

The effect of electron correlation on the charge density at the iron nucleus†

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Abstract. Numerical multi-configuration Hartree-Fock results are reported for the configurations, $3d^6(^5D)4s^n$, $n = 0, 1, 2$ of Fe^{2+} , Fe^+ and Fe respectively. Degeneracy effects, correlation between the $4s$ electrons and those in the M shell, and correlation within the $4s^2$ group were included in these calculations. Though the absolute values of the charge densities are not affected greatly by the above correlation, the charge density of Fe relative to Fe^+ decreased by 8.3%, whereas the same density relative to Fe^{2+} remained virtually unchanged.

1. Introduction

The determination of the isomer-shift calibration constant α from Mössbauer spectra requires knowledge of the nonrelativistic electron density at the nucleus $\rho(0)$, (Shirley 1964, Kalvins 1971). In effect, this constant incorporates the dependence of the isomer shift on nuclear and relativistic effects. Thus, once α is known, much valuable information may be deduced from a variety of isomer-shift measurements for atomic, molecular and biophysical applications (Goldanskii and Herber 1968).

A nucleus of considerable interest is ^{57}Fe . In a paper describing his own calibrations, Duff (1974) lists a total of seventeen different values which had been published over a period of thirteen years. The theoretical determination of the density is complicated by the fact that the Fe atom or ion is usually part of a compound and molecular-type calculations are required (Trautwein and Harris 1973, Duff 1974). For example, Duff found that the charge density at the iron nucleus of the cluster FeF_6^{3-} in K_3FeF_6 is $1.9 a_0^{-3}$ larger than in the free ion Fe^{3+} . Even so, assumptions concerning the free atoms or ions are often used (McNab *et al* 1971).

Many atomic properties have been shown to be affected by correlation, but so far no calculations have been performed to investigate its effect on $\rho(0)$ in ^{57}Fe . The measurements of McNab *et al* require the difference in charge densities between $^{57}Fe 3d^6 4s^2$ and $^{57}Fe^{2+} 3d^6$. In the former the $4s^2$ configuration is strongly correlated

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with $4p^2$, and this correlation could lead to a significant change in the difference of the charge densities.

This paper reports on an attempt to improve estimates of the charge densities for $\text{Fe}^+ 3d^6 4s(^6D)$ and $\text{Fe } 3d^6 4s(^5D)$ relative to $\text{Fe}^{2+} 3d^6(^5D)$ using a multi-configuration Hartree–Fock approximation. All calculations were performed using a slightly modified version of MCHF72 (Froese Fischer 1972) together with Hibbert's (1971) program for the determination of the energy interaction matrix.

2. Method of calculation

In the multi-configuration Hartree–Fock (MCHF) approximation, the total wavefunction for a many-electron system is approximated by a function $\psi(\gamma LS)$, which is a linear combination of configuration state functions, $\Phi(\gamma' LS)$. Thus

$$\psi(\gamma LS) = \sum_j c_j \Phi(\gamma_j LS) \quad (1)$$

where the coefficients c_j are 'mixing coefficients' and Φ is an antisymmetric state function for the vector-coupled configuration $\gamma_j LS$. Both the radial functions for the orbitals and the mixing coefficients are determined variationally.

In the cases considered here the dominant configuration is $3d^6(^5D)4s^n$, $n = 0, 1, 2$ for $\text{Fe}^{2+}(^5D)$, $\text{Fe}^+(^6D)$ and $\text{Fe}(^5D)$ respectively. Though there are several configurations in the complex (that is, several configurations have the same parity and the same set of principal quantum numbers (Layzer 1959)) their mixing coefficients are small except for $3d^6 4s^2$ where $3d^6 4p^2$ has a significantly large coefficient. Thus a reasonable definition of a zero-order approximation is the following:

$$\begin{aligned} \text{Fe}^{2+} \quad \psi^{(0)}(3d^6 ^5D) &= \Phi(3d^6 ^5D) \\ \text{Fe}^+ \quad \psi^{(0)}(3d^6(^5D)4s ^6D) &= \Phi(3d^6 4s ^6D) \\ \text{Fe} \quad \psi^{(0)}(3d^6(^5D)4s^2 ^5D) &= c_1 \Phi(3d^6 4s^2 ^5D) + c_2 \Phi(3d^6 4p^2 ^5D). \end{aligned}$$

A first-order approximation may be defined to include all those configurations which interact with $\psi^{(0)}$. The difference between the resulting approximation and the Hartree–Fock (HF) one is attributed to correlation. Consequently, the additional configuration state functions which enter in equation (1) are referred to as 'correlation functions' and any new orbitals as 'correlation orbitals'.

The number of configurations in the correlation function for these atoms or ions is large, but the configurations may differ from those in the zero-order approximation by no more than two electrons, and so may be classified according to the type of electron replacement that is involved. If we consider the core to be $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ and $4s^n$ to be the outer shell, then the possible two-electron replacements are either (i) core and core, (ii) core and outer, $n \geq 1$ or (iii) outer and outer, provided $n = 2$. The contributions to the correlation functions from core–core replacements are nearly the same for all the states (Layzer *et al* 1964). In isomer-shift calibrations the difference in charge densities is required. Correlation effects which are important in this difference are those which are not the same in each case, namely (ii) and (iii). At the same time, correlation between the outer $4s^n$ shell and the inner $1s^2 2s^2 2p^6$ core is likely to be small. With these assumptions, the present correlation problem can be simplified considerably.

In the core–core replacements, only configurations in the same complex were included, namely $3p^2 \rightarrow 3d^2$ replacements (the other configuration in the complex,

Table 1. Multi-configuration Hartree-Fock results for some Fe atoms and ions.

Configuration	Fe ²⁺ <i>n</i> = 0	Fe ⁺ <i>n</i> = 1	Fe <i>n</i> = 2
3p ⁶ 3d ⁶ (⁵ D)4s ₁ ⁿ	0.99829	0.99525	0.96170
3p ⁴ 3d ⁸ (³ F)4s ₁ ⁿ	-0.03903	-0.03749	-0.03746
(³ P)	-0.04339	-0.04166	-0.04155
3p ⁵ 3d ⁷ (⁴ F)4s ₂ ⁿ⁻¹ 4p ₁			
⁵ F ⁴ F		0.02520	-0.02080
⁵ F ⁶ F			0.02015
³ F ⁴ F			-0.00219
⁵ D ⁴ D		-0.03381	0.02797
⁵ D ⁶ D			-0.02809
³ D ⁴ D			0.00330
3p ⁵ 3d ⁷ (⁴ P)4s ₂ ⁿ⁻¹ 4p ₁			
⁵ D ⁴ D		-0.01360	0.01167
⁵ D ⁶ D			-0.01189
³ D ⁴ D			0.00121
⁵ P ⁴ P		0.02472	-0.01940
⁵ P ⁶ P			0.01964
³ P ⁴ P			-0.00226
3p ⁶ 3d ⁶ (⁵ D)4s ₂ ⁿ⁻¹ 4d ₁			
⁶ D		0.032291	0.01779
⁴ D			-0.02883
3p ⁶ 3d ⁵ (⁶ S)4s ₂ ⁿ⁻¹ 4p ₂ ² (¹ D)		-0.05216	-0.04753
(⁴ G)			-0.04819
(⁴ F)			-0.03477
(⁴ D)			-0.03769
(⁴ P)			-0.02755
3p ⁶ 3d ⁶ (⁵ D)4p ₃ ² (¹ S)			0.23898
3p ⁴ 3d ⁸ (³ F)4p ₃ ² (¹ S)			-0.00879
(³ P)			-0.00967
3p ⁶ 3d ⁶ (⁵ D)4d ₂ ² (¹ S)			-0.02320
4f ² (¹ S)			0.01315
5s ² (¹ S)			-0.03766
<i>E</i> ^{MCHF}	-1261.67142	-1262.23671	-1262.50639
<i>E</i> ^{HF}	-1261.65678	-1262.21301	-1262.44366
<i>E</i> ^{HF} - <i>E</i> ^{MCHF}	0.01464	0.02370	0.06273

but not in our first-order approximation, 3s3p⁴3d⁹, was found to have a mixing coefficient of 0.0013 in all cases and was neglected thereafter). The core-outer replacements considered were (3p → 3d; 4s → 4p), (3d → 4p; 4s → 4p) and (3d → 3d; 4s → 4d). The latter is a core-outer replacement since the 4d electron couples with the core in a different way to the 4s electron. The replacements (3d → 3d; 4s → 4f) were also checked, but since they had mixing coefficients of less than 0.0032 they were neglected. Finally, for *n* = 2, 4s² (or 4p²) was replaced by 4d², 4f² and 5s².

The results of these calculations are presented in table 1. For Fe²⁺ and Fe⁺, all interactions were included, but in Fe, because of the large number of coupling schemes for some of the configurations, only the interactions with $\psi^{(0)}$ were included. Not all orbitals were constrained to be the same. In particular, correlation orbitals were unconstrained so that as much correlation as possible be included by these configurations (Froese Fischer 1973).

Table 2. Analysis of energy differences (in atomic units).

	HF	MCHF	Observed
$E(\text{Fe}^{2+}) - E(\text{Fe}^+)$	0.55623	0.56529	0.59471
(% error)	(6.47)	(4.95)	
$E(\text{Fe}^+) - E(\text{Fe})$	0.23065	0.26968	0.29024
(% error)	(20.53)	(7.08)	

Table 2 shows that the error in the theoretical energy difference $\Delta E = E(\text{Fe}^+) - E(\text{Fe})$, has been reduced from 20.5% to 7.1%.

In table 3 the mean radii of the final orbitals are listed. The table shows that the mean radii of correlation orbitals are frequently smaller than those of an outer electron. Note in particular the different mean radii for $4p_1$, $4p_2$ and $4p_3$ in Fe. Each orbital represents a different correlation effect and therefore is localized in a different region. Values of $\langle r^{-3} \rangle$ are also listed.

3. The charge density

In the HF approximation, the charge density for a configuration is given by

$$\rho_\gamma(0) = \sum_{ns} q_{ns} R_{ns}^2(0)/4\pi \quad (2)$$

where $R_{ns}(0) = P_{ns}(r)/r$, $r \rightarrow 0$ and $P_{ns}(r)$ is the radial function for an s orbital; q_{ns} equals the number of ns electrons in the configuration γ . For the MCHF approximation considered here, the total charge density is

$$\rho(0) = \sum_j c_j^2 \rho_{\gamma_j}(0).$$

Table 3. Values of the mean radius $\langle r \rangle$ and $\langle r^{-3} \rangle$ for the MCHF orbitals.

Orbital	Fe^{2+}		Fe^+		Fe	
	$\langle r \rangle$	$\langle r^{-3} \rangle$	$\langle r \rangle$	$\langle r^{-3} \rangle$	$\langle r \rangle$	$\langle r^{-3} \rangle$
1s	0.0591	—	0.0591	—	0.0591	—
2s	0.2685	—	0.2685	—	0.2684	—
2p	0.2361	462.87	0.2364	462.23	0.2350	465.47
3s	0.8208	—	0.8204	—	0.8208	—
3p	0.8648	54.62	0.8651	55.21	0.8666	51.98
3d	1.0446	5.09	1.0650	5.00	1.0744	4.977
4s ₁	—	—	2.7863	—	3.1671	—
4s ₂	—	—	—	—	3.0962	—
4p ₁	—	—	1.9907	14.71	2.1313	13.00
4p ₂	—	—	3.1111	4.20	2.5968	6.71
4p ₃	—	—	—	—	3.2497	2.87
4d ₁	—	—	2.4572	2.16	2.7219	1.76
4d ₂	—	—	—	—	3.1169	0.85
4f	—	—	—	—	2.9950	0.06
5s	—	—	—	—	3.9047	—

Table 4. Values of $R_{ns}(0)$. In each case the Hartree-Fock value is given followed by the MCHF value.

Orbital	Fe ²⁺	Fe ⁺	Fe
1s	260.20127	260.20047	260.20026
	260.20139	260.20202	260.20031
2s	78.9055	78.9117	78.9115
	78.9083	78.9043	78.9163
3s	29.1593	29.2002	29.2286
	29.1494	29.2018	29.1945
4s ₁	—	7.6463	6.2521
	—	7.8302	6.5515
4s ₂	—	—	—
	—	—	7.2619
5s	—	—	—
	—	—	9.3739

Values of $R_{ns}(0)$ are given in table 4 for both HF and MCHF orbitals. Note that $R_{5s}(0)$ is larger than $R_{4s}(0)$, a result which is consistent with a correlation orbital being more contracted than an occupied orbital.

Table 5 lists the charge densities for the various cases. The present numerical HF values are compared with those which Bloomquist *et al* (1971) determined from an analytic basis. The present values are consistently smaller (by 1.975, 2.008 and 2.019 for Fe²⁺, Fe⁺ and Fe respectively). The absolute value of $\rho(0)$ depends critically on $R_{1s}(0)$; a change in the fifth significant digit could account for the discrepancy. It is possible that the analytic basis was still too limited. The present values for Fe²⁺ differ slightly from the numerical HF values published by Duff since the present calculations were performed for a particular *LS* state rather than for the average energy of the configuration. A striking feature of table 5 is the fact that in the HF approximation the first 4s electron added to the 3d⁶ core increases the charge density by $5.1 a_0^{-3}$, whereas the second adds only $1.8 a_0^{-3}$ more. This feature is enhanced somewhat in the MCHF results. Correlation has had little effect on the charge densities of Fe²⁺ and Fe (the difference in $\rho(0)$ has increased by 0.1%) but the charge density for Fe⁺ has increased somewhat. As a result, the difference in charge density between Fe and Fe⁺ has decreased 8.3%, whereas the difference between Fe⁺ and Fe²⁺ has increased 3.3%.

An interesting analysis is presented in table 6 where the contributions to the density from the individual orbitals are given for Fe⁺ and Fe. For Fe⁺ in going from HF to MCHF, there is some rearrangement in the core which allows the 4s orbital

Table 5. A comparison of charge densities $\rho(0)$.

Atom or ion	Analytic HF	Numerical HF	MCHF
Fe ²⁺ 3d ⁶ ⁵ D	11903.747	11901.772	11901.762
	5.156	5.123	5.286
Fe ⁺ 3d ⁶ 4s ⁶ D	11908.903	11906.895	11907.048
	1.820	1.809	1.655
Fe3d ⁶ 4s ² ⁵ D	11910.723	11908.704	11908.703

Table 6. An analysis of the change in $\rho(0)$ in Fe^+ and Fe.

		Contribution to $\rho(0)$		
	Orbital	HF	MCHF	MCHF - HF
Fe^+	1s	10775.472	10775.600	0.1284
	2s	991.067	990.881	-0.1859
	3s	135.704	135.719	0.0149
	4s ₁	8.868	9.758	0.8899
	Sum	11911.111	11911.958	0.8473
Fe	1s	10775.454	10775.458	0.0036
	2s	991.061	991.182	0.1212
	3s	135.968	135.651	-0.3167
	4s ₁	6.2212	6.3393	0.1181
	4s ₂	0.0	0.0528	0.0528
	5s	0.0	0.0198	0.0198
	Sum	11908.704	11908.703	-0.0011

to acquire a higher density at the nucleus. Generally, it is a more contracted orbital. For Fe, the increase from 4s is much less, probably because of the important correlation effect arising from the replacement of $4s^2$ by $4p^2$. Intuitively, this would decrease the s electron density at the nucleus. Because of this, the rearrangement in the core is quite different from that found in Fe^+ . There is virtually no change in the 1s contribution, in going from HF to MCHF, a slight increase in 2s and a considerable decrease in 3s. The correlation orbitals, 4s₂ and 5s, produce a small but significant increase to $\rho(0)$. The result of all of these opposing changes leaves $\rho(0)$ for Fe virtually unchanged.

4. Conclusion

Though the actual charge density is not affected greatly by correlation, the difference in charge densities of an atom and its ion may change significantly. For iron, the difference between Fe and Fe^+ has changed from $1.81 a_0^{-3}$ in the Hartree-Fock approximation to $1.66 a_0^{-3}$ when correlation is included.

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