (III) porphyrin chloride have been used in the calculation of the hyperfine field and quadrupole splitting at iron in hemin. The approximate treatment makes use in part of unrestricted Hartee-Fock results for atomic iron, and leads to good agreement with experiment.

The magnetic and spectral properties of porphyrin complexes are of considerable current interest because of the relationship of such molecules to hemoglobin. In a series of papers, Gouterman and co-workers treated the spectral properties of transition metal porphyrins by means of extended Hückel theory [1]. The extended Hückel MO's [1] were used by Weissbluth and Maling [2] in their calculation of the Mössbauer parameters (quadrupole splitting and isomer shift) for several hemoglobin derivatives. The quadrupole and zero-field splittings for a number of 5-coordinate iron porphyrin complexes have recently been calculated by Harris [3], using crystal field theory.

We propose to make a theoretical study of a number of the properties of one porphyrin complex, namely hemin chloride. We report here calculations of the hyperfine field and the electric field gradient at iron, and we compare our results to the experimental determination by Johnson [4].

The Hamiltonian under consideration for hemin chloride is given by

$$\mathscr{H} = g_e \beta_e \boldsymbol{H} \cdot \boldsymbol{S} + D\left(S_z^2 - \frac{1}{3} S^2\right) + A^* \boldsymbol{I} \cdot \boldsymbol{S} + B^*(2I_z S_z - I_x S_x - I_y S_y) + \frac{e^2 q Q}{4I(2I-1)} \left[3I_z^2 - I(I+1)\right] . \tag{1}$$

The last three terms in (1) were evaluated using extended Hückel MO's very similar to those of ZGK: we repeated the calculation of ZGK using the same input parameters for iron (III) porphyrin chloride and a modified version of Hoffmann's original MO program [5] capable of iteration to charge self-consistency with the inclusion of a transition metal. The molecular orbital results are nearly identical to those reported [1] earlier and will not be reported here.

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The hyperfine and effective fields are defined in (2):

$$\boldsymbol{H}_{\mathrm{eff}} = \boldsymbol{H}_{\mathrm{applied}} + \frac{\langle S \rangle}{S} H_{\mathrm{hyperfine}} \,. \tag{2}$$

Lang and Marshall [6] have shown that under the conditions of the Mössbauer experiments ($H_{\mathrm{applied}} \sim 30$ kG, $T = 1.65 - 4.2°$ K, polycrystalline hemin) the first two terms in (1) should give rise to a preferred orientation of the spins in the negative x direction with $\langle S_x \rangle \sim -2$. (The $+z$ direction is along the Fe–Cl bond axis, and the $+x$ direction is defined by the projection of $\boldsymbol{H}_{\mathrm{applied}}$ on the hemin plane).

The isotropic hyperfine coupling constant A^* is given by Eq. (3), where the χ are Clementi AO's [10] and the ψ_i are the MO's:

$$\begin{aligned} A^* = \frac{8\pi}{6S} g_e \beta_e g^*_{\mathrm{Fe}} \beta_{\mathrm{N}} \Bigg\{ & \sum_{\substack{i=\text{half-} \\ \text{filled MO's}}} |\psi_i(0)|^2_{\text{direct}} \\ & + \frac{3.138}{4} \left(\sum_{l=1s}^{3s} [|\chi_{l\alpha}(0)|^2 - |\chi_{l\beta}(0)|^2] \right. \\ & \left. + 0.20266 [|\chi_{4s\alpha}(0)|^2 - |\chi_{4s\beta}(0)|^2] \right) \Bigg\} . \end{aligned} \tag{3}$$

In Eq. (3), g^*_{Fe} corresponds to the metastable state ($I = 3/2$) of the iron nucleus and is equal to -0.1033 [6], and $S = 5/2$ for hemin chloride [7]. In the evaluation of A^*, we made use of the unrestricted Hartree-Fock calculation of Bagus and Liu [8] for the ^5D state of atomic iron (configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5_\alpha 3d^1_\beta 4s^2 4p^0$). The extended Hückel calculations for iron porphyrin chloride lead to the following configuration for the coordinated iron "pseudo-atom":

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d_\alpha^{4.952} 3d_\beta^{1.814} 4s_\alpha^{0.2046} 4s_\beta^{0.2026} 4p_\alpha^{0.3389} 4p_\beta^{0.2654} \,,$$

where the $3d$ populations reflect a $3d$ population of 3.138 electrons in half-filled MO's (on the basis of the usual Mulliken population analysis [9]). We make the reasonable assumptions that, for the calculation of core-polarization, the only important difference between ^5D iron and the hemin pseudoiron atom is in the number of unpaired spins, and that the extent of inner shell core polarization by the outer half-filled $3d$ orbitals is directly proportional to the number of unpaired spins. Thus arises the proportionality term 3.138/4 in Eq. (3), which relates the hemin MO results to the Bagus-Liu UHF calculation. The terms $|\chi_{l\alpha,\beta}(0)|^2$ are taken directly from the UHF results [8]. The quantity $\sum_i |\psi_i(0)|^2$ direct is taken from the half-filled extended Hückel MO coefficients in conjunction with Clementi's [10] $4s$ atomic orbital expression for ^5D iron. The quantity 0.2066 in Eq. (3) corresponds to one-half the total paired $4s$ electron density. In Eq. (3), we neglect the inner s shell polarization by the very small unpaired $4p$ electron density (0.0735). If the degree of inner shell polarization by the unpaired $4p$ electrons is nearly the same magnitude as the polarization by the unpaired $3d$ electrons, we expect a $4p$ contribution of only $\sim 2\%$ of the $3d$. This must be considered an upper limit, however, since the $4p$ orbitals are considerably more diffuse than the $3d$.

The dipolar (anisotropic) contribution to the hyperfine coupling constant is given by Eq. (4). In Eq. (4),

$$B^* = \frac{\gamma_e \gamma_{\mathrm{Fe}}^* \hbar^2}{2S} \sum_i \left\langle \psi_i \left| \frac{3\cos^2\theta_i - 1}{r_i^3} \right| \psi_i \right\rangle S_{iz} \tag{4}$$

the summation is limited to half-filled MO's, and θ_i is the angle between the coordinates of electron i and the z axis, with the origin at iron. Further, only the $3d$, $4s$ and $4p$ iron orbital contributions were considered. The contribution of unpaired electrons in ligand atomic orbitals was neglected, and is expected to be quite small, as in field gradient calculations [2]. The quantities $\langle r^{-3}\rangle_{3d}$, $\langle r^{-3}\rangle_{4p}$, and $\langle r^{-3}\rangle_{3d-4s}$, which arise in Eqs. (4) and (6) were evaluated from Clementi's functions for ^5D iron and have the values 4.9979 a.u., 2.0369 a.u., and 0.0013 a.u., respectively.

The calculated hyperfine field in terms of A^* and B^* is given by (5), where we have taken the transverse field to be

$$\begin{aligned} H_{\text{hyperfine}}^{\text{transverse}} &= \left(B^* - \left(A_{4s,\text{direct}}^* + A_{\text{core polarization}}^*\right)\right) \frac{S}{\gamma_{\mathrm{Fe}}^* \hbar} \, [\mathrm{kG}] \\ &= [-11.45 - (1.74 - 161.01)]\, S\, [\mathrm{kG}] = 370\ \mathrm{kG}\,. \end{aligned} \tag{5}$$

dominant in the polycrystalline sample because most of the spins are expected to be aligned in the molecular plane [4]. The calculated value of the hyperfine field is in very good agreement with the experimental value [4] of 480 kG, and the results indicate that the hyperfine field in hemin is strongly dominated by the core polarization term. The dipolar term in the hyperfine field ($-11.45\,S$ in the x direction or $+22.90\,S$ in the z direction) could lead to an observed anisotropy of 85.8 kG in a sufficiently strong applied field, and it would be of interest to observe this experimentally.

The magnitude and direction of H_{eff} in (2) depends upon the angle ϕ between the molecular x axis and the applied field direction. This dependence is given by (6), with the unit vectors defined by the molecular coordinate system.

$$\boldsymbol{H}_{\text{eff}} = \left(\frac{\langle S_x\rangle}{S} H_{\text{hyperfine}} + H_{\text{applied}} \cos\phi\right) \frac{\boldsymbol{X}}{|X|} + (H_{\text{applied}} \sin\phi) \frac{\boldsymbol{Z}}{|Z|} \tag{6}$$

With $\langle S_x\rangle \sim -2$, $H_{\text{applied}} = 30$ kG, and $H_{\text{hyperfine}} = 370$ kG, (6) gives $H_{\text{eff}} = -266$ kG for $\phi = 0°$, and $H_{\text{eff}} = -298$ kG for $\phi = 90°$. The entire range of values for H_{eff} should be observed in a polycrystalline sample. This range of calculated values for H_{eff} is again in surprisingly good agreement with the experimental value of -345 kG [4].

We now consider the field gradient q, calculated by Eq. (7), with the ψ_i again being the extended Hückel MO's, and $n(i)$ the occupation number of the ith MO.

$$q = V_{zz} = \sum_{\substack{\text{occupied} \\ \text{MO's}}} \left\langle \psi_i \left| \frac{3\cos^2\theta_i - 1}{r_i^3} \right| \psi_i \right\rangle \cdot n(i) \tag{7}$$

In the calculation of q, only integrals involving valence atomic orbitals of iron were considered, it being assumed that charge density on the ligands makes only a small contribution to q (see Ref. [2]). The table summarizes the main contributions to the field gradient, with contributions to q from filled and half-filled MO's indicated separately. The observed quadrupole splitting is related to the calculated value of q by relation (8):

$$\Delta E = \frac{e^2 q Q}{2}(1-R). \tag{8}$$

From (8), with $Q = 0.15$ barns, $q = +0.6626\, a_0^{-3}$, and the antishielding factor $(1-R) = 0.68$ (from Ref. [2]), the calculated value of ΔE is $+0.73$ mm/sec. The experimental value of $+0.76$ mm/sec (Ref. [4]) is therefore well reproduced by our calculations. The correct value of Q is still in doubt, with values from 0.15–0.41 barn having been reported [11–16].

Table. *Contributions to the field gradient in Hemin (in* a.u.*)*

	$\sum_{ml=-2}^{+2} q_{ml}^{3d}$	$\sum_{ml=-1}^{+1} q_{ml}^{4p}$	$q^{3d_{z^2}-4s}$	q_{total}
unpaired electrons	-0.9324	$+0.0172$	$<10^{-4}$	-0.9152
paired electrons	$+1.6420$	-0.0641	$<10^{-4}$	$+1.5779$
total	$+0.7095$	-0.0469	$<10^{-4}$	$+0.6626$

The positive sign of q indicates a greater electron density out of the heme plane than in the plane. In this connection it is observed that the contribution of unpaired electrons to q is negative, due mainly to the fact that d_{xy} is very slightly mixed with ligand orbitals. We note here that Eq. (9) derived by Lang and Marshall [6] properly

$$-B^* = 2g^*_{\text{Fe}}\beta_e\beta_{\text{Fe}}\langle r^{-3}\rangle_{3d}\left(\frac{4\Delta E}{105\ \text{mm/sec}}\right) \tag{9}$$

applies only to that part of ΔE arising from *unpaired* spins, a quantity which cannot be experimentally determined. Our results indicate that the contribution of half-filled MO's is smaller than and of opposite sign to the contribution of filled MO's (see table). These results strongly suggest that both paired and unpaired contributions to q must be considered for molecules with highly delocalized molecular orbitals. The very large contribution of paired MO's to the field gradient, as well as the experimentally observed large *ligand* hyperfine terms for hemin chloride and related molecules [18], suggest that crystal field theory is inadequate for the treatment of this problem. In addition, in the crystal field theory, the hyperfine field at iron will be overestimated by a factor of about two. This result follows because the crystal field theory predicts a $^6A_1$ ground state for ferric iron in hemin, which state is composed only of $3d$ orbitals, with the $4s$ orbital unoccupied. The hyperfine field in the crystal field model is therefore expected to be nearly the same as for free ferric iron. The hyperfine field at the nucleus in Fe^{+3} has been calculated to be -745 kG by the "moment-perturbation" method [19], which should be compared to the calculated MO result (Eq. (5)) of -370 kG, and to the experimental result of -480 kG [4]. The much better agreement of the MO result with experiment further emphasizes the inadequacy of crystal field theory.

The extended Hückel molecular orbitals for iron (III) porphyrin chloride are found to give very reasonable results in the calculation of the hyperfine field and the electric field gradient at iron in hemin chloride, which results complement the earlier successes [1, 2] for this and related molecules. In order to overcome the limitations of the "pseudoatom" treatment employed here, detailed calculations of the hyperfine field at iron in hemin by the "moment-perturbation" method [17] would be necessary. In progress are improved calculations of the field gradient, zero field splittings, and ligand hyperfine terms for iron porphyrin complexes, the results of which will provide additional tests of the molecular orbital theory.

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