Core-Electron Contributions to Fe$^{57m}$ Nuclear Quadrupole Interactions in Hemin*

Jane C. Chang and T. P. Das
Department of Physics, State University of New York, Albany, New York

Dennis Ikenberry
Department of Physics, California State College at San Bernardino

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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 $3p_{z,r}$ 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 hemin

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.

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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 question 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]

$$q_{Fe}^{\sigma^p} = -\sum_i \frac{3 \cos^2 \theta_{Fe,i} - 1}{r_{Fe,i}^3}$$ (1)

where $\theta_{Fe,i}$ 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. $r_{Fe,i}$ 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 $q_{Fe}^{\sigma^p}$

$$q_{Fe} = \langle \psi | q_{Fe}^{\sigma^p} | \psi \rangle = -\sum_j \left\langle \psi_j \left| \frac{3 \cos^2 \theta_{Fe} - 1}{r_{Fe}^3} \right| \psi_j \right\rangle .$$ (2)

$\psi$ representing the determinant wave-function of the whole molecule, while the $\psi_j$ 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,