Theoret. Chim. Acta (Berl.) 35, 361—368 (1974)
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Core-Electron Contributions to Fe^{57m} Nuclear Quadrupole Interactions in Hemin*

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Received December 19, 1973/June 19, 1974

In an attempt to resolve the difference between theory and experiment for nuclear quadrupole interaction of Fe^{57m} in hemin, we have examined the contribution from the core p electrons on the iron atom. This contribution arises from the different distortion of the $3p_{x,y}$ orbitals on the plane, as compared to the $3p_z$ orbital perpendicular to the plane of the hemin, through overlap with neighboring atoms. It leads to about seventy per cent of the local contribution from valence electrons calculated earlier from the molecular orbital picture. On combining this contribution with the calculated local valence contributions reported earlier, the net theoretical result is -0.16 mm/sec. This compares with the experimental value 0.76 mm/sec and the earlier local contribution of about the same magnitude but of opposite sign. Using the model for compression of the in-plane d-orbitals as compared to the out-of-plane d-orbitals, the new value of the contraction ratio, introduced in earlier work, is found to be 1.13, significantly smaller than the value 1.34 calculated previously.

Key words: Hemin – Nuclear quadrupole interactions in heminTearlier

1. Introduction

In recent years, a substantial amount of information regarding the electronic structure of heme compounds has emerged from the analysis of optical spectra and more recently of the hyperfine and magnetic properties obtained from the Mössbauer effect and magnetic resonance, both of the conventional and electron-nuclear double resonance types. The extended-Hückel procedure for obtaining wave-functions has proved to be rather suitable for a theoretical understanding of most of these properties. In particular, it has been rather successful in analyzing optical spectra [1], magnetic hyperfine constants [2, 3] at iron and nitrogen nuclei, and the zero-field splitting [4] of hemin. In earlier investigations [2, 5] we have studied the Fe^{57m} nuclear quadrupole interaction (field gradient) in hemin and have shown that the contributions from valence electrons, while of the same order of magnitude, is found to be of opposite sign to experiment [6]. This is not very surprising because the electronic configuration around the iron atom comes out close to spherical and small changes in the population of orbitals of one angular character as compared to others lead to reversal of sign of the field gradient.

* Supported by a grant from the Heart and Lung Institute of the National Institutes of Health.

In this paper we report a new source of contribution to the field gradient which had not been included before, and which, as we shall show, leads to a contribution to the field gradient in the right direction to improve agreement with experiment and should indeed be included in the future in the analysis of field gradients in other biological compounds containing iron. This contribution is connected with the distortion of the core orbitals due to overlap effect with neighboring nitrogen, chlorine and carbon atoms, leading to small changes in the populations of core $2p$ and $3p$ orbitals of iron in different directions. These small changes, because of the large contributions to $1/r^3$from the iron core orbitals near the nucleus, can lead to a substantial contribution to the field gradient.

In Section 2 we discuss the evaluation of the perturbed orbitals and obtain the contributions to the field gradient. In the concluding section, remarks are made about the possible sources that could provide the balance between experiment and theory. A reestimation is made of the required relative contraction of in and out-of-plane d-orbitals that had been proposed earlier [5]. The equestion of the non-local contribution obtained in earlier work is also briefly examined.

2. Procedure

The field gradient at a nucleus is described by the operator [7]

$$q_{\mathrm{Fe}}^{op} = -\sum_i \frac{3\cos^2\theta_{\mathrm{Fe},i} - 1}{r_{\mathrm{Fe},i}^3} \tag{1}$$

where $\theta_{\mathrm{Fe},i}$ is the angle made by the radius vector of the electron with the z-axis which is chosen in this case along the tetragonal Fe–Cl axis. $r_{\mathrm{Fe},i}$ is the magnitude of the radius vector of the iron nucleus, and the overall negative sign arises from the sign of the electric charge. The summation over i refers to all the electrons of the molecule. On taking the expectation value of this over a determinantal function involving all occupied orbitals in the molecule, we get for the expectation value of q_{Fe}^{op}

$$q_{\mathrm{Fe}} = \langle \Psi | q_{\mathrm{Fe}}^{op} | \Psi \rangle = -\sum_j \left\langle \psi_j \left| \frac{3\cos^2\theta_{\mathrm{Fe}} - 1}{r_{\mathrm{Fe}}^3} \right| \psi_j \right\rangle . \tag{2}$$

ψ representing the determinant wave-function of the whole molecule, while the ψ_j refer to the occupied molecular orbitals. In principle, this should include all the core electrons as well as the valence electrons. In earlier work [2], only the valence electrons had been considered and the contributions from the core electrons on the iron were neglected. This was a consequence of the assumption that the core p orbitals on the iron atom were nearly spherical since they were not expected to take part in the bonding or be influenced significantly in any other way by the neighboring atoms. Part of their effect has been included through the antishielding factor, but the latter represents only the influence of the distortion of core electrons due to the local anisotropic potential from the incomplete shell of the iron atom. But the influence that the core electrons can have through conjugation with neighboring atoms has so far not been taken into account. However,

since the core orbitals have very different energy from the $3d$ orbitals, and because their distances from the neighboring nitrogen and carbon atoms are large, we do not expect significant covalent bonding. On the other hand, there can be a small amount of distortion of these orbitals through overlap, or equivalently through the influence of the Pauli principle. This effect has been studied earlier in ionic crystals in terms of its influence on hyperfine properties in a number of systems [8–11]. To include this core distortion effect, one has to use for the ψ_j in Eq. (2), the distorted $2p$ and $3p$ orbitals in hemin. These distortions of the core orbitals can be obtained by considering their overlaps with the orbitals of neighboring nitrogen, chlorine and carbon atoms, and making them mutually orthogonal. There are a number of ways one could achieve this orthogonality. We shall choose here the Schmidt procedure. Thus, the orthogonalized $3p_z$ orbital is given by:

$$\psi^{\text{ortho}}_{\text{Fe},3p_z} = \frac{\psi_{\text{Fe},3p_z} - \sum_{i,\text{A}} S_{i\text{A},3p_z}\chi_{i\text{A}}}{\sqrt{1 - \sum_{i,\text{A}} S^2_{i\text{A},3p_z}}} \tag{3}$$

where the summation over A runs over all the neighboring atoms, and the summation over i runs over all valence orbitals of atom A. In principle, however, the important ones are expected to be orbitals on the four nearest nitrogen atoms, the chlorine atom and to a lesser extent, the four pairs of carbon atoms on the pyrrole rings that are the nearest neighbors of the four nitrogen atoms. Similar equations hold for the orthogonalized $3p_x$, $3p_y$, $2p_x$, $2p_y$, and $2p_z$. The overlap integral $S_{i\text{A},3pz}$ is given by:

$$S_{i\text{A},3p_z} = \langle \chi_{i\text{A}} | \psi_{\text{Fe},3p_z} \rangle$$

where $\chi_{i\text{A}}$ is the ith atomic orbital on atom A. Using the orthogonalized orbitals in (4), we can show that the local contribution to the field gradient from the $3p$ core electrons is given by:

$$\begin{aligned} q^{\text{core}}_{\text{Fe}} &= \sum_{i=x,y,z} \langle \psi^{\text{ortho}}_{\text{Fe},3p_i} | q^{op}_{\text{Fe}} | \psi^{\text{ortho}}_{\text{Fe},3p_i} \rangle \\ &= \frac{1}{\left[1 - \sum_{i,\text{A}} S^2_{i\text{A},3p_z}\right]} \langle 3p_z | q_{\text{Fe}} | 3p_z \rangle \\ &\quad - \frac{1}{2\left[1 - \sum_{i,\text{A}} S^2_{i\text{A},3p_x}\right]} \langle 3p_z | q_{\text{Fe}} | 3p_z \rangle \\ &\quad - \frac{1}{2\left[1 - \sum_{i,\text{A}} S^2_{i\text{A},3p_y}\right]} \langle 3p_z | q_{\text{Fe}} | 3p_z \rangle . \end{aligned} \tag{5}$$

In deriving the above expressions, use has been made of the fact that:

$$\begin{aligned} \langle 3p_z | q_{\text{Fe}} | 3p_z \rangle &= -2\langle 3p_x | q_{\text{Fe}} | 3p_x \rangle \\ &= -2\langle 3p_y | q_{\text{Fe}} | 3p_y \rangle . \end{aligned} \tag{6}$$

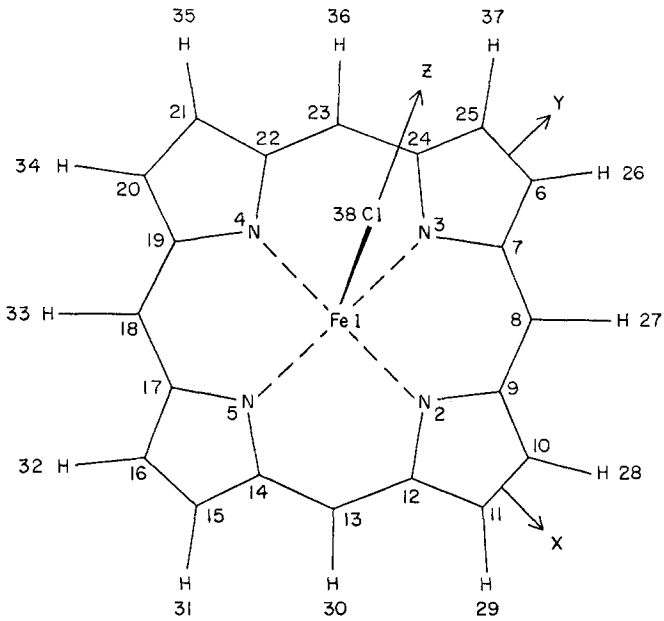

Fig. 1. Location of atoms in iron (III) porphyrin chloride (model used for hemin). The atoms are numbered consistently with those in the text

On including the influence of the nitrogen, chlorine and carbon atoms mentioned earlier, one gets:

$$q_{\mathrm{Fe}}^{\mathrm{core}} = q_x^{\mathrm{core}} + q_y^{\mathrm{core}} + q_z^{\mathrm{core}} \tag{7}$$

where q_x^{core}, q_y^{core}, q_z^{core} are respectively the contributions from the distorted $3p_x$, $3p_y$, $3p_z$ orbitals. Thus

$$\begin{aligned}
q_x^{\mathrm{core}} &= -\frac{\langle 3p_z | q_{\mathrm{Fe}} | 3p_z \rangle}{2\left[1 - \sum_{ij} S^2_{i\mathrm{N}(j),3p_x} - \sum_{ik} S^2_{i\mathrm{C}(k),3p_x} - \sum_{i} S^2_{i\mathrm{Cl},3p_x}\right]} \\
q_y^{\mathrm{core}} &= -\frac{\langle 3p_z | q_{\mathrm{Fe}} | 3p_z \rangle}{2\left[1 - \sum_{ij} S^2_{i\mathrm{N}(j),3p_y} - \sum_{ik} S^2_{i\mathrm{C}(k),3p_y} - \sum_{i} S^2_{i\mathrm{Cl},3p_y}\right]} \\
q_z^{\mathrm{core}} &= +\frac{\langle 3p_z | q_{\mathrm{Fe}} | 3p_z \rangle}{\left[1 - \sum_{ij} S^2_{i\mathrm{N}(j),3p_z} - \sum_{ik} S^2_{i\mathrm{C}(k),3p_z} - \sum_{i} S^2_{i\mathrm{Cl},3p_z}\right]}
\end{aligned} \tag{8}$$

where $\mathrm{N}_{(j)} = 2, 3, 4, 5$ and $\mathrm{C}_{(k)} = 7, 9, 12, 14, 17, 19, 22, 24$ are the four and eight N and C atoms respectively of heme as in Fig. 1. In carrying out the calculation of the contribution from all the iron core orbitals, we need to obtain only the values of the overlap integrals of the neighboring atomic orbitals with the iron $2p_{x,y,z}$ and $3p_{x,y,z}$ orbitals, since these are the only core orbitals that make finite contributions in the local approximation[1], a satisfactory one for the core electrons.

[1] For an explanation of the terms local, non-local and distant contributions to the field-gradient, see e.q. Ref. [5].

Fortunately, wavefunctions are available for iron atom in the configuration close to that in the metal [12], which is $3d^7 4s^1$, whereas the Mulliken population from our work leads to $3d^{6.7} 4s^{0.4} 4p^{0.6}$. While this is not exactly the same configuration for which the wavefunctions have been calculated for the metal, the radial parts of the $4s$ and $4p$ wave-functions are very similar, and the radial parts of the $3d$ orbitals are expected to be closer to that in the $3d^7 4s^1$ configuration than in the neutral $3d^6 4s^2$ iron. Consequently the core wave functions experience potentials similar to that in the configuration $3d^7 4s^1$ and the calculated cores in this configuration are adequate to use. Using these wavefunctions, the valence contribution to q has been recalculated, and is $-0.554\ a_0^{-3}$, which is somewhat smaller than the previous value of $-0.66\ a_0^{-3}$. This somewhat smaller result for the $3d^7 4s^1$ configuration as compared to the neutral atom $3d^6 4s^2$ can be understood by noting that the $4s$ electron has a larger density in the inner regions of the atom and therefore provides more shielding for the $3d$ orbitals. In obtaining the contributions from the $3p$ and $2p$ cores we need the overlap integrals $S_{iA,3p_j}$ and $S_{iA,2p_j}$ where

$$S_{iA,3p_j} = \langle \chi_{iA} | \chi_{3p_j} \rangle$$

and

$$S_{iA,2p_j} = \langle \chi_{iA} | \chi_{2p_j} \rangle \qquad (j = x, y, z)\,. \tag{9}$$

Table 1 gives the overlap integrals of the orbitals of $N_{(2)}$, $C_{(9)}$ and Cl with the Fe $2p$ and $3p$ orbitals. For the orbitals on nitrogen, chlorine and carbon atoms, the analytic Hartree-Fock orbitals given by Clementi [13] have been used. The important overlaps involving the other nitrogen and carbon atoms noted in Fig. 1 can be obtained from the numbers in Table 1 through application of symmetry operations. Using these, one gets from Eq. (7) for the distorted $3p_x$, $3p_y$ and $3p_z$ core states:

$$\begin{aligned} q_x = q_y &= +(21.903 + 0.291 + 0.028 + 0.0076)\, a_0^{-3} \\ q_z &= -(43.806 + 0.085 + 0.006 + 0.283)\, a_0^{-3} \end{aligned} \tag{10}$$

where the first term in each of the $q_i (i = x, y, z)$ is the field gradient from the undistorted cores, the second term is the contribution due to overlaps with nitrogen, the third from overlaps with carbon and the fourth term due to overlaps with chlorine. It is seen that q_z is smaller in magnitude and opposite in sign to the combined q_x and q_y contribution. This is understandable since all the $3p$ core orbitals on iron are being repelled by the orbitals of nitrogen, carbon and chlorine atoms, leading to greater concentration near the Fe nucleus and the effect of the overlap of the $3p_z$ orbital of iron with chlorine is more than compensated by the effect of the larger number of equivalent nitrogen atoms which overlaps more strongly with the $3p_x$ and $3p_y$ orbitals of Fe than with the $3p_z$. Therefore, one gets for the net result from the $3p$ electrons:

$$q_{Fe}^{core} = (0.497 + 0.050 - 0.267)\, a_0^{-3} = +0.280\, a_0^{-3} \tag{11}$$

where $+0.497\, a_0^{-3}$, $+0.050\, a_0^{-3}$, and $-0.267\, a_0^{-3}$ are respectively the contributions from the overlaps with the nitrogen, carbon and chlorine atoms.

Table 1. Overlap integrals between valence orbitals of $N_{(2)}$, $C_{(9)}$, and Cl with Fe $3p$ orbitals

		Fe $3p_x$	Fe $3p_y$	Fe $3p_z$	Fe $2p_x$	Fe $2p_y$	Fe $2p_z$
$N_{(2)}$	2s	0.0336	0	-0.0074	-0.0013	0	0.0003
	$2p_x$	0.0598	0	-0.0168	-0.0028	0	0.0008
	$2p_y$	0	-0.0159	0	0	0.0007	0
	$2p_z$	-0.0168	0	-0.0122	0.0008	0	0.0005
$C_{(9)}$	2s	0.0058	0.0022	-0.0009	-0.00021	-0.00008	0.00003
	$2p_x$	0.0137	0.0066	-0.0028	-0.00059	-0.00028	0.00012
	$2p_y$	0.0066	-0.0007	-0.0011	-0.00028	0.00003	0.00004
	$2p_z$	-0.0028	-0.0011	-0.0028	0.00012	0.00005	0.00012
Cl	3s	0	0	-0.0333	0	0	0.0012
	$3p_x$	0.0187	0	0	-0.0008	0	0
	$3p_y$	0	0.0187	0	0	-0.0008	0
	$3p_z$	0	0	-0.0731	0	0	0.0035

The net $3p$ core contribution of $0.28\, a_0^{-3}$ is to be compared with the local valence contribution $q_{\mathrm{val}}^{\mathrm{local}} = -0.554\, a_0^{-3}$. This local contribution from the valence orbitals had an additional factor [2] to be multiplied with, namely, the shielding which is 0.68. We do not have a comparable shielding factor here for the $3p$ core-contribution because the only orbitals that are internal to these are the $1s$, $2s$, and $2p$ orbitals, and not contribute significantly to the shielding factor[2].

It is clear then that the $3p$ cores make a significant contribution, opposite in sign to the earlier theoretical value, which is in the direction of improved agreement with experiment. Its magnitude is almost 75% of the local valence contribution after incorporating the shielding factor and also of the experimental value. The contribution to q due to $2p$ core orbitals is $2.13 \times 10^{-4}\, a_0^{-3}$, about 10^{-3} of the $3p$ core contribution. This small value is a consequence of the much smaller overlap of $2p$ orbitals of iron with the orbitals of neighboring atoms. In the next section, the consequences of the core contribution calculated here will be discussed.

[2] We have made this assumption on the basis that the $1s$, $2s$, and $2p$ orbitals were found to be in effect in antishielding calculations on Fe^{+3} ion due to an external point charge (see Ref. [14]). The $3p$ orbital is fairly external to the $2p$ orbitals, but perhaps not as external as the point charge in γ_∞ calculations, so the analogy may not be strictly justified. It would be desirable to test this point quantitatively, but this would be too complicated and beyond the scope of the present work and would not change our conclusions too significantly.

3. Discussion

From the results in the last section it appears that the core orbitals do provide a very significant contribution and in fact subtract off about 70% of the local valence contribution, making the net result only a third of the latter. The disagreement between experiment and theory is thus markedly reduced, but not enough to provide complete agreement. Further, there is also the non-local contribution [5] consisting of terms of the type:

$$q^{\mathrm{Cl}}_{\text{non-local}} = \langle \chi_{3p_z}(\mathrm{Cl}) | q_{\mathrm{Fe}} | \chi_{3d_{z^2}}(\mathrm{Fe}) \rangle$$

which have been evaluated only approximately before because of the difficulty in incorporating antishielding effects adequately in the overlap region of the two atoms, only the upper limit having been taken in previous work. The reformulation of this non-local contribution to include the antishielding effect more correctly requires substantial additional effort, although it is not beyond the realm of possibility, using a method similar to one that has proved quite adequate for the study of the influence of core polarization on hyperfine effects [11]. However, since most likely it is at present seriously overestimated, for the time being we will not include the non-local effect in the following considerations.

Using the core and local valence contributions we then obtain the coupling constant $e^2qQ(\mathrm{Fe}^{57m}) = -0.156$ mm/sec in comparison with the earlier [2] local valence contribution of -0.74 mm/sec and the experimental value of 0.76 mm/sec. Since we now have a smaller departure from experiment, this leads, using the same procedure as in previous work [5], to a smaller contraction ratio χ for the $\langle 1/r^3 \rangle$ from in-plane and out-of-plane $3d$ orbitals, namely

$$\chi = \frac{\langle 1/r^3 \rangle_{d_{xy}, d_{x^2-y^2}}}{\langle 1/r^3 \rangle_{d_{xz}, z^2}} = 1.13$$

instead of the previous value [5] of 1.34. While the difference from unity is now substantially smaller, it is still important to remember that the departure of this contraction ratio from unity remains to be explained. To understand the source of contraction, one has to improve the molecular orbital treatment to introduce greater in-plane and out-of-plane flexibility, and perhaps also include configuration interaction. However, the important result of the present work is that there is a significant contribution from the core electrons that has to be incorporated in future work in heme and other organic compounds containing iron.

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