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NUCLEAR HYPERFINE INTERACTION OF Fe IN CHLORO-HEMIN

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Résumé. — L'éclatement nucléaire hyperfin de l'ion ferrique dans la chlorohémine a été étudié théoriquement en calculant le gradient de champ électrique au noyau de fer à l'aide d'orbitales moléculaires multielectroniques construites dans le cadre des atomes qui se recouvrent. On montre que pour arriver aux principales contributions il faut considérer dans notre cas au moins les Cl- voisins, quatre atomes N et les huit atomes C les plus proches. La distorsion de la distribution de la charge du fer provient principalement des ligands chlore. La distorsion due aux atomes d'azote voisins produit des effets comparables et annule partiellement la contribution du chlore. Utilisant les données structurales de RX de Koenig, on a calculé l'éclatement hyperfin nucléaire du fer dans la chlorohémine dû aux effets de recouvrement et on a trouvé $+0.44$ mm/s ; le signe est correct et la valeur représente environ $57\%$ de la valeur expérimentale, $+0.78$ mm/s, observée par Johnson, Gonser et Grant, Shulman et Wertheim.

Notre calcul montre que le recouvrement dû aux électrons $2p^2$ des Cl les plus proches produit des effets importants sur l'éclatement hyperfin du fer. Ceci révèle qu'il existe un fort lien direct entre l'ion fer et les plus proches C dans la chlorohémine. Les effets des dipôles induits sur le chlore et les azotes ont aussi été étudiés par des méthodes autocohérentes. En tenant compte de ces effets, l'éclatement est réduit à $+0.14$ mm/s, si l'on prend pour la polarisation de Cl$^-$ une valeur aussi élevée que $2.97\,\text{Å}$. Par contre avec une faible polarisation de Cl$^-$ ($1\,\text{Å}$), la valeur calculée est remarquablement améliorée et devient $+0.79$ mm/s, en accord avec les expériences.

Abstract. — The nuclear hyperfine splitting of ferric iron in chloro-hemin has been studied theoretically by estimating the electric field-gradient at the iron nucleus employing the multi-electron molecular orbitals constructed in the frame-work of the overlapping atoms. It is shown that one must take into account as least the neighbouring Cl$^-$, four N's and eight nearest C's in our case to arrive at the most dominant contributions. The distortion of the iron charge distribution due to the chlorine ligand has been found to produce the dominant effect. The distortion due to the neighbouring nitrogen atoms produce comparable effects and partly nullify the chlorine contribution. Using the Koenig's X-ray structure data, the calculated nuclear hyperfine splitting of Fe in chloro-hemin due to the overlap effects has been obtained to be $+0.44$ mm/s which is of correct sign and about $57\%$ of the experimental value $+0.78$ mm/s as observed by Johnson, Gonser and Grant, and Shulman and Wertheim.

Our calculations show that the overlap due to the $2p^2$ electrons of the nearest C's produce important effects on the hyperfine splitting of Fe. This reveals that there exists a strong direct link between the iron ion and the nearest C's in chloro-hemin. The effects of the induced dipoles at chlorine and nitrogens have also been investigated by self-consistent methods. Inclusion of these effects reduce the splitting to $+0.14$ mm/s if the polarizability of Cl$^-$ is taken to be as large as $2.97\,\text{Å}$ whereas it improves the result drastically to $+0.79$ mm/s, in agreement with the experiments, if the polarizability of Cl$^-$ is assumed to be small ($1\,\text{Å}$).

Hemoglobins and the related compounds have recently been studied extensively by several groups [1-8]. Weissbluth and Maling [6] have interpreted the Mössbauer spectra of several derivatives of hemoglobin to understand the qualitative features of the quadrupole splitting. The theoretical investigation for the
asymmetry of the Mössbauer spectrum in chlorohemin has been investigated by Blume [2] and the Mössbauer isomer shift has been studied by Moutsos, Adams and Sharma [8]. The calculations of the nuclear hyperfine splitting of Fe in chlorohemin has been made by Han, Rettig, Ikenberry and Das [7] using the extended Hückel approximation. The hyperfine splitting, calculated by Han et al., has been found to be of opposite sign compared to the experimental result [3-5] and thus require further theoretical study.

We intend to inform an estimate of the nuclear hyperfine splittings of Fe$^{3+}$ in chlorohemin by extending the method used by one of us [9, 10] for evaluating the electric field-gradients (EFGs) in nonmetals. The multi-electron wave functions have been constructed in accordance with the Hund-Mulliken-Van Vleck [11] molecular orbital linear combination of the atomic orbitals involving overlap effects. The case of hemin is difficult in the sense that many more atoms (and electrons) surrounding the Fe are required to be taken into account than just the ligands to obtain the molecular orbitals. We show that the calculated splitting due to the overlap effects is of right sign and right order of magnitude in view of the experimental observations made by Johnson [3], Gonser and Grants [4] and Shulman and Wertheim [5].

The susceptibility and paramagnetic resonance measurements [12] have established that the Fe$^{3+}$ ion in chlorohemin carries the high spin $S = \frac{3}{2}$. This directs us to take the $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5$ electrons on the Fe$^{3+}$ ion in forming the molecular orbitals. Also, we take $3s^2$ and $3p^6$ orbitals of Cl$^-$, $2s^2$ and $2p^3$ orbitals of N and $2s^2$ and $2p^5$ orbitals of C in the linear combination of atomic orbitals to construct the molecular orbitals. As will be clear later, it is required to take account of only the neighbouring Cl$^-$, four N's and eight nearest C's in our case to obtain the most important contributions. The one-electron molecular orbitals $\psi_i$ are the antibonding (ab) and bonding (b) orbitals given by [9, 10]

\[
\psi_i = \left\{ \begin{array}{ll}
\psi_{a,b}^{\alpha} &= N_{\alpha}(\beta) S_{\alpha,\beta}(g) S_{\alpha,\beta}(a) \psi_{a,b}(a,\beta) \\
\psi_{a,b}(a,\beta) &= \chi_{a,b}(a,\beta)
\end{array} \right.
\]

where $\alpha$ designates the quantum numbers $n' L' M'$ of Fe$^{3+}$ orbitals and $\beta(g)$ the quantum numbers $nLM$ of the orbitals of the neighbouring atoms located at the site $g$. The parameters $S_{\alpha,\beta}(a,\beta)$ are the matrix elements $\langle \chi_{a,b}(a) | \chi_{a,b}(\beta) \rangle$ and $N_{\alpha}$ is the normalization constant.

Forming the many-electron wavefunction in the Hartree-Fock approximation as a Slater determinant of one electron molecular orbitals, the EFG due to the electrons is given by

\[
q_{ab} = e \sum_i e_i \langle \psi_i | (3 \cos^2 \theta_i - 1)/r_i^3 | \psi_i \rangle
\]

where $e$ is the electron charge (including sign) and $e_i$ is the number of electrons in the molecular orbital $\psi_i$. Incorporating the effects of the Sternheimer shielding and taking account of the charges on the nuclei of the surrounding atoms under consideration, the total contribution to the EFG (denoted by $q$) may be written as [9, 10, 13]

\[
q = (1 - R) (q_a^0 + q_b^0) + (1 - \gamma_a) (q_a^0 + q_b^0 + q_a^0)
\]

where $(1 - R)$ and $(1 - \gamma_a)$ are the Sternheimer shielding factors; $q_a^0, q_b^0$ and $q_a^0$ are the «local», «non-local» and «distant» contributions arising from the antibonding orbitals whereas $q_{ab}^0$ is the (distant) contribution due to the bonding orbitals; $q_a^0$ is the contribution from the nuclei of the surrounding atoms under consideration. The expressions for $q_a^0$, etc., in eq. (3) are similar to those obtained in ref. [13] except that they are more involved since many more atoms contribute to the results than just the nearest neighbours.

As for the calculations we have restricted (as mentioned above) the surrounding atoms to the Cl$^-$, the four N's and the eight nearest C's in order that the calculations remain manageable and still give the dominant contributions. The required atomic wavefunctions of Fe$^{3+}$, Cl$^-$, N and C taken for our calculations are those of Clementi [14]. The overlap and two-center integrals involved in the local, etc., expressions are evaluated by making use of a general expression [15] of the Löwdins $\alpha$-function.

The calculated EFG components have been tabulated in Table I using the X-ray structure parameters of Koenig [16]; the contributions arising from various Fe-orbitals are separately shown (whenever possible) for the four neighbouring N's, Cl$^-$ and eight nearest C's for the purposes of comparison. The most dominant contribution comes from the N's, next from Cl$^-$ and from C's. Other atoms in hemin are farther away and give only a small contribution. Taking $1 - R = 0.68$ [17] and $1 - \gamma_a = 10 \times 14$ [18], we obtain the total EFG as $q = +7.189 \times 10^{14}$ esu which yields the quadrupole splitting

\[
\Delta E = \frac{e q}{2} = +0.44 \text{ mm/s}
\]

(using $q = +0.20$ [10] b for Fe) which is of correct sign and about 57 per cent of the experimental result [3-5] $0.78 \pm 0.03$ mm/s. Our results may also be compared with the previously calculated value [7]

\[
\Delta E = - 1.47 \text{ mm/s}
\]

using the extended Hückel approximation. Considering the approximate nature of our starting wavefunctions, the agreement with the experiment is remarkably good. Our rough estimates indicate that further improvements may be made if one also includes the contributions from the other neighbouring atoms.

Since in hemin the iron is in the state Fe$^{3+}$ and the chlorine in the state Cl$^-$ it is expected that these ions will induce the polarizations in the system. Thus, it is worthwhile to consider the effects of the induced
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Dipoles at Cl⁻ and nearest nitrogens no the electric field-gradient at iron. We use the self-consistent method of calculating [19] the induced dipoles on Cl⁻ and four nitrogens neglecting the induced dipoles on the remaining atoms. We find that for the polarizability values, α(N) = 1.13 Å³ and α(Cl⁻) = 2.97 Å³ the splitting reduces to +0.14 mm/s, retaining the correct sign. If, however, α(Cl⁻) is taken as 1 Å³ while keeping α(N) constant (1.13 Å³) one obtains the splitting as +0.79 mm/s, in agreement with the experimental value. Though it is difficult to say what value of α(Cl⁻) is appropriate for heme, it looks that the value 2.97 Å³ for α(Cl⁻) is somewhat large and, therefore, good agreement with the reduced value of α(Cl⁻) is encouraging.

Precise analysis of our results reveal that the distant 3p-orbitals of Fe is dominant (see Table I). In the previous calculations of EFG by Han et al. [7] in heme such contributions gave zero result since the 3p-orbitals were isotropic in their model. We expect that our results will give impetus to the more detailed molecular orbital calculations (such as self-consistent Hartree-Fock calculations) in which the particular emphasis will be placed on including the effects of 3p-iron orbitals.

<table>
<thead>
<tr>
<th>Field-gradient Components</th>
<th>Fe-orbital</th>
<th>N</th>
<th>Cl⁻</th>
<th>C</th>
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<tr>
<td></td>
<td>3d</td>
<td>1.313</td>
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<td></td>
<td>(total)</td>
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References