Theoret. chim. Acta (Berl.) 30, 45—58 (1973)

Molecular Orbital Structure, Mössbauer Isomer Shift, and Quadrupole Splitting in Iron Complexes*

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Received January 18, 1973

Molecular orbital calculations are made on six iron complexes, using iterative Hückel methods and, where required for proper description of spin states, a spin-projected semi-empirical configuration interaction (CI). Many integrals are avoided in the CI studies by making direct calculation of energy differences between states. From the calculations are obtained charge and spin bond order matrices, dipole moments, and atomic orbital charges. These quantities are used to calculate charge densities at the Fe nucleus, nuclear quadrupole splittings, and spin populations. From calculations of all six complexes we estimate an Fe^{57} Mössbauer isomer-shift calibration $\alpha \equiv \Delta\delta/\Delta\varrho(0) = -0.31$ to $-0.38 a_0^3$ mm/sec.

Mit Hilfe iterativer Hückel-Methoden werden MO-Rechnungen für sechs Eisenkomplexe durchgeführt. Wo es für die Beschreibung der Spinzustände notwendig ist, wird nach einem CI-Verfahren mit Spinprojektion gearbeitet. Durch direkte Berechnung von Energiedifferenzen zwischen den einzelnen Zuständen werden viele Integrale in den CI-Berechnungen vermieden. Aus den Rechnungen erhält man die Matrizen der Ladungs- und Spin-Bindungsordnungen, Dipolmomente und AO-Ladungsverteilungen. Diese Größen werden zur Berechnung der Ladungsdichte am Fe-Kern, der Kernquadrupolaufspaltung und der Spinpopulation verwendet. Aufgrund der Berechnungen aller sechs Komplexe wird die Fe^{57}-Mößbauer-Isomerieverschiebung auf $\alpha \equiv \Delta\delta/\Delta\varrho(0) = -0{,}31$ bis $-0{,}38 a_0^3$ mm/sec geschätzt.

Introduction

The essential role of iron complexes in biological processes makes particularly interesting and important a good understanding of the electronic structures of such complexes. This understanding can to some extent be obtained experimentally, but there remain many questions which theoretical studies might resolve. Since the complexes involve to varying extents covalent binding between iron and ligands and charge rearrangements within the ligand structure, a theoretical description cannot justifiably be limited to an iron atom and its

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* Supported in part by U.S. National Science Foundation Grant GP-31373X, in part by an award from the Biomedical Sciences Support Grant at the University of Utah (U.S. Public Health Service Grant RR 07092), and in part by the Centre Européen de Calcul Atomique et Moléculaire, Orsay, France.

** Supported at the Centre Européen de Calcul Atomique et Moléculaire, Orsay, France by a fellowship (No. 531) of the European Molecular Biology Organization and by the French Government through Monsieur le Ministre des Affaires Etrangères, de la République Francaise (No. 12778 CT/b/1).

immediate neighbors. Moreover, the three-dimensional structure of the complexes contraindicates approximations which do not include all relevant valence electrons.

Rigorous all-valence-electron treatments of systems as large as typical iron complexes are prohibitive in cost, even at the self-consistent-field (SCF) level of approximation. It is even extremely costly to pursue semi-empirical antisymmetrized molecular orbital theory or approximations based on neglect of differential overlap, such as the CNDO/2 method. The key simplification appearing to permit calculation at reasonable cost is the avoidance of constructing an explicit antisymmetrized many-electron wavefunction; methods in this category include those of the Hückel type and the "multiple-scattering $X\alpha$ method" of Johnson *et al.* [1]. The present paper describes theoretical studies based on an iterative extended Hückel method previously described by one of the authors [2]. The iterative feature gives the method SCF character, and "extended" indicates the application to all valence electrons.

The Hückel model is inadequate to distinguish spin eigenstates and to calculate energy differences between them, and many iron complexes exist in "high-spin" states necessitating the use of singly-occupied molecular orbitals (MO's). For such problems we supplemented the Hückel calculations by proceeding to a limited configuration interaction (CI), simplifying the computations by using the Hückel SCF MO's to construct configurations, by calculating only energy differences, and by using approximate integrals.

In semi-empirical studies such as that reported here, the success of the description should rest on the capability for inter-relating a variety of data on a variety of systems. We show here the extent to which our studies agree with conventional spectral data, such as ligand field splittings, and also with Mössbauer data, such as isomer shifts and quadrupole splittings. By comparing calculations for six different complexes, we are able to obtain information regarding the calibration constant relating the Mössbauer isomer shift to the charge density at the iron nucleus.

Hückel Calculations

Iterative extended Hückel calculations were carried out by methods described in detail previously [2]. The Hückel one-electron Hamiltonian H was assumed to have diagonal elements $H_{aa} = -\alpha_a - q_a \Delta\alpha_a$, where α_a is the "α" parameter for atomic orbital a (of real form) in a neutral atom, q_a is the net charge of the atom at which orbital a is centered, and $\Delta\alpha_a$ is an additional parameter controlling the variation of H_{aa} with net atomic charge. The off-diagonal elements H_{ab} were determined from H_{aa} and H_{bb} by the Cusachs approximation [3] $H_{ab} = S_{ab}(1 - \frac{1}{2}|S_{ab}|)(H_{aa} + H_{bb})$. Here S_{ab} is the overlap integral of atomic orbitals a and b, calculated assuming Slater-type orbitals (STO's). In evaluating H_{ab}, all operations are performed in a coordinate system passing through the orbital centers so as to retain full invariance with respect to rotation of the molecule in the coordinate system.

Iterations were carried out until the occupied-orbital solutions of the matrix equation $(\boldsymbol{H} - E_i\boldsymbol{S})\,\boldsymbol{c}_i = 0$ were consistent with the net atomic charges used in calculating $\boldsymbol{H}$. Here E_i is the orbital energy of the molecular orbital whose atomic-orbital coefficients are represented by the vector c_i. The overlap matrix S is built from the S_{ab} as already defined. The iterative process must be sophisticated enough to overcome the strong nonlinearity of the theory; we use a combination of damping and second-order extrapolations and thereby ordinarily achieve convergence to ± 0.01 units in atomic charge in five to ten iterations. The net atomic charges are obtained by apportioning exactly-computed overlap charges among the atoms involved, in a fashion which preserves the projection of the charge centroid on the intercenter line. This causes the atomic charges to be approximately consistent with computed dipole moments and to reflect the actual charge distribution far better than would an equal division of overlap charge.

The Hückel-method output includes orbital energies and corresponding MO's, the bond-order matrix, net atomic and orbital charges, and the molecular dipole moment. All programming is in FORTRAN, and is set up for a Univac 1108 system. The Hückel program, the CI program described in the next section, and all data storage for calculations involving a maximum of 60 atomic orbitals fit into approximately 50,000 words of core and run without the use of peripheral equipment for intermediate storage. Typical SCF computation times for the iron

Table 1. Approximate molecular-orbital calculations of small fluorine compounds

Molecule[a]	Method[b]	Energy sequence[c] (valence orbitals)	Dipole moment (D)[d]	Ionization potential (eV)
FH	CNDO/2	$\sigma^2 \sigma^2 \pi^4$	1.86	15.77
	INDO		1.98	21.14
	IEHT		2.36	14.61
	expt.		1.82	19.96
F_2	CNDO/2	$\sigma_g^2 \sigma_u^2 \pi_u^4 \sigma_g^2 \pi_g^4$	0	15.7
	INDO		0	19.19
	IEHT		0	17.68
	expt.		0	18.32
CF_2	CNDO/2	$a_1^2 b_2^2 a_1^2 \underline{b_2^2 a_1^2 b_1^2} a_2^2 b_2^2 a_1^2$	0.53	—
	INDO	$\underline{b_2^2 a_1^2 b_1^2}$	0.26	—
	IEHT	$\underline{b_1^2 a_1^2 b_2^2}$	0.75	14.21
NF_2	CNDO/2	$a_1^2 b_2^2 a_1^2 \underline{b_1^2 a_1^2 b_2^2} a_2^2 b_2^2 a_1^2 b_1$	−0.12	—
	INDO	$\underline{b_1^2 a_1^2 b_2^2}$	−0.38	—
	IEHT	$\underline{b_2^2 b_1^2 a_1^2}$	−0.21	13.03
OF_2	CNDO/2	$a_1^2 b_2^2 a_1^2 \underline{b_1^2 a_1^2 b_2^2} a_2^2 b_2^2 a_1^2 b_1^2$	−0.21	—
	INDO	$\underline{b_1^2 a_1^2 b_2^2}$	−0.40	—
	IEHT	$\underline{b_2^2 a_1^2 b_1^2}$	−0.61	15.32
	expt.		±0.30	—
FH_2	CNDO	$\sigma_g^2 \sigma_u^2 \pi_u^4 \sigma_g$	0	—
	INDO		0	—
	IEHT		0	1.89

[a] Geometries: HF, $R = 0.917$ Å; F_2, $R = 1.435$ Å; CF_2, $R_{CF} = 1.32$ Å, $\measuredangle_{FCF} = 104°$; NF_2, $R_{NF} = 1.35$ Å, $\measuredangle_{FNF} = 104°$; OF_2, $R_{OF} = 1.41$ Å, $\measuredangle_{FOF} = 104°$; FH_2, $R = 0.92$ Å, $\measuredangle_{HFH} = 180°$.

[b] CNDO/2 and INDO calculations and experimental data as reported by Pople and Beveridge (Ref. [4]); IEHT are iterative extended Hückel calculations of this work.

[c] Energy sequences agree for all methods except where underlined portions are repeated.

[d] Dipole moment of AB or AB_2 molecules is + in the direction A^-B^+ or $A^-B_2^+$.

Table 2. Orbital parameters for Hückel and CI calculations: ζ = STO screening parameters; α, $\Delta\alpha$ = Hückel energy parameters; h = atomic core energy; γ = single-center repulsion energy

		ζ	α	$\Delta\alpha$	h	γ
Fe	3d	2.87	7.0	8	135	23.5
	4s	1.40	7.5	8	56	6.0
	4p	1.40	6.5	8	64	8.0
F	2s	2.60	34.0	18	130	16.0
	2p	2.60	18.5	15	115	14.0
O	2s	2.275	33.0	15		
	2p	2.275	14.0	15		
N	2s	1.95	30.0	12		
	2p	1.95	11.5	12		
C	2s	1.625	25.0	11		
	2p	1.625	10.0	11		
H	1s	1.20	11.6	14		

Table 3. Geometries used for iron complexes. Principal symmetry axis taken in z direction; octahedral ligands also in $\pm z$ and $\pm y$ directions

$Fe(CN)_5NO^{-2}$	Symmetry C_{4v}, data based on $Na_2Fe(CN)_5NO \cdot 2H_2O$[a] Cartesian coordinates (Å): Fe(0, 0, 0), N_1(0, 0, 1.63), O(0, 0, 2.76), C_1(0, 0, −1.91), N(0, 0, −3.07), C(±1.90, 0, −0.20), C(0, ±1.90, −0.20), N(±3.05, 0, −0.32), N(0, ±3.05, −0.32)
$Fe(CO)_5$[b]	Symmetry D_{3h} $R_{Fe-C} = 1.84 \pm 0.03$ Å; $R_{C-O} = 1.15 \pm 0.04$ Å All R_{Fe-C} equal; all R_{C-O} equal. Trigonal bipyramid; C_1, C_2, C_3 equatorial; C_4, C_5 polar
$Fe(CN)_6^{-3}$	Symmetry O_h, data based on $K_3Fe(CN)_6$[c] $R_{Fe-C} = 1.89$; $R_{C-N} = 2.157$
$Fe(CN)_6^{-4}$	Symmetry O_h, data based on $K_4Fe(CN)_6 \cdot 3H_2O$[d] $R_{Fe-C} = 1.91$; $R_{C-N} = 2.157$
FeF_6^{-3}	Symmetry O_h, data based on FeF_3[e] $R_{Fe-F} = 1.92$ Å
FeF_6^{-4}	Symmetry O_h, data based on $KFeF_3$[f] $R_{Fe-F} = 2.06$ Å

[a] Wyckoff, R. W. G.: Crystal structures, second ed., Vol. 3, p. 623. New York: Interscience 1965.

[b] Tables of interatomic distances and configurations in molecules and ions, ed. L. E. Sutton. London: Chemical Society 1958.

[c] Kohn, J. W., Townes, W. D.: Acta crystallogr. **14**, 617 (1961).

[d] Wyckoff, R. W. G.: Crystal structures, second ed., Vol. 3, p. 687. New York: Interscience 1965.

[e] Tables of interatomic distances and configurations in molecules and ions, ed. L. E. Sutton. London: Chemical Society 1965.

[f] Wells, A. F.: Structural inorganic chemistry. Oxford: Oxford University Press 1962.

complexes reported here are 1–2 min. A Hückel program version handling up to 140 atomic orbitals and using intermediate drum storage and approximately 50000 words of core has also been implemented; a typical 130-orbital, 138-electron SCF calculation requiring 8 iterations ran in 12 min.

The calculations in this paper include all valence orbitals, i.e. $1s$ for H; $2s$ and $2p$ for C, N, O, and F; and $3d$, $4s$, and $4p$ for Fe. For H, C, N, and O, the orbital parameters α_a, $\Delta\alpha_a$, and ζ_a (the STO screening parameters) were taken from previous iterative Hückel calculations [2].

For fluorine, we used values of ζ_{2s} and ζ_{2p} calculated by Slater's rules, and chose α_a and $\Delta\alpha_a$ values after study of a set of six molecules: HF, F_2, CF_2, NF_2, F_2O, and H_2F. Starting from α_a and $\Delta\alpha_a$ values as reported in the literature [4], we made adjustments to optimize the consistency with the parameters already adopted for H, C, N, and O. Our criteria included the energy sequences of the MO's, the ionization potentials, and the dipole moments. Our calculations for the fluorine compounds, previous calculations, and experimental data are summarized in Table 1.

For iron, we used values of ζ_{4s} and ζ_{4p} as given for the neutral atom by Clementi and Raimondi [5]. Starting from ζ_{3d}, α_a and $\Delta\alpha_a$ values given by Zerner *et al.* [6], we made slight adjustments to fit the ligand field splittings for $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$, and to have the Fe $3d_t$ orbitals as major components of the highest occupied MO's for both compounds.

The orbital parameters for all atoms entering the Hückel calculations are listed in Table 2. The molecular geometries used for the iron complexes are given in Table 3.

CI Calculations

As even a limited CI study is expensive for large systems, and since our present needs were to characterize the MO structure and to intercompare different spin states, we confine attention to the calculation of energies relative to that of a "reference configuration". If the reference configuration has energy E_0, energies relative thereto can be obtained as eigenvalues of $H - E_0 S$, where H and S now refer to many-electron space-spin states of appropriate symmetries. As E_0 can be written in terms of the integrals occurring in the elements of H, the elements of $H - E_0 S$ will depend only upon the orbitals affected by passage from the reference configuration to the configurations actually used in H and S. The foregoing statements have been written carefully to avoid the implication that the reference configuration necessarily refers to a specific spin state; on the contrary, if different spin states are to be compared, it must be the same for all states and should be chosen to cause a maximum degree of integral cancellation.

The definition we have found most satisfactory for a reference configuration is that which results if we assume its singly-occupied orbitals are averaged over spin orientations. Letting $(i|h|j)$ refer to a matrix element of the one-electron part of the Hamiltonian between MO's i and j, letting $\langle i|j\rangle$ stand for a MO overlap integral, and letting $[ij|mn]$ stand for an MO electron repulsion integral in Mulliken notation

$$[ij|mn] = \int \phi_i^*(1)\,\phi_j(1)\,r_{12}^{-1}\,\phi_m^*(2)\,\phi_n(2)\,d\tau_1\,d\tau_2\,,$$

we have

$$E_0 = \sum_{i_0}(i_0|h|i_0) + \sum_{i_0<j_0}\left([i_0 i_0|j_0 j_0] - \tfrac{1}{2}(1 - <i_0|j_0>)\,[i_0 j_0|j_0 i_0]\right),$$

where the summations are over all electrons and $i_0(j_0)$ refers to the MO of the $i^{\text{th}}(j^{\text{th}})$ electron before antisymmetrization. The MO's may be doubly occupied, but distinct MO's are assumed orthogonal.

The many-electron states used in H and S are constructed by antisymmetrization and spin projection [7] of spinorbital products. As in the preceding paragraph, we assume the spatial orbitals to be chosen from a set of orthogonal MO's. The matrix elements of H and S can then be written in terms of spatial integrals and spin projection (Sanibel) coefficients [8]. If two configurations μ and ν have different MO occupancies, $S_{\mu\nu}$ will vanish, $(H - E_0 S)_{\mu\nu}$ will be identical with $H_{\mu\nu}$, which may be evaluated by existing formulas. The important point here is that $H_{\mu\nu}$ will depend only upon two-electron integrals containing MO's whose occupancy differs in configurations μ and ν, and therefore will at worst involve a number of integrals comparable to the number of electrons.

When μ and ν refer to configurations with the same spatial MO occupancy (μ and ν may differ in spin assignment), then $E_0 S_{\mu\nu}$ does not vanish and $(H - E_0 S)_{\mu\nu}$ can be simplified. Using the expression already given for E_0 and the published expressions for $H_{\mu\nu}$ and $S_{\mu\nu}$, one may derive

$$\begin{aligned}(H - E_0 S)_{\mu\nu} = C_k \Big[&\sum_i (i|h|i) - \sum_p (p|h|p) + \sum_{ir} \{[ii|rr] - \tfrac{1}{2}[ir|ri]\} \\ &- \sum_{pr} \{[pp|rr] - \tfrac{1}{2}[pr|rp]\} + \sum_{i<j} \{[ii|jj] - \tfrac{1}{2}[ij|ji]\} \\ &- \sum_{p<q} \{[pp|qq|] - \tfrac{1}{2}[pq|qp]\} \Big] + \sum_{l<m} (\tfrac{1}{2} C_k - C_{\bar{k}})\,[lm|ml]\end{aligned}$$

In this equation, summations of i and j range over electrons in MO's of μ which are unoccupied in the reference configuration; p and q summations are over electrons in reference MO's not occupied in μ; r ranges over electrons in MO's common to μ and the reference configuration; and l and m range over electrons in singly-occupied MO's of μ. The symbol C_k stands for the Sanibel coefficient appropriate to the spin state and the relative spin assignments of the MO's in μ and ν; when $C_{\bar{k}}$ occurs within a summation over l and m, it denotes the Sanibel coefficient which is appropriate after the spin assignments of electrons l and m are interchanged in configuration μ. The key feature of this equation for $(H - E_0 S)_{\mu\nu}$ is that very few integrals are needed for configurations differing little from the reference configuration in MO occupancy.

The integrals needed for the CI calculations were calculated using approximations of types common in semi-empirical MO theory, However, the large size of the molecules involved made it necessary to use relatively simple approximations and to be careful to obtain proper cancellation of long-range opposing electrostatic forces. Expanding each MO into atomic orbitals, the atomic-orbital integral $(a|h|b)$ is related to "core energies" h_a, h_b and to point charge nuclear-attraction energies e_a, e_b:

$$(a|h|b) = S_{ab}(1 - \tfrac{1}{2}|S_{ab}|)\,(h_a + h_b) - \tfrac{1}{2} S_{ab}(e_a + e_b)$$

Here h_a, h_b are input parameters, and $e_a = \sum_{b \neq a} Z_b/R_{ab}$, where the sum is over all atoms except that on which orbital a is centered, Z_b is the core charge of atom b, and R_{ab} is the distance between the center of orbital a and atom b. Note that the Cusachs approximation is used for the two-center contributions for the core energies, but that a normal Mulliken approximation [10], is used for the two-center nuclear attraction energies. The evaluation of $(a|h|b)$ must be carried out in a rotationally invariant manner.

Atomic-orbital electron repulsion integrals are also evaluated using a Mulliken approximation:

$$[ab|cd] = \tfrac{1}{2} S_{ab}\, S_{cd} \{[aa|cc] + [bb|cc] + [aa|dd] + [bb|dd]\} ,$$

and $[aa|bb]$ are evaluated by the modified point-charge formula of Mataga and Nishimoto [11]:

$$[aa|bb] = (R_{ab} + [2/(\gamma_a + \gamma_b)])^{-1} ,$$

where γ_a and γ_b are empirical parameters describing single-center electron repulsions for orbitals a and b.

After obtaining CI wavefunctions, charge and spin (i.e., first-order density) matrices were obtained for states of interest. The charge bond order matrix $\boldsymbol{P}$ is first generated in the MO basis. For a state formed from configurations Ψ_μ by $\sum\limits_{\mu} c_\mu \Psi_\mu$, the element P_{ij} is simply

$$P_{ij} = \sum_{\mu\nu} c_\mu^* c_\nu < \Psi_\mu | B | \Psi_\nu > ,$$

where B is the one-electron operator built from $|j\rangle\langle i|$. These one-electron matrix elements can be calculated from published spin-projection formulas [9]. After finding $\boldsymbol{P}$ in the MO basis, it is transformed to the atomic-orbital basis and presented as output.

Similar methods yield the spin bond-order matrix $\boldsymbol{Q}$, with the exception that the one-electron operator B is now spin-dependent, being built from $|j\rangle s_z \langle i|$, where s_z is the operator for the z component of the electron spin. Convenient formulas for spin-projected matrix elements of spin-dependent operators for wavefunctions built from orthogonal MO's had not been published, and we therefore had to derive such formulas by specialization of more general relationships [12]. These formulas will be reported elsewhere.

The CI calculations described here were carried out for the fluoride complexes FeF_6^{-3} and FeF_4^{-4}, and we therefore needed h_a and γ_a parameters for Fe and F. Using ionization potentials, atomic energy levels, and STO atomic electron-repulsion integrals as a guide, we adjusted the parameter values for maximum consistency with experimental data. The parameters as finally adopted are included in Table 2.

Isomer Shifts

The isomer shift in Mössbauer spectroscopy, δ, depends upon the electron density at the nucleus under study, $\varrho(0)$. Values of δ are proportional to changes in $\varrho(0)$ from a reference compound: $\delta = \alpha \Delta \varrho(0)$, where α is known as the calibration constant. We are concerned here with application to Fe^{57}. We may estimate isomer shifts from our MO calculations, using the approximation that atomic orbitals on other centers have no density at the Fe nucleus. As the

Fe $3d$ and $4p$ orbitals also vanish at the Fe nucleus, the only contributing atomic orbital in our calculations is Fe $4s$. However, the Fe inner-shell densities are also affected by the molecular structure and at least the Fe $3s$ contribution cannot be neglected. Following ideas developed by Flygare and Hafemeister [13], we estimate the Fe $3s$ contribution by considering its lack of orthogonality to the valence orbitals of neighboring ligands. This nonorthogonality can be interpreted as requiring a renormalization of the wavefunction, with a consequent change in the Fe $3s$ orbital density. We also consider differences in shielding associated with changes in the Fe $3d$ orbital occupancy.

The Fe $4s$ density at the nucleus is obtained by multiplying $|\psi_{4s}(0)|^2$ by $P_{4s,4s}$, its coefficient as given in the bond-order matrix. There is some uncertainty as to the optimum value of $|\psi_{4s}(0)|^2$. Walker *et al.* [14] give the value $2|\psi_{4s}(0)|^2 = 15\,a_0^{-3}$ calculated using the (nonrelativistic) Fermi-Segré-Goudsmit formula and a relativistic correction term $S'(Z)$ which is about 1.3 for iron [15]. This method of calculation assumes no screening of inner s electrons by an additional $4s$ electron. However, Blomquist *et al.* [16] report the smaller value $|\psi_{4s}(0)|^2 = 6.7\,a_0^{-3}$ for the electron density produced at the nucleus of an iron atom by a single $4s$ electron of configuration $3d^6 4s^1$, based on nonrelativistic Hartree-Fock calculations with the $S'(Z)$ correction. In the present work we use both values for comparison.

The Fe $3s$ density at the nucleus, including $3d$ shielding effects but before the nonorthogonality correction, is taken as

$$2|\psi_{3s}(0)|^2 = 138.2 - 1.762(\Sigma_{3d} P_{3d,3d} - 5)\,.$$

This formula is based on Hartree-Fock atomic-orbital values for various electronic configurations of Fe and its ions [17].

The nonorthogonality of Fe $3s$ to other orbitals has the effect of changing the coefficient of $|\psi_{3s}(0)|^2$ away from 2, even though the Fe $3s$ orbital is assumed to remain fully occupied. The effect can be calculated by orthogonalizing the Fe $3s$ orbital to the other occupied MO's. The results are invariant with respect to the orthogonalization procedure chosen, and we therefore found it simplest to achieve orthogonality through changes of the Fe $3s$ orbital only, leaving all other MO's unaltered. This approach eliminates approximations attendant upon the use of the symmetric orthogonalization procedures, and which are only marginally justified for the degree of overlap encountered in the complexes presently under study. We therefore write

$$\phi_{3s} = N\left[\psi_{3s} - \sum_{i \neq 3s} \langle \phi_i | \psi_{3s} \rangle\, \phi_i\right],$$

where

$$N = \left(1 - \sum_{i \neq 3s} |\langle \phi_i | \psi_{3s} \rangle|^2\right)^{-\frac{1}{2}},$$

the ϕ_i are occupied MO's and ψ_{3s} is the $3s$ Hartree-Fock atomic orbital.

Now the density at the Fe nucleus may be written

$$\begin{aligned}\varrho(0) &= P_{4s4s}|\psi_{4s}(0)|^2 + 2N^2|\phi_{3s}(0)|^2 \\ &= P_{4s,4s}|\psi_{4s}(0)|^2 + \frac{2}{1-A}|\psi_{3s}(0) - B\psi_{4s}(0)|^2\end{aligned}$$

where $A=\frac{1}{4}\sum_{ab} P_{ab} S_{a,3s} S_{3s,b}$ and $B=\frac{1}{2}\sum_{a} P_{4s,a} S_{a,3s}$. In using this expression for $\varrho(0)$, we assume that the overlap integrals are to be evaluated using Hartree-Fock atomic orbitals, as STO's give a qualitatively incorrect overlap with Fe 3*s*. We may then omit Fe 4*s* from the summations in A and B, as $S_{3s,4s}=0$. We have omitted the 1*s* and 2*s* contributions to $\varrho(0)$ because they are assumed to be constant for all the complexes under study.

Quadrupole Splitting

The Mössbauer quadrupole splitting ΔE_Q is proportional to the electric quadrupole moment Q of the Mössbauer nucleus and to the electric field gradient there, q: $\Delta E_Q=\frac{1}{2}e^2 qQ$. The field gradient is calculated here from contributions of the Fe 3*d* and Fe 4*p* orbitals, plus contributions from ligand orbitals estimated from the distribution of net atomic charge.

Complexes of symmetry O_h have no quadrupole splittings, while those of symmetry C_{4v} or D_{3h} have splittings given in the above-described approximation by

$$\Delta E_Q=\tfrac{1}{2}e^2 Q\left\{(1-R)\langle r^{-3}\rangle\left(\sum_{3d} P_{3d,3d} f_{3d}+\sum_{4p} P_{4p,4p} f_{4p}\right)\right.$$
$$\left.+(1-\gamma_\infty)\sum_a q_a(3z_a^2-r_a^2)/r_a^5\right\}.$$

The 3*d* and 4*p* summations are over the appropriate sets of Fe orbitals, the *a* summation is over all atoms other than Fe; and q_a, z_a, r_a are the net charge, *z* coordinate and distance (from Fe) of atom *a*. We actually limited the sum over *a* to the nearest neighbors of the Fe atom. The quantity $\langle r^{-3}\rangle$ is the common radial factor resulting from taking the expectation value of $(3z^2-r^2)/r^5$; angular factors needed for individual 3*d* and 4*p* orbitals of varying magnetic quantum number are indicated as f_{3d}, f_{4p}. These factors are $f_{3d\pm 2}=4/7$, $f_{3d\pm 1}=-2/7$, $f_{3d0}=-4/7$, $f_{4p\pm 1}=2/5$, $f_{4p0}=-4/5$. The quantities $(1-R)$ and $(1-\gamma_\infty)$ are Sternheimer shielding corrections [19]; $1-R$ represents the shielding effect experienced by charge on the Fe atom, while $1-\gamma_\infty$ gives the antishielding factor to be applied to charge far removed from the Fe atom. In this work $1-\gamma_\infty$ was assigned the value 10.1.

The major uncertainties in the calculation of ΔE_Q are the assignments of values to Q and $(1-R)\langle r^{-3}\rangle$. The value of $\langle r^{-3}\rangle$ should be expected to depend upon the electronic configuration of the Fe atom. The quantity $\Delta E_Q^0=\frac{1}{2}e^2 Q(1-R)\langle r^{-3}\rangle\frac{4}{7}$ has been measured by McNab *et al.* [20] in an Fe dimer, with the result $\Delta E_Q^0=4.05$ mm/sec. This dimer is interpreted as having Fe electronic configuration $3d^6$, for which $(1-R)\langle r^{-3}\rangle$ has been calculated to have the value 3.3 a.u. [21]. These data yield for the relevant state of Fe^{57} the value $Q=0.21$ barn, which was the value adopted in the present work. The literature, however, contains other estimates of Q ranging from 0.17 barn [22] to 0.41 barn [23].

The compound $\mathrm{Fe(CO)_5}$ has a calculated Fe electronic configuration $3d^6 4s^{0.08} 4p^{0.43}$, and we have assumed the 4*s* and 4*p* occupancy to have little effect on the value of $\langle r^{-3}\rangle$. We have consequently assumed that for $\mathrm{Fe(CO)_5}$

we may use $\Delta E_Q^0 = 4$ mm/sec, essentially the same value measured for a $3d^6$ configuration. However, our other compound with quadrupole splitting, $Fe(CN)_5NO^{-2}$, has a calculated Fe electronic configuration with a higher $3d$ occupancy, and this will lead to a reduction in $\langle r^{-3} \rangle$ [22] which we have accounted for by reducing ΔE_Q^0 by 10%.

Results and Discussion

In Table 4 we present calculated data indicating some features of the charge distributions in the six iron complexes under study. Two of these complexes, FeF_6^{-3} and FeF_6^{-4}, are largely ionic, while the remaining four complexes have considerably more covalent character. The fluoride complexes are "high-spin" compounds, and were studied by the CI method; for the other complexes only Hückel calculations were made. As is generally true of well-calibrated semi-empirical studies, the methods used here probably suffice to give qualitatively reasonable charge distributions in the occupied MO's. In Table 5 we give experimental and calculated values of quantities related to spectroscopic observations.

Let us start by considering the Mössbauer isomer shifts δ. Considerable previous work has dealt with the evaluation of isomer shifts and their relation to calculated charge densities $\varrho(0)$ at the Fe^{57} nucleus [24–35]. However, some of these studies differ from the present work in that they have not fully included the effect of changes in the Fe electronic configuration from one compound to another. Examining first the two fluoride complexes, we note that the δ and $\varrho(0)$ values correspond to a calibration constant $\alpha = \Delta\delta/\Delta\varrho(0) = -0.38\, a_0^3$ mm/sec, in qualitative agreement with the values -0.4 of Ingalls *et al.* [24] and -0.34 of Chappert *et al.* [25]. This α value differs substantially, however, from the

Table 4. Diagonal bond-order matrix elements P_{aa} and atomic charges of iron complexes. Data calculated by Hückel method except for the fluoride complexes, for which spin-projected CI was used. Atomic charges obtained using centroid projection method described in the text. Orientation of complexes in the coordinate system is specified in Table 3

P_{aa}	$Fe(CN)_5NO^{-2}$	$Fe(CO)_5$	$Fe(CN)_6^{-3}$	$Fe(CN)_6^{-4}$	FeF_6^{-3}	FeF_6^{-4}
$a = d_{x^2-y^2}$	1.10	1.30	1.05	0.95	1.33	1.23
$d_{3z^2-r^2}$	0.90	0.82	1.05	0.95	1.33	1.23
d_{xz}, d_{yz}	1.33	1.31	1.53	1.69	1.23	1.08
d_{xy}	1.83	1.30	1.53	1.69	1.23	2.00
s	0.10	0.08	0.11	0.15	0.15	0.14
p_z	0.22	0.17	0.23	0.24	0.15	0.13
p_x, p_y	0.20	0.26	0.23	0.24	0.15	0.13
Atomic charges						
	Fe: 0.27 N_1: -0.06 C_1: -0.16 C_{2-5}: -0.14	Fe: 0.40 C_{1-3}: 0.07 C_{4-5}: 0.08	Fe: 0.14 C: -0.31	Fe: -0.03 C: -0.38	Fe: 0.52 F: -0.59	Fe: 0.40 F: -0.72

Table 5. Isomer shifts δ, charge densities at Fe nucleus $\varrho(0)$[a], quadrupole splittings ΔE_Q, ligand field splittings 10 Dq, and spin populations at Fe n_s. Calculated data by Hückel method except for the fluoride complexes, for which spin-projected CI was used, with $S=5/2$ for FeF_6^{-3}, $S=2$ for FeF_6^{-4}

Compound	$Fe(CN)_5NO^{-2}$	$Fe(CO)_5$	$Fe(CN)_6^{-3}$	$Fe(CN)_6^{-4}$	FeF_6^{-3}	FeF_6^{-4}
δ, exptl. (mm/sec)	-0.560 ± 0.003[d]	-0.44 ± 0.01[e]	-0.413 ± 0.003[d]	-0.333 ± 0.005[d]	0.687[f]	1.59 ± 0.011[f]
$\varrho(0)$, calc. (a_0^{-3})[q]	141.3	140.7 ± 0.2	141	140.7	143.1	140.7
					144.8[b]	142.2[b]
					143.4[c]	139.9[c]
	140.9[q]	140.3 ± 0.2[q]	140.5[q]	140.2[q]	142.4[q]	140.0[q]
ΔE_Q, exptl. (mm/sec)	1.73[d], 1.85[g], 2[h]	2.53[e] – 2.58[i]				
calc.	2.3	2.5				
Sign of q, exptl.	Positive[k]	Positive[l]				
calc.	Positive	Positive				
10 Dq, exptl. (cm^{-1})			35000[m]	31000[n]	14000[o]	7600 – 10000[o]
calc.			36000	30000		22000[p]
n_s calc. (a_0^{-3})	0	0	0	0	1.80	1.67

[a] Not including 1s and 2s contributions.

[b] Using Fe 4s orbital charge rather than $P_{4S,4S}$; see text.

[c] Neglecting $3s_{Fe} - 2s_F$ overlap integrals; see text.

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[p] Shulman and Sugano (Ref. [32]) reported a value of about 20,000 cm^{-1}.

[q] Individual entries marked "q" are calculated using the Blomquist value for $|\psi_{4s}(0)|^2$ (see text). All other $\varrho(0)$ entries are based on the Walker value of $|\psi_{4s}(0)|^2$.

value −0.15 obtained by Šimańek and Šroubek [26] through consideration of FeO and Fe_2O_3, and a similar value obtained by Šimańek and Wong [27] on FeF_2 and FeF_3.

Upon examining the work of Šimańek *et al.*, we note that they made several different approximations than were used in our work. In including the correction for orbital nonorthogonality in the fluorides, they neglected the overlap of Fe $3s$ and F $2s$ orbitals, retaining only the Fe $3s - \mathrm{F}\ 2p\sigma$ overlap. They also assumed the fluorine $2s$ orbitals to be fully occupied, whereas we took the fluorine orbital occupancies from our MO calculations. To determine more fully the results of these approximations, we repeated our calculations of $\varrho(0)$ neglecting the Fe $3s - \mathrm{F}\ 2p\sigma$ overlap, but retaining our charge distributions as calculated. The result, shown in Table 5, leads to a reduction of the calibration constant to $\alpha = -0.26\, a_0^3$ mm/sec, halfway to the value of Šimańek *et al.*

Šimańek and Šroubek observed that the large change in δ on going from Fe^{+2} to Fe^{+3} salts could be consistent with their calibration if the Fe $4s$ occupancy were considerably higher in the trivalent salts. However, this hypothesis does not agree with our MO calculations; we find very little increase, from $P_{4s,4s} = 0.142$ in FeF_6^{-4} to $P_{4s,4s} = 0.145$ in FeF_6^{-3}. If we look at the $4s$ orbital charge as obtained from a Mulliken population analysis, the corresponding numbers are 0.37 and 0.33. The value 0.33 for trivalent Fe is in good agreement with an earlier estimate of 0.32 made by Danon [28] and by Viste and Gray [29]. Our work suggests a $\Delta\varrho(0)$ between divalent and trivalent fluorides somewhat smaller than postulated by Šimańek and Štroubek, and mainly due to changes in overlap integrals with internuclear distance and to changes in $3d$ shielding. In summary, even for these relatively ionic compounds it may be a serious oversimplification to approach too closely descriptions such as Fe^{++} and F^-.

To assess further the reliability of our calibration, we made one additional auxiliary calculation in which we used the Mulliken-population orbital charge instead of $P_{4s,4s}$ as a measure of the Fe $4s$ orbital occupancy. This is probably a poorer measure of the $4s$ contribution to $\varrho(0)$, as the overlap charge causing an occupancy difference from $P_{4s,4s}$ is for the most part not near the Fe nucleus. Even so, the calibration was only altered slightly, from −0.38 to $-0.35\, a_0^{-3}$ mm/sec.

We now turn to the more covalent compounds. Attempts to relate these to the fluorides fail, most probably because small inconsistencies in the parametrization of F in relation to C, N, and O can produce systematic changes in charge distribution of a magnitude sufficient to obscure the tiny effect under study. However, meaningful comparisons can be made within the group of more covalent compounds.

Our first observation in these compounds is that their differences in $\varrho(0)$ are small, in agreement with the narrow range of observed δ. If we allow for the uncertainty in the calculated $\varrho(0)$ for $Fe(CO)_5$ (this uncertainty comes from that in the Fe–C bond length) and if we use the Blomquist value for $|\psi_{4s}(0)|^2$, we find that the $\varrho(0)$ values are consistent with a calibration in the range $\alpha = -0.31$ to $-0.38\, a_0^3$ mm/sec, in agreement with our analysis of the fluorides, and in agreement with our recent isomer shift calibration using multivalent states of ^{57}Fe in $KMgF_3$ [30]. Furthermore our molecular orbital study of Mössbauer results on iron dissolved in solid noble gases [31] supports the choice of 6.7 a_0^{-3} for the electron density produced at the nucleus of an iron atom by a single $4s$ electron of configuration $3d^6 4s^1$.

The cyanide complexes have previously been studied by Shulman and Sugano [32], who attributed the small $\Delta\delta$ between $\mathrm{Fe(CN)}_6^{-4}$ and $\mathrm{Fe(CN)}_6^{-3}$ to nearly unchanged $P_{4s,4s}$ and $\Sigma_{3d} P_{3d,3d}$ in both compounds. We find this to be nearly consistent with our MO studies, which show that a small change in $\varrho(0)$ due to change in $P_{4s,4s}$ is nearly exactly compensated by a small change in $\Sigma_{3d} P_{3d,3d}$. In contrast to the fluoride compounds, the Fe–C bond distances remain almost unchanged on going from $\mathrm{Fe(CN)}_6^{-4}$ to $\mathrm{Fe(CN)}_6^{-3}$, so that changes in overlap integrals are unimportant.

Thus far, we have not emphasized the fact that all our nonorthogonality corrections in $\varrho(0)$ have been based on Hartree-Fock atomic orbitals rather than STO's. The STO's seriously underestimate the overlaps and cannot realistically be used in this context. Moreover, the nonorthogonality of Fe $3s$ and $4s$ STO's would introduce a correction of questionable value.

To summarize, our study of both ionic and covalent iron complexes leads to an Fe^{57} Mössbauer calibration value in the range $\alpha = -0.31$ to $-0.38\ a_0^3$ mm/sec.

The reliability of the MO studies can also be studied by examining other calculated quantities. In the present work, these include quadrupole splittings ΔE_Q, ligand field splittings 10 Dq, and atomic spin populations at Fe n_s. Two of the compounds under study have nonvanishing ΔE_Q; both calculated values are in qualitative accord with experiment. The 10 Dq values are also satisfactory, and the spin densities (only applicable to the high-spin compounds) look reasonable.

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