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Calibration constant for ^{57}Fe Mössbauer isomer shifts derived from *ab initio* self-consistent-field calculations on octahedral FeF$_6$ and Fe(CN)$_6$ clusters*

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Ab initio self-consistent-field molecular-orbital calculations were performed on octahedral FeF$_6$ and Fe(CN)$_6$ clusters using extensive basis sets of Gaussian-type functions. Two distances relevant for ferrous and ferric compounds are considered. In this paper, we report the part of our results that is relevant for a determination of the isomer-shift calibration constant for Fe. Good overall consistency with available ^{57}Fe Mössbauer data is found resulting in a value of $\alpha_{\mathrm{HF}} = (-0.30 \pm 0.03) a_0^3 \mathrm{mm\,sec}^{-1}$ for the calibration constant to be used in conjunction with densities on the nucleus calculated in the spin- and symmetry-restricted Hartree-Fock approximation. This value is compared with previous estimates, a number of which can be corrected on the basis of the present work and are then shown to agree with our results. Recent attempts to obtain quantitative relativistic corrections by solving the Fock-Dirac equations for Fe and its ions are discussed. A value for the calibration constant appropriate to densities calculated by this method of $\alpha_{\mathrm{FD}} = (-0.22 \pm 0.02) a_0^3 \mathrm{mm\,sec}^{-1}$ is tentatively derived.

I. INTRODUCTION

During the last decade many papers have been published dealing with the ^{57}Fe isomer-shift calibration constant in Mössbauer spectroscopy and the correlation of isomer shifts with the characteristics of the chemical bond between Fe and its surroundings. Some recent examples are the work by Duff,[1] Trautwein and Harris,[2] and Blomquist, Roos, and Sundbom.[3,4] The values put forward for the calibration constant vary between $0.1a_0^3$ and $0.7a_0^3$ mm/sec^{-1} depending on the way the necessary charge densities on the iron nucleus in various compounds are obtained. From calculated nonrelativistic[5,6] charge densities (ρ_i) and measured isomer shifts (δ_i) the calibration constant α is determined by[5,7]

$$\delta_i - \delta_j = \alpha[\rho_i(0) - \rho_j(0)], \tag{1}$$

where the lower index refers to different chemical compounds.

Trautwein and Harris[2] computed $\rho(0)$ for various iron compounds from molecular orbitals obtained by an iterative semiempirical procedure. However, their results for high-spin and low-spin compounds when considered together are not consistent with the experimental data.[6,8] Duff[1] has presented results from an *ab initio* spin-unrestricted self-consistent-field (SCF) calculation on the FeF$_6^{3-}$ complex ion. For the ferrous analog the charge density on the iron nucleus was obtained from the free-ion value for Fe^{2+} with a correction of $0.1a_0^{-3}$ estimated by Goldanskii *et al.*[9] on qualitative grounds.

The work reported here intends to improve on the previous work by applying one and the same *ab initio* computation scheme consistently to a number of iron-ligand clusters varying in chemical character from highly ionic to highly covalent in the usual chemical parlance. More specifically, the method chosen is the restricted SCF method as described by Roothaan[10] with expansion functions of the Gaussian type.[11,12] The clusters treated are FeF$_6^{4-}$ as found in KFeF$_3$ ($R_{\text{Fe-F}} = 2.06$ Å),[13,14] FeF$_6^{3-}$ as found in FeF$_3$ ($R_{\text{Fe-F}} = 1.92$ Å),[14,15] [Fe(CN)$_6$]$^{4-}$ and [Fe(CN)$_6$]$^{3-}$ both with $R_{\text{Fe-C}} = 1.90$ Å and $R_{\text{C-N}} = 1.157$ Å.[16,17] In all cases high- and low-spin configurations are considered. Moreover the ferrous and ferric fluorides are both studied at the two Fe-F distances given. Octahedral symmetry has been assumed for all clusters. The main purpose of this paper is to present an improved theoretical estimate of the calibration constant for which we shall give and discuss a number of computational results. Additional results of relevance to the interpretation of isomer shifts will be presented and discussed in a subsequent paper.

II. DETAILS OF THE CALCULATIONS

All calculations are carried out within the framework of the spin- and symmetry-restricted nonrelativistic Hartree-Fock approximation[10] using the program system SYMOL developed in this laboratory by van der Velde.[18] This program uses a fixed set of Cartesian Gaussian orbitals as a basis for the expansion of atomic and molecular orbitals and its principal feature is the advantage it takes of most of the spatial symmetry present. In the cases at hand this means that fairly large basis sets can be employed. For Fe we used 14 *s*, 11 *p*, and 6 *d* primitive Gaussians, contracted to 9 *s*,

TABLE I. Exponents α and contraction coefficients cc of the Gaussian basis set for Fe.

s type		p type		d type	
α	cc	α	cc	α	cc
257 539	0.000 29	1678.40	0.002 49	41.452 6	0.025 11
38 636.9	0.002 26	396.392	0.020 15	11.540 3	0.136 26
8 891.44	0.011 52	128.598	0.091 99	3.885 43	0.353 23
2 544.01	0.045 66	49.115 8	0.259 91	1.323 80	1.0
844.777	0.140 35	20.503 5	0.428 87	0.416 68	1.0
312.527	0.314 20	8.987 12	1.0	0.2	1.0
125.593	1.0	3.682 49	1.0		
53.498 7	1.0	1.521 75	1.0		
17.715 1	1.0	0.592 684	1.0		
7.376 77	1.0	0.259	1.0		
2.018 47	1.0	0.111	1.0		
0.779 935	1.0				
0.286	1.0				
0.105	1.0				

7 *p*, and 4 *d* basis functions. This basis set, given in Table I, is essentially that of Wachters[19] except for two additional diffuse functions of 4*p* type and one additional function of 3*d* type. Moreover the two diffuse functions of 4*s* type given by Wachters were replaced by two less diffuse functions in order to have a better description of the region between metal and ligands. The overall quality can be judged from Table II where orbital energies and total energies for Fe^{2+} and Fe^{3+} are compared with numerical Hartree-Fock results.[20] The agreement shown in the table does not imply an equally satisfactory agreement between the computed densitities at the iron nucleus. This is, however, of little consequence for the purpose of this paper as will be discussed in Sec. III. The F, C, and N ligand atoms are described by the 10 *s* and 6 *p* primitive Gaussians given by Huzinaga,[21] which are contracted into 5 *s*, 3 *p* set listed in Table III. The total SCF energies for the ground states of F^- and CN^- calculated in this basis are respectively −99.436 785 and −92.280 98 a.u. Hence, in total 251 (138) and 419 (222) functions were used in the fluoride and cyanide calculations, respectively, where the numbers in brackets refer to the contracted functions. The set of primitive Gaussians used by Duff[1] in his work on FeF_6^{3-} in K_3FeF_6 is somewhat smaller than ours (14 *s*, 11 *p*, 5 *d* for Fe; 8 *s*, 5 *p* for F: total 215) and more contracted (8 *s*, 4 *p*, 3 *d* for Fe; 3 *s*, 2 *p* for F: total 92). His paper does not contain information to allow a comparison as given in Table II.

III. RESULTS

A. Free-ion densities

Densities at the nucleus for the ground states of Fe^{2+} and Fe^{3+} calculated with the present basis set are listed in Table IV and compared with the corresponding numerical Hartree-Fock densities. As alluded to in Sec. II one sees that the two sets of results differ appreciably in magnitude (≅3%) which reflects the fact that it is very difficult to satisfy the cusp conditions[22] on the atomic nuclei with Gaussians. The deviations are highly systematic, however, so that the relevant quantities, the density differences between the ions, do not differ much (again ≅3%). This is a satisfying result because the density differences among the complex ions to be discussed are of the same order of magnitude as the Fe^{2+} – Fe^{3+} difference. It shows the usefulness of Gaussian orbitals in an area where this might not be expected at first thought.

B. Iron densities in the fluoride complexes

Electron densities at the Fe nucleus calculated for the ferrous and ferric fluoride clusters are displayed in Table V. Results are given for high-

TABLE II. Comparison of free-ion orbital energies ϵ_i and total energies E_{total} (atomic units).

	$Fe^{2+}(^5D)$		$Fe^{3+}(^6S)$		Δ_ϵ [b]	
	NHF [a]	This work	NHF	This work	NHF	This work
$-\epsilon_{1s}$	262.0469	262.0526	262.7620	262.7657	−0.7151	−0.7131
$-\epsilon_{2s}$	32.5965	32.5905	33.3355	33.3287	−0.7390	−0.7382
$-\epsilon_{3s}$	4.8296	4.8282	5.5218	5.5205	−0.6922	−0.6923
$-\epsilon_{2p}$	28.0786	28.0894	28.8147	28.8245	−0.7361	−0.7351
$-\epsilon_{3p}$	3.4100	3.4100	4.0851	4.0853	−0.6751	−0.6753
$-\epsilon_{3d}$	1.3169	1.3161	2.0732	2.0724	−0.7563	−0.7563
$-E_{\text{total}}$	1261.6569	1261.5715	1260.6151	1260.5302	1.0418	1.0413

[a] NHF: numerical Hartree-Fock results, Ref. 20.

[b] Δ_ϵ: Fe^{2+}-Fe^{3+} energy differences.

TABLE III. Exponents α and contraction coefficients cc of Gaussian basis sets for F, C, and N.

F		C		N	
s type		*s* type		*s* type	
α	cc	α	cc	α	cc
22 686.837	0.000 42	9470.52	0.000 45	13 325.646	0.000 43
3 366.268	0.003 32	1397.56	0.003 59	1 980.864 7	0.003 41
752.639 44	0.017 57	307.435 96	0.019 32	439.806 72	0.018 28
208.968 15	0.070 72	84.605 726	0.077 36	120.976 6	0.073 9
66.728 149	0.213 06	26.921 792	0.226 4	38.480 343	0.219 32
23.252 786	0.422 22	9.412 992	0.428 43	13.460 245	0.424 49
8.613 801	1.0	3.479 82	1.0	4.977 794	1.0
2.681 264	1.0	1.071 231	1.0	1.567 68	1.0
1.000 775	1.0	0.400 792	1.0	0.579 0799	1.0
0.328 900	1.0	0.135 166	1.0	0.192 2706	1.0
p type		*p* type		*p* type	
α	cc	α	cc	α	cc
66.621 738	0.008 56	25.620 81	0.008 61	36.847 115	0.008 79
15.518 396	0.056 44	5.846 072	0.053 84	8.570 870	0.054 51
4.851 131	0.192 19	1.799 35	0.183 82	2.712 196	0.181 186
1.728 951	0.365 42	0.654 333	0.360 09	0.990 762	0.596 5
0.617 222	1.0	0.248 692	1.0	0.371 763	1.0
0.206 217	1.0	0.090 9266	1.0	0.133 898	1.0

and low-spin states at $R_{\text{Fe-F}} = 2.06$ Å and for the high-spin states at $R_{\text{Fe-F}} = 1.90$ Å. They include the contributions of each totally symmetric molecular orbital. These results will be discussed in the next sections, but we want to draw attention here to the fact that significant changes in $\rho(0)$ with respect to the free-ion results of Table IV occur even for the ferrous fluoride. The calculated change in this case of about $1.2a_0^{-3}$ differs considerably from the estimate of $0.1a_0^{-3}$ referred to earlier[9] and which has been used, e.g., by Duff,[1] in his calculation of the calibration constant.

A quantitative demonstration of the predominance of the shape and occupation of the metal *s* orbitals in determining $\rho(0)$ is given in Table VI, where the separate contributions of metal, metal-ligand, and ligand distributions are displayed for two representative cases. The last two terms are small and, more importantly, their effect on the density differences is only very small.

C. Iron densities in the cyanide complexes

In Table VII the calculated densities for the ferrous and ferric cyanides complexes are listed. Again the total density at the Fe nucleus and the contributions of the appropriate molecular orbitals are given for both low- and high-spin states. The extent to which overlap and ligand distributions contribute to $\rho(0)$ in this case is illustrated in Table VIII. As expected the magnitudes of these terms are larger than in the case of fluorides although their effect on the density differences is even smaller.

TABLE IV. Calculated orbital and total free ion densities at the nucleus, $\rho_i(0)$, and their differences.

	$Fe^{2+}(^5D)$		$Fe^{3+}(^6S)$		Δ_ρ[b]	
	NHF[a]	This work	NHF[a]	This work	NHF	This work
$\rho_{1s}(0)$	10 775.537	10 456.667	10 775.193	10 456.298	0.344	0.369
$\rho_{2s}(0)$	990.910	1 018.713	990.863	1 018.633	0.047	0.080
$\rho_{3s}(0)$	135.325	140.247	137.931	142.971	−2.607	−2.724
$\rho_{\text{total}}(0)$	11 901.772	11 615.628	11 903.987	11 617.902	−2.215	−2.274

[a] Numerical Hartree-Fock results.

[b] Δ_ρ: Fe^{2+}-Fe^{3+} density differences.

TABLE V. Molecular-orbital (MO) contributions to the electron density at the Fe nucleus and their sum $\rho_{\text{total}}(0)$ in FeF_6 clusters (in units of a_0^{-3}).

	$R_{\text{Fe-F}} = 2.06$ Å [a]				$R_{\text{Fe-F}} = 1.92$ Å [b]	
	FeF_6^{4-}		FeF_6^{3-}		FeF_6^{4-}	FeF_6^{3-}
MO [c]	t^4e^2, $^5T_{2g}$	t^6, $^1A_{1g}$	t^3e^2, $^6A_{2g}$	t^5, $^2T_{2g}$	t^4e^2, $^5T_{2g}$	t^3e^2, $^6A_{2g}$
$1a_1$	10 456.603	10 456.525	10 456.233	10 456.180	10 456.578	10 456.209
$2a_1$	1 018.644	1 018.755	1 018.559	1 018.741	1 018.585	1 018.499
$4a_1$	140.007	140.566	142.536	142.889	139.736	142.241
$5a_1$	0.175	0.175	0.234	0.226	0.369	0.466
$6a_1$	1.393	1.418	2.096	2.057	1.902	2.534
$\rho_{\text{total}}(0)$	11 616.822	11 617.439	11 619.657	11 620.092	11 617.171	11 619.949

[a] $R_{\text{Fe-F}}$ in $KFeF_3$.

[b] $R_{\text{Fe-F}}$ in FeF_3.

[c] $3a_1$ ($1s_F$) does not contribute to $\rho(0)$.

IV. COMPARISON WITH MEASURED ISOMER SHIFTS

A. Selection of data

The data to be considered are collected in Table IX together with the appropriate calculated values of $\rho(0)$. The data listed have been selected because they are recent and because they are as much as possible determined by the same authors. Thus the isomer shifts taken for $KFeF_3$ and FeF_3 are those reported by Perkins and Hazony,[23] the ones for $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ are those Ref. 8. Other reasonable values can be found, notably for $KFeF_3$ (1.38 instead of 1.34)[6,22] and $K_4Fe(CN)_6$ (−0.045 instead of − 0.02).[6,23–26] The experimental accuracy is generally reported to be within ±0.01 mm/sec. It will be seen, however, that these discrepancies have little influence on the conclusions to be drawn from our calculations.

B. Qualitative considerations

The most conspicuous features of the data presented in Table IX are the quite different positions of the isomer shifts for the high-spin fluorides compared to those for the low-spin cyanides and the fact that the difference of the shifts found for the ferrous and ferric fluorides is much larger than that found for the ferrous and ferric cyanides. A cursory inspection of the calculated densities listed in the same table immediately shows that these features are quite well reproduced. Thus, taking $\rho(0)$ for the free Fe^{2+} ion as our reference, we calculate a change of $1.2a_0^{-3}$ in $\rho(0)$ for FeF_6^{4-} against a change of $5.3a_0^{-2}$ for $[Fe(CN)_6]^{3-}$. Furthermore the density difference for the fluorides is calculated to be $3.1a_0^{-3}$ compared to only $1.2a_0^{-3}$ for the cyanides. It seems warranted therefore to proceed with a more quantitative comparison in order to arrive at an estimate of the calibration constant α.

TABLE VI. Contributions to $\rho_{\text{total}}(0)$ of metal, $\rho_M(0)$, metal-ligand overlap, $\rho_{ML}(0)$, and ligand, $\rho_L(0)$, distributions in Fe fluorides.

	$\rho_M(0)$	$\rho_{ML}(0)$	$\rho_L(0)$	$\rho_{\text{total}}(0)$
FeF_6^{4-} [a]	11 616.912	−0.092	0.002	11 616.822
FeF_6^{3-} [b]	11 620.094	−0.147	0.002	11 619.949

[a] $^5T_{2g}$, $R_{\text{Fe-F}} = 2.06$ Å.

[b] $^6A_{2g}$, $R_{\text{Fe-F}} = 1.92$ Å.

C. Calibration constant

The $\rho(0)$ and σ values listed in Table IX are plotted in Fig. 1. They are well correlated by the linear expression

$$\rho_{\text{SCF}}(0) = 11\,621.49 - 3.4\delta \qquad (2)$$

corresponding to a value for α_{SCF} of $-0.29a_0^3$ mm sec^{-1} with a standard deviation of 0.03. In assessing this result a number of remarks are in order. Firstly, we can consider the discrepancies

TABLE VII. Molecular orbital (MO) contributions to the electron density at the Fe nucleus and their sum $\rho_{\text{total}}(0)$ in $Fe(CN)_6$ clusters (in units of a_0^{-3}).

	$Fe(CN)_6^{4-}$ [a]		$Fe(CN)_6^{3-}$ [a]	
MO [b]	t^6, $^1A_{1g}$	t^4e^2, $^5T_{2g}$	t^5, $^2T_{2g}$	t^3e^2, $^6A_{2g}$
$1a_1$	10 456.133	10 456.283	10 455.976	10 456.050
$2a_1$	1 018.836	1 018.544	1 018.773	1 018.414
$5a_1$	141.393	140.340	142.314	141.855
$6a_1$	0.049	0.051	0.062	0.070
$7a_1$	3.869	3.883	4.465	4.653
$8a_1$	0.693	0.640	0.573	0.501
$\rho_{\text{total}}(0)$	11 620.973	11 619.801	11 622.164	11 621.543

[a] Fe–C = 1.90 Å, C–N = 1.157 Å.

[b] $3a_1$ ($1s_N$) and $4a_1$ ($1s_C$) do not contribute to $\rho(0)$.

TABLE VIII. Contributions to $\rho_{\mathrm{total}}(0)$ of metal $\rho_M(0)$, metal-ligand overlap, $\rho_{ML}(0)$, and ligand, $\rho_L(0)$, distributions in Fe cyanides.

	$\rho_M(0)$	$\rho_{ML}(0)$	$\rho_L(0)$	$\rho_{\mathrm{total}}(0)$
$\mathrm{Fe(CN)_6}^{4-}$ [a]	11 621.346	−0.377	0.004	11 620.973
$\mathrm{Fe(CN)_6}^{3-}$ [b]	11 622.547	−0.387	0.004	11 622.164

[a] Low-spin states, distances as in Table VII.

in the isomer-shift data quoted earlier. Least-squares fits employing the alternative data yield changes smaller than 0.01 in α, however, and hence are all within the standard deviation. Secondly, we may look into the deviations of our SCF densities, $\alpha_{\mathrm{SCF}}(0)$, from the true restricted Hartree-Fock (HF) densities, $\rho_{\mathrm{HF}}(0)$ that one would prefer to use. It has already been shown that these deviations in spite of their large magnitudes seem to have little influence on density differences. When the data in Table IX are used to obtain a linear relationship between $\rho_{\mathrm{HF}}(0)$ and $\rho_{\mathrm{SCF}}(0)$ a small correction to α can be established leading to

$$\alpha_{\mathrm{HF}} = \alpha_{\mathrm{SCF}}/0.974 = (-0.30 \pm 0.03)a_0^3 \text{ mm sec}^{-1} .$$

Some remarks concerning the adequacy of, respectively, the isolated cluster model and the HF approximation will be made at the end of this paper.

V. COMPARISON WITH OTHER CALCULATIONS OF α

A. Nonrelativistic calculations

Some 16 estimates of the (nonrelativistic) calibration constant have been listed and discussed by Duff.[1] They include two high values, −0.51 and −0.62, eight low values ranging from −0.11 to −0.20, and five medium values lying between −0.28 and −0.38. Considerations of overlap distortions of free-ion HF wave functions and the use of effective charges or effective orbital populations in conjunction with theoretical free-ion densities characterize most of the work underlying the various estimates.

TABLE IX. Comparison of measured isomer shifts, δ, and calculated densities, $\rho(0)$.

	$\mathrm{KFeF_3}$	$\mathrm{FeF_3}$	$\mathrm{K_4Fe(CN)_6}$	$\mathrm{K_3Fe(CN)_6}$
δ [a]	1.34 [b]	0.48 [b]	−0.02 [c]	−0.13 [c]
$\rho(0)$ [d]	11 616.822	11 619.949	11 620.973	11 622.164

[a] In mm/sec, Fe metal reference, room temperature.

[b] Reference 21.

[c] Reference 8.

[d] In a_0^{-3}.

Duff has added a value of −0.23 to the list, which he obtained from an *ab initio* SCF calculation on $\mathrm{FeF_6}^{3-}$ in $\mathrm{KFeF_3}$ and an estimate of the density for $\mathrm{FeF_6}^{4-}$ in $\mathrm{FeF_2}$. Very recently Bagus, Walgren, and Almlof[27] extracted a value of −0.18 from an *ab initio* SCF calculation on ferrocene, $\mathrm{Fe(C_5H_5)_2}$.

At first sight these new results seem to be of little help in narrowing the bandwidth of the α spectrum indicated above. A closer study reveals, however, that both values are quite consistent with our results. First of all we recall from Sec. III B that $\rho(0)$ in the ferrous fluoride shows a substantial shift of $1.2a_0^{-3}$ with respect to the free ferrous ion. This is for 77% an overlap distortion effect obtained in the first step of our self-consistent-field procedure, where the free-ion densities are supplied and subsequently are renormalized to yield the initial cluster wave function. Duff used an estimate of $0.1a_0^{-3}$ for this shift in $\mathrm{FeF_2}$, while the authors of Ref. 27 neglected it altogether because of its supposed smallness. Since Duff's ferric fluoride result is not very different from ours, we can simply supplement his calculation with the additional ferrous shift found here. This changes his value for α by a factor of $\frac{4}{3}$ to −0.31. Applying the same correction to the work of Bagus *et al.* changes their value to −0.25. The isomer shift for ferrocene of 0.65 mm/sec (reference stainless steel, 310 SS) used in this estimate is, however, not consistent with the more recent data used by us.[8] In Ref. 8, 0.27 mm/sec (reference Pd) is reported for ferrocene at room temperature. This value corresponds to 0.45 mm/sec in our reference scheme (Fe) and to 0.53 in reference to 310 SS.[6] The latter value would lead to a 20% increase in

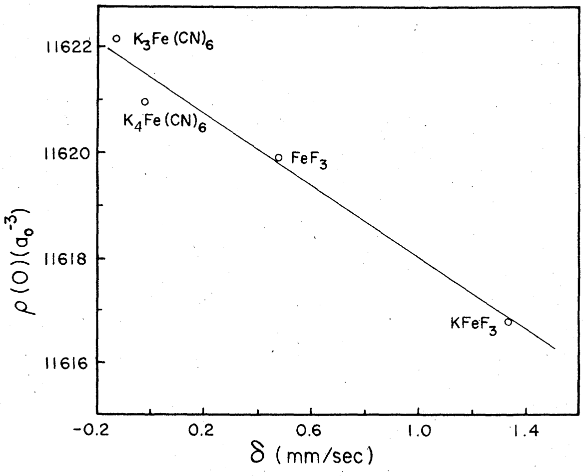

FIG. 1. Least-squares fit of calculated $\rho(0)$ values versus measured isomer shifts: $\rho(0) = 11\,621.39 - 33.8\delta$.

α, again in complete accord with our result.

It is worth noting at this point that the two isomer shift data sources used here (Sec. IV A), although not allowing a direct comparison, can be shown to be consistent with each other on the basis of our results. In Ref. 8 a shift of 0.24 mm/sec (Pd) is listed for K_3FeF_6 ($R_{Fe\text{-}F} = 1.85$ Å) corresponding to 0.42 mm/sec in reference to Fe metal. Reference 23 on the other hand, gives 0.48 mm/sec for FeF_3 ($R_{Fe\text{-}F} = 1.92$ Å), the value used in our work. From Table V we see that a shift in $\rho(0)$ of 0.30 a_0^{-3} occurs in the ferric fluoride when the Fe-F distance is decreased by 0.14 Å. A linear extrapolation of this observation yields a further increase of $\rho(0)$ by 0.15 a_0^{-3} for the Fe-F distance observed in K_3FeF_6. Using our value for α_{SCF} this increase is seen to lead to a predicted value of 0.43 mm/sec for the isomer shift of K_3FeF_6.

Similar to what was done in Sec. IV C to obtain α_{HF} we can use our free-ion densities and those of Ref. 27 to obtain a linear relation between our calculated densities and the ones of Ref. 27. In this way an approximate value of 11 619.5a_0^{-3} can be derived for ferrocene which together with the corresponding isomer shift of 0.45 mm/sec can be incorporated in our results. As was to be expected from the discussion given a least squares fit including these values gives essentially the same results.

We consider finally the isomer shift of −0.98 mm/sec (−2.32 mm/sec with respect to FeF_2) found for Fe atoms trapped in rare-gas matrices.[28] As a first approximation we can take $\rho_{SCF}(0)$ for the free Fe atom ($3d^6$, $4s^2$, ^5D) which has the value 11 623.947 a_0^{-3} in our basis. Including this value and the corresponding isomer shift in our data and carrying out a new least-squares fit yields a value of $\alpha = -0.31 a_0^3$ mm/sec. This surprisingly good agreement must of course not be taken too seriously since we do not know to what extent the free-atom density would change if a cluster calculation consistent with our other calculations were undertaken.[29] Lacking more precise information at present we can do no more than state that if $\rho(0)$ is varied from the free-atom value over a range of $\pm 1.0 a_0^{-3}$, the α values obtained from least-squares fits range from −0.28 to −0.34. Nevertheless, we feel that the fact that our results behave consistently even when extrapolated over such a wide range of isomer shifts strongly supports their credibility.

A final comment on the α value of −0.33 reported by McNab *et al.*[28] is in order. If we follow these authors and take just the $\rho(0)$ values for Fe^{2+} and Fe we find $\alpha = -0.28$ instead. A comparison of the calculated $\rho(0)$ values used by McNab *et al.*[30] and our own suggests that this discrepancy finds its origin in the abnormally low value of $\rho(0)$ for the Fe atom reported in Ref. 30. This in turn may be a consequence of the use in the latter work of different sets of s basis functions for Fe^{2+} and Fe, respectively.

B. Relativistic corrections

For more than a decade it has been customary to account for relativistic effects in the evaluation of isomer shifts by multiplying the nonrelativistic densities by a relativistic correction factor $S'(Z)$.[5] For Fe this factor was estimated to be 1.29, no distinction being made for different charge states, different configurations, or different configurational states. Only very recently attempts have been made to investigate these effects more closely at least at the level of the self-consistent-field approximation.[31,32] Unfortunately the methods as well as the results of the two investigations differ on essential points so that a completely unambiguous relativistic adjustment of our calibration constant cannot be made. The work of Trautwein and co-workers is most consistent with our work in the sense that they solve the relativistic analog of HF equations, the Dirac-Fock equations, straightforwardly for mixed j configurations corresponding closely to the appropriate Russell-Saunders states. Also $\rho(0)$ is associated directly with the density at the nuclear position. The authors of Ref. 32 do not use mixed j configurations. They further deviate from Ref. 31 by imposing Slater's local density approximation on the exchange potential and by taking explicit account of the finite size of the nucleus. The latter is assumed to be a homogeneously filled sphere with a given radius and $\rho(0)$ is consistently replaced by the average value of the electron density in the nuclear region. The results differ quantitatively from those of Ref. 31. That is, if we use the results for Fe^{2+} and Fe^{3+} to relate Hartree-Fock densities, $\rho_{HF}(0)$, linearly to Fock-Dirac densities, $\rho_{FD}(0)$, we find $\Delta\rho_{FD} = 1.579\Delta\rho_{HF}$ from Ref. 32, and $\Delta\rho_{FD} = 1.346\Delta\rho_{HF}$ from Ref. 31, where $\Delta\rho$ indicates the difference of the ion densities. We do not know how much of the difference between the two expressions must be attributed to the local exchange approximation and how much to the interesting extension of the usual point-charge model of the nucleus. In the nonrelativistic case, using the same local exchange potential, we found the $Fe^{3+} - Fe^{2+}$ density difference to be $2.7 a_0^{-3}$ which differs significantly from the numerical HF result of $2.2 a_0^{-3}$. (We thank Dr. F. Herman, IBM Research Laboratory, San Jose, for providing the program for this calculation.) In fact if this difference persists in the relativistic calculation it would completely explain the discrepancy between Refs. 31 and 32. Another valid criticism on the use of the results of Ref. 32 would be that a consistent linear fit to nonrelativistic densities requires the latter to be obtained also from a calculation in which the nucleus is given a finite size. Given these uncertainties we must consider Ref. 31 as the best basis for the relativistic adjustment of our calibration constant. Thus we arrive at the value $\alpha_{FD} = \alpha_{HF}/1.346 = (-0.22 \pm 0.02)a_0^3$ mm sec^{-1} for the calibration constant to be used in conjunction with densities at the iron nucleus calculated by the Fock-Dirac method.

VI. INFLUENCE OF THE CLUSTER ENVIRONMENT

In order to account for the influence of the surroundings, in a way consistent with our localized cluster approach, the cluster calculations can be carried out in the fixed potential field of the rest of the crystal considered as a collection of ions at appropriate lattice positions. Such a field can be thought to consist of two contributions, a long-range electrostatic potential or Madelung part and a short-range pseudopotential or Born repulsion part. Of these two contributions we can at present only consider the first part. We have investigated its effect on the density on the iron nucleus in FeF_6^{4-} and FeF_6^{3-} clusters with Fe-F distances and Madelung potential corresponding to the FeF_2 crystal.[33,34] (We thank Dr. C. Bauschlinger, Battelle Laboratories, Columbus, Ohio, for his cooperation in obtaining these results.) It was found that the inclusion of the Madelung potential lowered $\rho(0)$ by $-0.14a_0^{-3}$ in FeF_6^{4-} and by $-0.17a_0^{-3}$ in FeF_6^{3-}. Changes of this magnitude have no consequences for the conclusions drawn from our free-cluster results. These results are consistent with earlier work on $KNiF_3$,[35] where it was also found that the Madelung potential has only a small effect on the charge distribution of the NiF_6^{4-} cluster. Its effect on the total energy is often sufficiently large, however, to make its inclusion essential for obtaining the correct equilibrium distance in the cluster.[36]

At present we do not have similar results for the cyanides, but we have no reason to believe that their behavior will be so different from that of the fluorides as to alter our estimate of the calibration constant. Of course the Madelung potential can be of significance when comparing ferrous and ferric cyanides on account of the small difference in density on the nucleus.

No attempt will be made to estimate the effect of the short-range part of the lattice potential, work on this point is in progress. That the overall effect on the densities of the remainder of the crystal will be small can be inferred from experimental data on the isomer shifts of the same cluster in different surroundings. For example, for $M_4Fe(CN)_6$, $M=$ K, Cu, Ag one finds[26] $\delta = -0.394$, -0.445, and -0.469 mm/sec, respectively, and $\delta = -0.471$, -0.507, and -0.494 mm/sec for $M_3Fe(CN)_6$ (room temperature, Pt reference). Also, for K_3FeF_6 $\delta = 0.24$ mm/sec and for NH_4FeF_6 $\delta = 0.25$ mm/sec (room temperature, Pd reference).[8]

VII. CONCLUDING REMARKS

The main result of the work reported here is that a satisfactory linear relationship is shown to exist between nonrelativistic self-consistent-field densities at the iron nucleus calculated for a number of iron-ligand clusters and Mössbauer isomer shifts observed in materials containing these clusters. The materials chosen, $KFeF_3$, FeF_3, $K_4Fe(CN)_6$, and $K_3Fe(CN)_6$, exhibit isomer shifts that cover a wide range of values running from 1.40 to -0.15 mm/sec with respect to iron metal at room temperature. For this reason we consider the derived nonrelativistic calibration constant $\alpha_{HF} = -0.30a_0^3$ mm sec^{-1} to be a reliable value. Moreover, theoretical and experimental evidence suggests that taking the cluster surroundings into account has only minor consequences.

The question whether exact nonrelativistic densities on the nucleus, if they could be obtained, would yield essentially the same calibration constant cannot be answered at present. Two possible sources for deviations can be considered. First, within the cluster approximation, the influence of correlation corrections to the Hartree-Fock densities must be dealt with. These corrections probably will be qualitatively different for the fluorides and cyanides, respectively, on account of the differences in electron shell structure and excitation spectra. Preliminary investigations show that the density changes induced by single and double excitations out of the metal 3*s*-, 3*p*-, and 3*d*-like orbitals and the highest occupied ligand orbitals occur with positive and negative signs and can have comparable magnitudes. Their evaluation therefore requires a fairly extensive configuration interaction calculation. Our present estimate is that the density differences can be affected by a few tenths.

Finally the cluster approximation itself can be questioned. For the type of insulating compounds considered here it seems reasonable to approach a property like the isomer shift from a localized point of view in which only the electronic structure of an iron atom with its nearest neighbors is explicity taken into account. The main deficiency lies in the treatment of the ligand valence electrons which one would rather deal with as forming part of a ligand valence-band structure. At present we have no way of assessing the influence of this deficiency on properties calculated for the free cluster.

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[*] A summary of the conclusions pertaining to the nonrelativistic calibration constant has been communicated by Dr. G. A. Sawatsky at the Congress on Applications of the Mössbauer Effect, Bendor, France, 1974.

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