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Variational Calculation of the Sternheimer Factors for the Ferrous Ion*

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The Sternheimer factors for the ferrous ion are calculated using the free-ion wave functions of Watson and the variational method of Das and Bersohn. The results of this calculation are $R=+0.22$ and $\gamma_\infty=-10.6$. With these factors and previously published ferrous quadrupole splitting data, the quadrupole moment of the first excited state of iron-57 is estimated to be $+0.15$ b.

INTRODUCTION

RECENT Mössbauer experiments[1] with ferric[2,3] (Fe^{3+}) and ferrous[4-6] (Fe^{++}) compounds have provided two different ways of determining the electric quadrupole moment, Q, of the first excited state of the iron-57 nucleus. As we shall see, this is because the relative roles of ionic versus lattice contribution to the electric field gradient, q, at the iron-57 nucleus (which must be calculated for each compound), are opposite in the ferric compounds to those in the ferrous.

In lowest order, the ferric ion is in a spherical ^6S state ($3d^5$) so that the field-gradient calculation for ferric substances involves a lattice sum,[7,8] q_{lat}. This sum must then be multiplied by the Sternheimer correction,[9] $(1-\gamma_\infty)$, to account for the appreciable first-order distortion of the ferric core by the lattice[10]:

$$q=(1-\gamma_\infty)q_{\text{lat}}. \tag{1}$$

As shown by Burns,[11] when such lattice sums are performed and combined with experimental data of Wertheim[3,12] the values of Q appear to center around $+0.4$ b.

In contrast, the lowest-order state of the ferrous ion is ^5D ($3d^6$) which may be pictured as the spherical ferric-like "core" plus an unpaired $3d$ "valence" electron. The ionic contribution to q then contains the field gradient due to the valence electron, q_{val}. This in turn must be multiplied by the Sternheimer correction[9] $(1-R)$, to include the polarization of the core by the valence electron. The field gradient in ferrous substances is then approximately

$$q=(1-R)q_{\text{val}}+(1-\gamma_\infty)q_{\text{lat}}. \tag{2}$$

Several investigators[5,6,13] have pointed out that the lattice term in (2) may be neglected. In addition, if the factor, R, is assumed to be small compared with unity, the field gradient in ferrous compounds is simply:

$$q=-\langle(3\cos^2\theta-1)/r^3\rangle_{3d}. \tag{3}$$

If the restricted Hartree-Fock free-ion $3d$ wave function of Watson[14] is used to compute the above expectation value, the quadrupole moment, Q, turns out to be on the order of $+0.1$ b.[5,6,13]

In view of the surprisingly different values of Q that one obtains, depending upon which ion is used, and the various approximations employed, it seems advisable also to determine the Sternheimer factor, R, in (2). Such a calculation, using the simple variational procedure of Das and Bersohn[15] and the free ferrous wave functions of Watson,[14] is reported in this paper. Since they require very little extra computation, the main contributions to the factor, γ_∞, in (2) are also included and compared to the similar factor in (1) which is calculated by Burns and Wikner.[10]

METHOD OF CALCULATION[16]

The factors, R and γ_∞, may be obtained as special cases of the general quadrupole polarizability, $\gamma(r)$, which occurs when a charge, Z, described by the coordinates, r and θ, perturbs a core electron at r_c and θ_c through the interaction:

$$H_1=-\tfrac{1}{2}Z(3\cos^2\theta-1)\times(3\cos^2\theta_c-1)\begin{cases} r_c^2/r^3 & \text{for } r_c\leqslant r \\ r^2/r_c^3 & \text{for } r_c\geqslant r. \end{cases} \tag{4}$$

If the zero-order wave function for a core electron is $u_0(nlm_l)$, corresponding to the central field Hamiltonian, H_0, the first-order perturbation, $u_1(nlm_l)$, caused by

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[16] This section is taken in part from references 9, 15, and also E. G. Wikner and T. P. Das, Phys. Rev. **109**, 360 (1957). As in these references, this present treatment uses atomic units.

H_1 obeys the first-order wave equation

$$(H_0-E_0)u_1=-(H_1-E_1)u_0, \tag{5}$$

where

$$E_0=\langle u_0|H_0|u_0\rangle,\quad E_1=\langle u_0|H_1|u_0\rangle,$$

and

$$\langle u_0|u_1\rangle=0. \tag{6}$$

The quadrupole polarizability is then given by

$$\gamma(r)=\left(Z\frac{3\cos^2\theta-1}{r^3}\right)^{-1}\sum_{\text{core}}2\left\langle u_0\left|\frac{3\cos^2\theta_c-1}{r_c{}^3}\right|u_1\right\rangle. \tag{7}$$

The factor, R, is then calculated by letting the perturbing charge be the $3d$ valence electron and taking the appropriate expectation value

$$R=\langle\gamma(r)r^{-3}\rangle_{3d}/\langle r^{-3}\rangle_{3d}, \tag{8}$$

while the factor, γ_∞, is obtained by assuming the lattice ions to be point charges, completely outside the ferrous ion ($r_c<r$):

$$\gamma_\infty=\lim_{r\to\infty}\gamma(r). \tag{9}$$

The zero-order wave function for each core electron may be written

$$u_0(nlm_l)=u_0'(nl)Y_l{}^{m_l}(\Omega_c),$$

where $u_0'(nl)$, the radial function of r_c, is normalized as follows:

$$\int_0^\infty[u_0'(nl)]^2dr_c=1.$$

Therefore Eq. (5) is seen to separate if u_1 is written

$$u_1(\mathbf{r};nlm_l)=\sum_{l'}u_1(\mathbf{r};nl\to l',m_l)$$

or, more specificially,

$$u_1(\mathbf{r};nlm_l)=\sum_{l'}Z(3\cos^2\theta-1)c(l\to l',m_l)\times Y_{l'}{}^{m_l}(\Omega_c)u_1'(r;nl\to l'). \tag{10}$$

The coefficients, $c(l\to l',m_l)$, in (10) are obtained from the expansion

$$H_1u_0(nlm_l)=-\tfrac{1}{2}\sum_{l'}Z(3\cos^2\theta-1)c(l\to l',m_l)\times Y_{l'}{}^{m_l}(\Omega_c)u_0'(nl)\begin{cases}r_c{}^2/r^3 & \text{for } r_c\leqslant r\\ r^2/r_c{}^3 & \text{for } r_c\geqslant r,\end{cases} \tag{11}$$

or

$$c(l\to l',m_l)=\int_0^{4\pi}[Y_{l'}{}^{m_l}(\Omega_c)]^*(3\cos^2\theta-1)Y_l{}^{m_l}(\Omega_c)d\Omega_c, \tag{12}$$

and the "excitation," $u_1'(r;nl\to l')$, is a function of r_c as well as r. Selection rule considerations show that $l'=l$ or $l'=l\pm2$. Excitations for which $l'=l$ are termed "radial," while those for which $l'=l\pm2$ are termed "angular."

Inserting (10) into (7) and performing the part of the core summation which is over m_l, one obtains

$$\gamma(r)=\sum_{n,l\to l',m_s}\gamma(r;nl\to l'), \tag{13}$$

and

$$\gamma(r;nl\to l')=4C(l\to l')r^3\int_0^\infty u_0'(nl)u_1'(r;nl\to l')r_c{}^{-3}dr_c, \tag{14}$$

where

$$C(l\to l')=\sum_{m_l=-l}^{l}[c(l\to l',m_l)]^2.$$

In particular, $C(s\to d)=C(d\to s)=1/5$, $C(p\to p)=6/25$, $C(p\to f)=9/25$, $C(d\to d)=2/7$, and $C(d\to g)=18/35$.

For each excitation, $u_1'(r;nl\to l')$, it is customary to choose a trial wave function of the form

$$u_1'(r;nl\to l')=u_0'(nl)\sum_{i=1}^{i\text{max}}\lambda_i(r;nl\to l')r_c{}^{i+k}, \tag{15}$$

where the λ_i are variation parameters and the integer, k, permits one to vary the start of the series solution. One then minimizes the second-order energy associated with each excitation:

$$E_2(\mathbf{r};nl\to l')=\phi_1(\mathbf{r};nl\to l')+\phi_2(\mathbf{r};nl\to l'), \tag{16}$$

where

$$\phi_1(\mathbf{r};nl\to l')=\sum_{m_l=-l}^{l}2\langle u_0(nlm_l)|H_1(\mathbf{r})|\times u_1(\mathbf{r};nl\to l',m_l)\rangle, \tag{17}$$

and

$$\phi_2(\mathbf{r};nl\to l')=\sum_{n_l=-l}^{l}\langle u_1(\mathbf{r};nl\to l',m_l)|H_0-E_0|\times u_1(\mathbf{r};nl\to l',m_l)\rangle. \tag{18}$$

The $nl\to l$ notation is now deleted and the functions, $\gamma(r)$, $\phi_1(\mathbf{r})$, and $\phi_2(\mathbf{r})$, associated with each excitation, $u_1'(r)$, are written in matrix notation.[17] Let $\Lambda(r)$ be a column matrix composed of the $\lambda_i(r)$. In addition, components of column matrices G and $S(r)$ and the symmetric matrix T are defined as follows:

$$g_i=\int_0^\infty[u_0'(nl)]^2r_c{}^{i+k-3}dr_c, \tag{19}$$

$$s_i(r)=2\left[r^{-3}\int_0^r[u_0'(nl)]^2r_c{}^{i+k+2}dr_c+r^2\int_r^\infty[u_0'(nl)]^2r_c{}^{i+k-3}dr_c\right], \tag{20}$$

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[17] R. Ingalls, Ph.D. thesis, Department of Physics, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, May, 1962 (unpublished).

$$t_{ij}=2[l'(l'+1)-l(l+1)+(i+k)(j+k)] \times\int_0^\infty [u_0'(nl)]^2 r_c^{i+j+2k-2}dr_c. \quad (21)$$

With these definitions one may derive the matrix equations[17]

$$\phi_1(\mathbf{r})=-CD(\theta)\tilde{S}(r)\Lambda(r), \quad (22)$$

$$\phi_2(\mathbf{r})=\tfrac{1}{2}CD(\theta)\tilde{\Lambda}(r)T\Lambda(r), \quad (23)$$

and

$$\gamma(r)=4Cr^3\tilde{G}\Lambda(r), \quad (24)$$

where $D(\theta)=(3\cos^2\theta-1)^2$. Minimizing the energy, E_2, with respect to the variation parameters, λ_i, one obtains the set of simultaneous equations:

$$T\Lambda(r)=S(r), \quad (25)$$

with the solutions

$$\Lambda(r)=T^{-1}S(r), \quad (26)$$

so that

$$\gamma(r)=4Cr^3\tilde{G}T^{-1}S(r). \quad (27)$$

It should be remarked that not only must the λ_i satisfy equations (26), but that they must also satisfy two important orthogonality conditions. Equation (6) reduces to a restriction on $\lambda_i(r;nl\rightarrow l)$:

$$\int_0^\infty u_0'(nl)u_1'(r;nl\rightarrow l)dr_c=0. \quad (28)$$

This condition must be met for the radial excitations, $2p\rightarrow p$, $3p\rightarrow p$, and $3d\rightarrow d$. The fact that the total wave function for any two electrons must be orthogonal connects $\lambda_i(r;n_1l_1\rightarrow l_2)$ with $\lambda_j(r;n_2l_2\rightarrow l_1)$. To first order in the λ_i

$$\int_0^\infty [u_0'(n_1l_1)u_1'(r;n_2l_2\rightarrow l_1) +u_0'(n_2l_2)u_1'(r;n_1l_1\rightarrow l_2)]dr_c=0. \quad (29)$$

This equation connects excitations $2p\rightarrow p$ with $3p\rightarrow p$, as well as $3s\rightarrow d$ with $ns\rightarrow d$ ($n=1$, 2, or 3). In principle, (28) and (29) are equations of constraint, and each equation should be used to eliminate a variation parameter before the energy, E_2, is minimized.

NUMERICAL RESULTS

The results of the calculations outlined in the previous section are listed in Table I. Included are the partial factors, $R(nl\rightarrow l')$, and also the major contributions to γ_∞, namely, the radial factors, $\gamma_\infty(nl\rightarrow l)$. In this table, the m_s summation of (13) has been performed, that is, (14) has been multiplied by two for every excitation except $3d\rightarrow g$, $3d\rightarrow d$ and $3d\rightarrow s$. Also listed is the minimized second-order energy, $E_2(nl\rightarrow l')$, assciated with each partial factor. The various integrals which contributed to these results are tabulated in reference 17.

TABLE I. The partial results which contribute to the Sternheimer factors for the ferrous ion, R and γ_∞. The minimized second-order energy, E_2, (in atomic units), associated with each partial factor is also given.

$nl\rightarrow l'$	$R(nl\rightarrow l')$	$\langle E_2(r;nl\rightarrow l')\rangle_{3d}$	$\gamma_\infty(nl\rightarrow l)$	$E_2(r;nl\rightarrow l)\times r^6$
$3d\rightarrow d$	$+0.015$	-1.88×10^{-3}	-2.39	-3.63×10^{-1}
$3p\rightarrow p$ (a)	$+0.365$	-1.52×10^{-4}	-5.98	-2.28×10^{-2}
$3p\rightarrow p$ (b)	$+0.073$	-2.80×10^{-4}	-9.98	-2.37×10^{-2}
$3p\rightarrow p$ (c)	-0.252	-3.24×10^{-4}	-14.14	-2.39×10^{-2}
$2p\rightarrow p$ (a)	-0.318	-0.61×10^{-4}	-0.73	-0.00×10^{-2}
$2p\rightarrow p$ (b)	-0.201	-0.21×10^{-4}	$+0.78$	$+0.03\times10^{-2}$
$2p\rightarrow p$ (c)	-0.098	$+1.11\times10^{-4}$	$+2.07$	$+0.11\times10^{-2}$
$3d\rightarrow g$	$+0.018$	-4.76×10^{-3}		
$3d\rightarrow s$	$+0.00$	-2.46×10^{-4}		
$3s\rightarrow d$	$+0.071$	-4.24×10^{-3}		
$3p\rightarrow f$	$+0.042$	-4.82×10^{-3}		
$2p\rightarrow f$	$+0.064$	-2.16×10^{-4}		
$2s\rightarrow d$	$+0.087$	-2.42×10^{-4}		
$1s\rightarrow d$	$+0.050$	-3.32×10^{-7}		
		Totals		
	$R(\text{rad})=-0.11$[b]		$\gamma_\infty(\text{rad})=-11.6$[b]	
	$R(\text{ang})=+0.33$		$\gamma_\infty(\text{ang})=+1.0$[d]	
	$R=+0.22$		$\gamma_\infty=+10.6$	

[a] $E_2(2p\rightarrow p)$ was minimized first, then $\lambda_1(3p\rightarrow p)$ eliminated before $E_2(3p\rightarrow p)$ was minimized.

[b] $E_2(2p\rightarrow p)+E_2(3p\rightarrow p)$ was minimized as a unit.

[c] Similar to case (a) except that $E_2(3p\rightarrow p)$ was minimized first, etc.

[d] See reference 10.

In the above calculations, several values of the parameter, k, of (15) were tried ($k=+1$, 0, and -4). It was found that the results were quite insensitive to the actual value of k used. In the few instances where different values of this parameter led to different results, the value of $R(nl\rightarrow l')$ or $\gamma_\infty(nl\rightarrow l)$ corresponding to the lowest value of the energy, $E_2(nl\rightarrow l')$, was adopted. In most cases six or seven variation parameters were used with the partial results for $E_2(nl\rightarrow l')$ converging rather well to a lowest value as the number of variation parameters was increased.

Although the variation parameters leading to $R(ns\rightarrow d)$ and $R(3d\rightarrow s)$ are, in principle, related by (29), this complex condition appeared to have minor influence on the final results and was therefore ignored. On the contrary, the $2p\rightarrow p$ and $3p\rightarrow p$ results for both factors, R and γ_∞, were found to be affected greatly by (29) and also extremely sensitive to the way this requirement was satisfied. In principle, one may (a) minimize $E_2(2p\rightarrow p)$ and then eliminate one of the $\lambda_i(3p\rightarrow p)$ before $E_2(3p\rightarrow p)$ is minimized; or (b) minimize $E_2(2p\rightarrow p)+E_2(3p\rightarrow p)$ simultaneously satisfying the constraint imposed by (29); or, finally, use the method corresponding to (a), except that $E_2(3p\rightarrow p)$ is minimized first, etc. As is evident from Table I, each method gave a different result for R and also γ_∞. Although methods (a) and (c) appeared to give the same energy, $E_2(2p\rightarrow p)+E_2(3p\rightarrow p)$, method (b) gave even lower values for this energy so that the results adopted here are obtained using (b), that is: $R=+0.22$ and $\gamma_\infty(\text{rad})=-11.6$.

It should be remarked that the much less important $\gamma_\infty(\text{ang})$ is not included here because the variational method appeared to diverge when applied to $\gamma_\infty(3s\rightarrow d)$ for $k=+1$ or 0 (the integrals involved in this calculation diverge if $k<0$). This was not investigated further, nor the complicated orthogonality conditions applied, since the ferric γ_∞(ang), which is expected to be very similar, had already been calculated via the Thomas-Fermi method and reported by Burns and Wikner.[10] Using their value (γ_∞(ang) $=+1.04$) the ferrous factor, γ_∞, may be stated as $\gamma_\infty=-10.6$.

DISCUSSION

In discussing the above results, one should bear in mind that free-ion wave functions have been used. A more detailed treatment should, in any case, include the crystalline field, so that R (and, perhaps, γ_∞) would be expected to vary from compound to compound. There is also the characteristic disadvantage of the variational method, in that one is at the mercy of a judicious choice of a trial wave function. It is conceivable that some other choice would provide lower energy and different Sternheimer factors.

In addition, exchange has been left out of this calculation, although its relative importance here is not known. One could perhaps include exchange with either the more accurate method of Sternheimer,[9,18] or even the more preferable general second-order perturbation treatment of Dalgarno.[19] Perhaps it would be even advantageous to start from the beginning and obtain better free-ion wave functions without the central field restriction. Watson[20] and Freeman have, in fact, carried out m_s and m_s, m_l unrestricted Hartree-Fock calculations for the free ferrous ion, obtaining R(rad). Although their value for R(rad) is negative and in qualitative agreement with the results in this paper [$R(2p\rightarrow p)$ negative, $R(3p\rightarrow p)$ and $R(3d\rightarrow d)$ positive], the corresponding value of R(ang) is not contained in their calculation, so that no conclusion about the accuracy of the present R value may be made. It may also be noted that the R results here are similar to the R results for the Cu atom as calculated by Sternheimer (see page 161 of the last reference in footnote 9). Thus, for Cu, the factors are R(rad) $=-0.02$ and R(ang) $=+0.27$, so that $R=+0.25$. These may be compared with the present ferrous results of -0.11, $+0.33$ and $+0.22$, respectively. Moreover, for Cu, $R(2p\rightarrow p)$ also gives antishielding, while $R(3p\rightarrow p)$ and $R(3d\rightarrow d)$ each give shielding.

In estimating Q, one finds that spin-orbit coupling and also the lattice contribution generally tend to reduce the field gradient, q.[17,21] Therefore, if spin-orbit coupling and the effects of the lattice are to be ignored in (2) and (3), it is advisable to use the largest available ferrous quadrupole splittings, namely, $|\frac{1}{2}e^2qQ|=0.36$ cm/sec for $Fe_2SO_4\cdot 7H_2O$,[5] or 0.37 cm/sec for $FeSiF_6\cdot 6H_2O$.[6] In calculating q_{val} in (3), if one also uses the free-ion expectation values,[13,17] $|\langle 3\cos^2\theta-1\rangle_{3d}|=4/7$ and $\langle r^{-3}\rangle_{3d}=5.1$ au, one obtains $(1-R)Q=0.12$ b or $Q=0.15$ b.

In comparing this Q value with the larger one of Burns,[11] it should be mentioned that the similar calculation of the ferric factors, $\gamma_\infty(2p\rightarrow p)$ and $\gamma_\infty(3p\rightarrow p)$ by Burns and Wikner[10] was done using method (a) of the last section.[22] For comparison, the γ_∞(rad) results for the two ions, using method (a) are

Ion	$\gamma_\infty(3d\rightarrow d)$	$\gamma_\infty(2p\rightarrow p)$	$\gamma_\infty(3p\rightarrow p)$
Ferric	-1.53	-0.68	-5.00
Ferrous	-2.39	-0.73	-5.98

Watson[20] mentions that it is reasonable to expect the more contracted ferric ion (particularly in the $3d$ wave function) to give smaller γ_∞ values. However, it is very likely that a method (b) calculation would yield a better value for the ferric γ_∞, which would probably be about -8.1 instead of -6.2, thereby reducing the Q estimate by Burns. Covalent effects in the ferric compounds would reduce it still more.[6,17] On the other hand, Burns[22] remarks that the spin-orbit coupling constant, which goes roughly as $\langle r^{-3}\rangle_{3d}$, is somewhat reduced in going from the free ion to the solid, so that, therefore, the ferrous estimate of q_{val} should possibly also be reduced. This, in turn, would increase the value of Q as calculated from the ferrous data. Thus, although there is still much work in order concerning this matter, the two methods of determining Q show signs of converging, possibly around the value of $+0.2$ b.

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[21] An analysis of the temperature dependence of the quadrupole splitting in several ferrous compounds (see reference 5), which includes spin-orbit coupling, is in progress.

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