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Extended Hückel Treatment of the Fe^{57m} Nuclear Quadrupole Interaction in Hemin

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Improvement of the previous method of calculation of the field gradient at iron in hemin is reported. The earlier attempt included only the local contribution (electron density localized on iron) to the field gradient and that calculation gave the wrong sign of q. Reported here are the contributions of non-local and distant terms to the observed field gradient. It is found that the distant terms are negligible, and that non-local effects are of comparable size and the same sign as local terms. Thus with the available extended Hückel wave-functions, a more complete calculation of q leads to a worsening of the results. Further analysis leads to the conclusion that a correct estimate of q may be obtained by means of contracting the radial parts of the in-plane d-orbitals (those which interact most strongly with the porphyrin nitrogen lone pairs). Greatly results are obtained with only a moderate and physically reasonable change in the orbital exponents. Also presented is a calculation of the quadrupole coupling at ligand chlorine.

Die frühere Methode der Berechnung des Feldgradienten am Eisenatom in Hämin wird verbessert. In der damaligen Arbeit war nur der lokale Anteil (Elektronendichte am Eisenatom) am Feldgradienten berücksichtigt worden, und es ergab sich ein falsches Vorzeichen für q. In der vorliegenden Arbeit werden die Beiträge von nicht lokalen und entfernten Termen zum beobachteten Feldgradienten erfaßt. Man findet, daß die entfernten Termen vernachlässigt werden können, während die nichtlokalen Effekte vergleichbare Größen und dasselbe Vorzeichen wie die lokalen Terme haben. Auf diese Weise führt eine umfangreiche Berechnung von q mit der Wellenfunktion nach der erweiterten Hückelmethode zu einerVerschlechterung der Ergebnisse. Die weitere Untersuchung führt zu dem Ergebnis, daß eine richtige Abschätzung von q erzielt werden kann, wenn die Radialanteile der in der Ebene liegenden d-Orbitale (derjenigen d-Orbitale, die am stärksten mit den einsamen Elektronenpaaren des Stickstoffs im Porphyrin wechselwirken) kontrahiert werden. Stark verbesserte Resultate werden so schon mit geringen und physikalisch sinnvollen Änderungen des Orbitalexponenten erreicht. Weiterhin wird die Quadrupolkopplung am Chlorliganden berechnet.

Compte rendu de l'amélioration de la méthode antérieure pour le calcul du gradient du champ sur l'atome de fer de l'hème. La tentative précédente ne tenait compte que de la contribution locale (densité électronique localisée sur le fer) au gradient du champ et ce calcul donnait le mauvais signe pour q. On donne ici les contributions des termes non locaux et éloignés. Les termes éloignés sont négligeables, quant aux effets non locaux ils sont de grandeur comparable avec les termes locaux et de même signe. Aussi, avec les fonctions d'onde Hückel Etendu disponibles, un calcul plus complet de q conduit à une détérioration des résultats. Une analyse plus approfondie conduit à la conclusion

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qu'une estimation correcte de q peut être obtenue en contractant les parties radiales des orbitales d dans le plan (celles qui interagissent le plus fortement avec les paires libres de l'azote de la porphyrine). Des résultats fortement améliorés sont obtenus au moyen d'un changement modéré et physiquement raisonnable des exposants orbitaux. On présente aussi un calcul du couplage quadrupolaire sur le ligand chlore.

1. Introduction

In our series of theoretical investigations [1–4] on the iron-porphyrin complexes, we have given an analysis of the magnetic and hyperfine effects in hemin. One of our objectives is to determine the accuracy of extended Hückel wave-functions on the calculation of molecular properties. Satisfactory use of the extended Hückel method has already been made in the interpretation of optical spectra [5, 6]. However, our earlier extended Hückel calculation [1, 2] of the electric field gradient q at iron in hemin was in disagreement with experiment in that the wrong sign was obtained. In this paper we report new results which are in better agreement with the experimental field gradient. The improvement in the results was effected by a more complete calculation using modified extended Hückel wave-functions, rather than by a new procedure for molecular orbital calculation.

In our earlier field gradient calculation, we included only the local contributions. The non-local contributions involving two-center expectation values of the field gradient operator were neglected. However, recent results for alkali halides and alkali halide solid solutions indicate that the non-local contributions may be substantial [7]. We therefore include here a discussion of the non-local contributions to q at iron in hemin. The results indicate that explicit inclusion of non-local effects does not improve agreement with experiment. In order to improve our calculation, we find that the various d-orbitals on iron must have different radial dependencies, a feature which is not included in the original extended Hückel method, but which we have introduced as an approximation.

In Sect. 2, the details of the procedure and results of the non-local calculation of q are presented. The necessity of d-orbital contraction is discussed in Sect. 3. Sect. 4 is devoted to calculation of the field gradients of Cl in hemin. Sect. 5 presents a summary of our present understanding of the magnetic and hyperfine properties of hemin.

2. Non-Local Contribution to the Field Gradient

The earlier work [1, 2] on the Fe^{57m} nuclear quadrupole interaction included only the local contribution to the field gradient. Thus, for axial symmetry in hemin chloride;

$$\mathscr{H}_Q = \frac{e^2 qQ}{4I(2I-1)} [3I_z^2 - I^2] \tag{1}$$

where

$$q = -\left\langle \Psi \middle| \sum_i \frac{\partial^2 (1/r_i)}{\partial z_i^2} \middle| \Psi \right\rangle \tag{2}$$

and only one-electron integrals involving orbitals on the iron atom alone were retained. The many electron expectation value in Eq. (2) can be expressed as a sum of expectation values over all the molecular orbitals of hemin, and not only the half filled orbitals as in the case for the anisotropic electron-nuclear hyperfine constant [1]. The core orbitals on the iron are assumed to be spherically symmetric and thus do not contribute directly to the electric field gradient, q. However, the core orbitals may be electrostatically polarized by the valence electrons, and may thus shield the nuclear quadrupole moment from the valence electrons. A shielding factor $R = 0.32$ (appropriate for the free iron atom), leading to a fractional reduction to $(1-R) = 0.68$ of the valence electron field gradient, was used earlier [1, 2]. This was combined with a valence electron local contribution to q from extended Hückel wave-functions and a nuclear quadrupole moment of 0.15 barns to yield $e^2qQ = -0.73$ mm/sec as compared to the experimental $+0.76$ mm/sec. Because of uncertainties in Q and $(1-R)$, the exact magnitude of the theoretical e^2qQ is some doubt. However, the disagreement in sign is significant. The calculated result implies that the out-of-plane electron density in hemin is greater than that in-the-plane, while the experimental result indicates the reverse (assuming only local contributions to q). These conclusions can be definitely established only after all contributions to q have properly included. There are two main contributions which were earlier neglected and which arise when one introduces the complete expressions for the molecular orbitals comprising the many electron function Ψ in Eq. (2). These contributions are termed "distant" and "non-local". The "distant" terms are composed of matrix elements of the field gradient operator for Fe^{57m} with orbitals exclusively on neighboring atoms. Actually, these matrix elements are combined with the field gradients from the effective charges (ζ) on the atoms. Thus,

$$\begin{aligned} q_{\text{distant}} = {} & \sum_{A} \frac{2\zeta}{R_A^3}(1-\gamma_\infty) \\ & -2\sum_{\mu}\sum_{A,B} C_{\mu A} C_{\mu B} \left\langle \psi_{\mu A} \left| \frac{3\cos^2\theta - 1}{r^3} \right| \psi_{\mu B} \right\rangle (1-\gamma_\infty). \end{aligned} \tag{3}$$

In the last term of Eq. (3), only the terms corresponding to $A = B$ are significant. The antishielding factor $(1-\gamma_\infty)$ is somewhat uncertain. The atomic charge on iron in hemin, according to the Mulliken population analysis, is about $+0.75$, so the antishielding factor is likely to be intermediate between Fe^+ and Fe^0. Using a value of [8] 10.14 for $(1-\gamma_\infty)$, and on effective charge $+0.169$ on each nitrogen atom from extended Hückel calculation, the contribution from a single nitrogen atom was found to be $0.013\ a_0^3$, which is an order of magnitude smaller than the local contribution. Considering that there is likely to be some cancellation of the in-plane nitrogen distant contribution by the axial chlorine distant contribution, we feel that q_{distant} may be safely neglected.

This brings us to consideration of $q_{\text{non-local}}$, which is made up of matrix elements in which one orbital is on iron and the other is on a ligand atom. The influence of $q_{\text{non-local}}$ has recently been found to be significant in alkali halide solutions and alkali-halide molecules [7]. The reason one might expect $q_{\text{non-local}}$ to be large is as follows. $q_{\text{non-local}}$ involves a significant contribution from electron density in the region between the iron and ligand atoms; this overlap charge density is not completely internal to the iron core and so it may lead to a significant anti-shielding effect. Recently, Moss [9] utilized Mulliken orbital populations to derive the field gradient at iron in hemin. This procedure incorporates part of the non-local effect because half of the overlap population is assigned to each of a neighboring pair of atoms. However, the quantitative significance of this procedure for including non-local effects is ambiguous first because it implies the use of the approximation:

$$\langle \psi_A | 1/r_A^3 | \psi_B \rangle = S \langle \psi_A | 1/r_A^3 | \psi_A \rangle \tag{4}$$

where

$$S = \langle \psi_A | \psi_B \rangle \tag{5}$$

which leads to a gross overestimate [10]. Second, it is not clear how one should apply the anti-shielding factors to the overlap density.

We now discuss our procedure for calculation of $q_{\text{non-local}}$. We have to include the contributions from nitrogen and chlorine orbitals separately. As a typical example, we describe in detail the process for evaluation of $q_{\text{non-local}}$ from the chlorine 3*s* orbital.

$$q_{\text{non-local}}^{\text{Cl}(3s)} = -2 \sum_{\mu=1}^{66} n(\mu) \sum_{i=\text{Fe}(3d)} a_{\mu,i} a_{\mu,\text{Cl}(3s)} \cdot \left\langle i \left| \frac{(3\cos^2\theta - 1)}{r_{\text{Fe}}^3} \right| 3s(\text{Cl}) \right\rangle . \tag{6}$$

Here μ represents a summation index over the 66 occupied molecular orbitals and i a summation over the Fe basis atomic orbitals. Since the chlorine ligand in hemin chloride lies on the molecular z-axis above the iron, as shown in Fig. 1, no coordinate rotations are necessary. The chlorine 3*s* AO is defined as in Eq. (7) below where $R_{\text{Cl}(3s)}$ is the Clementi atomic radial function for 3*s* and a_{Cl} refers to the Fe-Cl distance. To calculate the integral in Eq. (6), we utilized the two-center expansion in Eq. (7) by the alpha function technique, [11]

$$\begin{aligned} 3s(\text{Cl}) &= R_{\text{Cl}(3s)}\, Y_0^0(\theta_{\text{Cl}}, \varphi_{\text{Cl}}) \\ &= \sum_{l=0}^{\infty} \alpha_l(300 | a_{\text{Cl-Fe}}, r_{\text{Fe}})\, Y_l^0(\theta_{\text{Fe}}, \varphi_{\text{Fe}}) \end{aligned} \tag{7}$$

which expresses the chlorine 3*s* atomic orbital as a linear combination of alpha functions centered at iron. Substituting (7) into (6) and utilizing angular momentum selection rules, we get

$$q_{\text{non-local}}^{\text{Cl}(3s)} = -2 \sum_{\mu=1}^{66} a_{\mu,\text{Fe}(dz^2)} a_{\mu,\text{Cl}(3s)} n(\mu) \cdot \left\langle d_{z^2}(\text{Fe}) \left| \frac{3\cos^2\theta - 1}{r^3} \right| 3s(\text{Cl}) \right\rangle \tag{8}$$

where

$$\begin{aligned} \left\langle d_{z^2}(\text{Fe}) \left| \frac{(3\cos^2\theta - 1)}{r^3} \right| 3s(\text{Cl}) \right\rangle &= \sqrt{\frac{16\pi}{5}} \\ &\cdot \{ \langle R_d | \alpha_0(300 | a_{\text{Cl-Fe}}, r_{\text{Fe}}) \rangle \langle Y_2^0 | Y_2^0 | Y_0^0 \rangle \\ &+ \langle R_d | \alpha_2(300 | a_{\text{Cl-Fe}}, r_{\text{Fe}} \rangle \langle Y_2^0 | Y_2^0 | Y_2^0 \rangle \\ &+ \langle R_d | \alpha_4(300 | a_{\text{Cl-Fe}}, r_{\text{Fe}}) \langle Y_2^0 | Y_2^0 | Y_4^0 \rangle \} . \end{aligned} \tag{9}$$

On carrying out the angular integrations involving the spherical harmonies and the radial integrals in (9) using Clementi's neutral atom orbitals for iron, we get

$$\left\langle d_{z^2}(\mathrm{Fe}) \left| \frac{(3\cos^2\theta-1)}{r^3} \right| 3s(\mathrm{Cl}) \right\rangle = 0.0663\,(\mathrm{a.u.})\,. \tag{10}$$

Next, substituting for the coefficients $a_{\mu,\mathrm{Fe}(dz^2)}$ and $a_{\mu,\mathrm{Cl}(3s)}$ from the MO calculations, we find that

$$\sum_{\mu=1}^{66} 2a_{\mu,\mathrm{Fe}(dz^2)}a_{\mu,\mathrm{Cl}(3s)}n(\mu) = 0.0190\,. \tag{11}$$

Inserting the values of (10) and (11) into (8), we finally get $q^{\mathrm{Cl}(3s)}_{\text{non-local}}$ as in Eq. (12).

$$q^{\mathrm{Cl}(3s)}_{\text{non-local}} = -0.001260\,(a.u.)\,. \tag{12}$$

For the contributions from the p orbitals of chlorine, we have to use the symmetry properties of the p and d orbitals to reduce the number of two-center integrals involved. The non-vanishing angular integrals of the type

$$\left\langle d_i(\mathrm{Fe}) \left| \frac{(3\cos^2\theta-1)}{r^3} \right| p_i(\mathrm{Cl}) \right\rangle$$

are shown in the Table where the x and y axes are taken as indicated in Fig. 1.

Table. *Selection rules of angular integrals of the type* $\left\langle d_i(\mathrm{Fe}) \left| \frac{(3\cos^2\theta-1)}{r^3} \right| p_j(\mathrm{Cl}) \right\rangle$

d_i(Fe) / p_j(Cl)	$d_{x^2-y^2}$	d_z^2	d_{xz}	d_{zy}	d_{xy}
p_x	0	0	non-zero	0	0
p_y	0	0	0	non-zero	0
p_z	0	non-zero	0	0	0

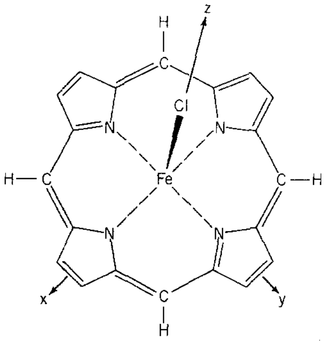

Fig. 1. Molecular geometry and coordinate axes for iron (III) Porphyrin chloride

Using the Table, we get

$$q^{\mathrm{Cl}(3s)}_{\text{non-local}} = -\frac{8\sqrt{\pi}}{\sqrt{5}} \sum_{\mu=1}^{66} n(\mu) \cdot \left\{ a_{\mu,\mathrm{Fe}(dz^2)} a_{\mu,\mathrm{Cl}(3s)} \left\langle d_{z^2}(\mathrm{Fe}) \left| \frac{Y_2^0}{r^3} \right| p_z(\mathrm{Cl}) \right\rangle + 2a_{\mu,\mathrm{Fe}(dxz)} a_{\mu,\mathrm{Cl}(p_x)} \left\langle d_{xz}(\mathrm{Fe}) \left| \frac{Y_2^0}{r^3} \right| p_x(\mathrm{Cl}) \right\rangle \right. \tag{13}$$

where use has been made of the axial symmetry of hemin in replacing the d_{yz} contribution to $q^{\mathrm{Cl}(3p)}_{\text{non-local}}$ by the d_{xz} term, leading to the factor of 2 in the last term of (13). The two center integrals in Eq. (13) can be evaluated in the same manner as that in Eq. (8) for the 3*s* contribution. On carrying out the necessary steps, we get

$$q^{\mathrm{Cl}(3p)}_{\text{non-local}} = -0.10023\,(a.u.) \tag{14}$$

leading to a net non-local contribution from the chlorine atom orbitals of

$$\begin{aligned} q^{\mathrm{Cl}}_{\text{non-local}} &= q^{\mathrm{Cl}(3s)}_{\text{non-local}} + q^{\mathrm{Cl}(3p)}_{\text{non-local}} \\ &= -0.00126 - 0.10023 \\ &= -0.10149\,(a.u.)\,. \end{aligned} \tag{15}$$

For the calculation of the nitrogen non-local contribution to *q*, coordinate rotations are required because the Fe–N line for any particular nitrogen atom does not coincide with the molecular *z*-axis as was the case for chlorine. The rotation process consists of expressing the nitrogen orbitals in a co-ordinate system with *z*-axis along the Fe–N line, then applying the α-function expansion and subsequently rotating the angular functions so obtained back to a co-ordinate system coinciding with the molecular axis [13]. Other than this, the process of calculation of $q_{\text{non-local}}$ is identical to that for the chlorine orbitals and lead to the result:

$$\begin{aligned} q^{\mathrm{N}}_{\text{non-local}} &= 4(q^{\mathrm{N}(2s)}_{\text{non-local}} + q^{\mathrm{N}(2p)}_{\text{non-local}}) \\ &= 0.00210 + 0.00885 \\ &= 0.01095\,(\mathrm{a.u.})\,. \end{aligned} \tag{16}$$

Combining the results of Eqs. (15) and (16), the final $q_{\text{non-local}}$ is given by

$$q_{\text{non-local}} = -0.0905\,. \tag{17}$$

While this value of $q_{\text{non-local}}$ appears to be only about 1/6 of q_{local} obtained earlier, the actual effect of $q_{\text{non-local}}$ is expected to be comparatively larger from a consideration of anti-shielding effects. The antishielding factor $(1-\gamma'_\infty)$ for the non-local field-gradient is expected to be intermediate between those for the local and distant terms and is dependent upon the variation of the anti-shielding factor with the distance *R* between the nucleus and a point-charge producing the field-gradient. For Cu^+ ion involving *d*-shell electrons, the variation in $(1-\gamma(R))$ with *R* is found to be rather slow, in contrast to the behavior of other positive ions with valence *p*-shells [14]. Thus a choice

$$\begin{aligned}(1-\gamma'_\infty) &= (1-\gamma_\infty)/2 \\ &= 10.14/2\,(a.u.) \\ &= 5.07\ a.u.\end{aligned} \tag{18}$$

appears reasonable and perhaps a slight underestimate. With this choice and $Q=0.15$ barns [15] we get for the non-local contribution to the quadrupole coupling parameters for Mössbauer spectra, the value

$$\Delta E_{\text{non-local}} = \frac{e^2Q}{2}(-.46) = -0.74\ \text{mm/sec}. \tag{19}$$

On combining this with ΔE_{local} we find net calculated Mössbauer quadrupole splitting:

$$\Delta E = -1.47\ \text{mm/sec}. \tag{20}$$

This analysis shows that it is important to include non-local contributions to the quadrupole coupling constant of Fe^{57m} since it is seen to be comparable in magnitude and have the same sign as the local effect. The inclusion of the non-local effect however widens the difference between theory and experiment. Hence the burden of obtaining the proper sign has to be placed on some other mechanism. One of the possibilities that can explain the disagreement between theory and experiment for ΔE involves expansion or contraction of the radial parts of the atomic orbitals, for which there is no prescription in the extended Hückel theory. This possibility has also been mentioned by Moss [9]. We expect that the in-plane *d*-orbitals of hemin are somewhat contracted relative to the out-of-plane orbitals, due to the interaction with the lone pair electrons on the four ligand nitrogens.

3. Anisotropic Contraction of Iron *d*-Orbitals

A knowledge of the net theoretical value of ΔE in (20) allows us to make an estimate of the contraction needed for the in-plane *d*-orbitals. Thus if we make the reasonable assumption that the non-local contribution to q is affected minimally by contraction, then the experimental ΔE requires $q_{\text{local}} = 1.69\ a.u.$ The extent of contraction necessary to obtain $q_{\text{local}} = 1.69\ a.u.$ is found as follows:

Using the neutral atom out-of-plane orbitals,

$$\langle 1/r^3\rangle_{dz^2} = \langle 1/r^3\rangle_{dxz} = 4.978\,(a.u.) \tag{21}$$

we introduce a relative scale factor χ for the in-plane orbitals, that is

$$\langle 1/r^3\rangle_{dx^2-y^2} = \langle 1/r^3\rangle_{dxy} = 4.978\,\chi. \tag{22}$$

This scale factor may be obtained by matching experimental and theoretical values of the field gradient,

$$\chi = \frac{\left(\dfrac{7}{4\times 4.978}\,q_{\text{local}}\right) + \sum_{\mu=1}^{66} n(\mu)\,(a^2_{\mu,\text{Fe}(dz^2)} + a^2_{\mu,\text{Fe}(dxy)})}{\sum_{\mu=1}^{66} n(\mu)\,(a^2_{\mu,\text{Fe}(dx^2-y^2)} + a^2_{\mu,\text{Fe}(dxy)})} = 1.34. \tag{23}$$

We thus find for the in-plane $\langle 1/r^3 \rangle$:

$$\langle 1/r^3 \rangle_{dx^2-y^2} = \langle 1/r^3 \rangle_{dxy} = 6.670 (a.u.) . \tag{24}$$

The values of $\langle 1/r^3 \rangle$ for neutral iron atom and ions with various charges can be obtained using wave-functions obtained by Clementi [12]. The contracted value for $\langle 1/r^3 \rangle$ in Eq. (24) corresponds roughly to the value expected for iron with a charge of about $+4.5(4s^0 3d^{3.5})$. This does not mean that the d_{xy} and $d_{x^2-y^2}$ orbitals are experiencing a higher core charge than in neutral iron, but it does suggest that the required contraction of in-plane *d*-orbitals is physically reasonable.

It is our feeling, however, that the contracted $\langle 1/r^3 \rangle = 6.670$ (a.u.) in Eq. (24) is likely to be an overestimate, since the extended Hückel calculation should be brought to self-consistency with the contracted in-plane orbitals. For example, if we would reduce the in-plane *d*-orbital ligand overlaps to reflect the contraction, the calculation would no longer be self consistent in charge. Iteration to self-consistency with this partially contracted basis would probably lead to less iron-nitrogen covalency (the iron *d*-orbital coefficients in plane would become closer to unity). Since the in-plane population would therefore increase, the degree of contraction necessary to reproduce the experimental ΔE would decrease, and so on for the next iteration. We therefore would have to iterate both the overlap and the charge. Thus, a theory which employs a contractible basis along with charge self-consistency would probably give a very reasonable value for ΔE, with lesser contractions of the orbitals than obtained here. It is worthwhile to note that the expected reduced covalency in the heme plane (σ-covalency for the nitrogen orbitals) is in the right direction to reduce the calculated anisotropy in the hyperfine interaction [3] at the nitrogen nucleus. The earlier calculation [3] overestimated this anisotropy.

4. Electric Quadrupole Interaction at Cl^{35} Nucleus

Also of interest as an index of our knowledge of the electronic structure of hemin are the hyperfine interactions of the ligand Cl^{35} nucleus and the field gradient at Cl^{35}. No data are currently available on either, but such data should become available from experiment in the near future. An analysis of the magnetic hyperfine constants would require a knowledge of the moment perturbation wave-function or Brueckner-Goldstone type analysis for Cl atom [3]. Since neither are available, we have therefore investigated only the quadrupole interaction of Cl^{35}. The field gradient at the Cl^{35} nucleus is again composed of local, non-local, and distant terms. We have only considered the local term because of the fact that due to the strong contribution from holes in the $3p$-shell of the chlorine atom, non-local and distant terms are usually of minor importance [16]. Thus, taking account of the axial symmetry of the charge distribution on the chlorine atom, the local field gradient is given by

$$q_{\text{local}} = -4/5 \langle r^{-3} \rangle_{3p} \sum_{\mu=1}^{66} (a^2_{\mu,pz} - a^2_{\mu,px})\, n(\mu) \tag{25}$$

where $a_{\mu,pz}$ and $a_{\mu,px}$ are MO coefficients associated with chlorine $3p_z$ and $3p_x$ orbitals, $n(\mu)$ is the population in the μ^{th} MO and $\langle r^{-3} \rangle_{3p}$ is the expectation value of r^{-3} over the chlorine $3p$ orbitals where antishielding effects involving interaction between valence and core orbitals have been neglected. Using the results of the MO calculation, we obtain,

$$\begin{aligned}\sum_{\mu=1}^{66}(a_{\mu,pz}^2-a_{\mu,px}^2)\,n(\mu)&=1.5864-1.8266\\&=-0.2402\,.\end{aligned}\tag{26}$$

The quadrupole coupling energy, corresponding to the difference in energy between $\pm 3/2$ and $\pm 1/2$ levels in zero-magnetic field, is given by

$$\Delta E=e^2Qq/2=-4/5\langle r^{-3}\rangle_{3p}e^2Q(-0.1201)\,.\tag{27}$$

Using

$$\langle r^{-3}\rangle_{3p}=6.75596/a_0^3\tag{28}$$

from Clementi $3p$ orbitals and the Cl^{35} nuclear quadrupole moment [17]

$$Q=-7.9\times 10^{-2}\ \text{barns}\tag{29}$$

we get

$$\Delta E=-12.04\ \text{mc/sec}\,.\tag{30}$$

An alternate approach which avoids explicit knowledge of the nuclear quadrupole moment and the local antishielding effect is to use the Townes-Dailey procedure [18] and the population factor in Eq. (31) together with coupling constant per p-hole in the atom [16], namely,

$$e^2Qq_{\text{atom}}=109.74\ \text{mc/sec}\,.\tag{32}$$

Such an analysis leads to the slightly larger magnitude for

$$\Delta E=e^2Qq_{\text{atom}}(-0.1201)=-13.18\ \text{mc/sec}\tag{33}$$

as compared to (30). This net theoretical value of ΔE would require a knowledge of the non-local contribution to the field-gradient, but because of the larger local departure from sphericity for the chlorine atom as compared to iron, the relative importance of non-local effects is expected to be less pronounced.

The value of ΔE in Eq. (30) indicates that while the Fe–Cl bond in hemin is not as covalent as for example the C–Cl bond in organic compounds, there is still substantial departure from a purely ionic bond. It would be very interesting to make a comparison of the theoretical prediction for e^2Qq with experiment when the latter becomes available.

5. Conclusion

The work in this series of investigations of hemin including that in the present paper was aimed at quantitative understanding of the origin of magnetic and hyperfine properties of hemoglobin derivatives. In particular, we had intended to test if one had as much success in interpreting magnetic properties as in the case of optical properties. From these investigations it appears that extended Hückel wave-functions give fairly good results for properties that depend upon over-all charge and spin densities such as the isotropic hyperfine constant [3] and zero-field splitting parameter [4]. On the other hand, properties that depend upon the local anisotropy such as dipolar hyperfine interaction at the nitrogen nuclei and Fe^{57m} quadrupole interaction seem to come out rather poorly with the extended Hückel wave-function. We have no experimental data on N^{14} and Cl^{35} quadrupole interactions to check if the same points hold in the latter cases. From estimates in this paper it appears that a plausible remedy is the use of different radial characters for atomic orbitals which are in very different bonding situations. For large molecules such as hemin, it might be possible to achieve such differing in-plane and out-of-plane radial character by modifying the EH program to include a $4d$ basis function. Since the $3d$ and $4d$ orbitals have differing radial character, the coefficients $a_{\mu,\mathrm{Fe}(3d)}$ and $a_{\mu,\mathrm{Fe}(4d)}$ could adjust in such a way to give the desired radial character.

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References

1. Rettig, M. F., Han, P. S., Das, T. P.: Theoret. chim. Acta (Berl.) **12**, 178 (1968).
2. — — — Theoret. chim. Acta (Berl.) **13**, 432 (1969).
3. — — — Theoret. chim. Acta (Berl.) **16**, 1 (1970).
4. Han, P. S., Das, T. P., Rettig, M. F.: J. chem. Physics (in press).
5. Zerner, M., Gouterman, M.: Theoret. chim. Acta (Berl.) **4**, 44 (1966).
6. — — Kobayashi, H.: Theoret. chim. Acta (Berl.) **6**, 363 (1966).
7. Ikenberry, D., Das, T. P.: Physic Rev. **184**, 989 (1969).
8. Ingalls, R. I.: Physic. Rev. **128**, 1155 (1962).
9. Moss, T., Bearden, A. J., Caughey, W. S.: J. chem. Physics **51**, 2624 (1969).
10. For example, compare with results in: Ikenberry, D., Das, T. P.: Physic. Rev. **138**, A 822 (1965).
11. Löwdin, P. O.: Advan. Physics **5**, 1 (1956).
12. Clementi, E.: Tables of atomic functions. IBM Corp. 1965.
13. Han, P. S.: Ph. D. Thesis, University of California, Riverside, California.
14. See: Ramsey, N. F.: Molecular beams, p. 318. London: Oxford Univ. Press 1966.
15. Sawatzky, A., Hupkes, Juhlke: Physic. Rev. Letters **25**, 100 (1970).
16. Das, T. P., Hahn, E. L.: Nuclear quadrupole resonance spectroscopy. New York: Academic Press 1959.
17. Fuller, G. H., Cohen, V. W.: Nuclear Data Tables **5**, 433 (1969).
18. Townes, C. H., Dailey, B. P.: J. chem. Physics **17**, 782 (1949).

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