Antishielding of Magnetic and Electric Hyperfine Interactions in Open Shell Ions

A. J. Freeman

National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts, and
U. S. Army Materials Research Agency, Watertown, Massachusetts*

AND

R. E. Watson

*Bell Telephone Laboratories, Murray Hill, New Jersey, and Atomic Energy Research Establishment,
Harwell, England*

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In a previous paper, a method was presented for determining, within the framework of the unrestricted Hartree-Fock formalism, the contribution of closed atomic shells (called Sternheimer antishielding) to magnetic and electric hyperfine interactions. We here discuss and apply this method to the study of the antishielding of both magnetic dipole and electric quadrupole interactions associated with the aspherical valence electrons of atoms and ions. In addition to closed shell antishielding, it is shown that there are repercussions within the open shell which are significant for hyperfine interactions. Results of specific computations for the free Fe^{2+} ion and the Cl atom are given, and comparisons are made with earlier perturbation theory results. An estimate is made of the quadrupole moment of the excited state of Fe^{57}. Finally, the serious symmetry problem, which is associated with polarization investigations applied either to atoms or solids, is discussed.

I. INTRODUCTION

THE importance of the contribution of closed atomic shells to both magnetic and electric hyperfine interactions has been strongly emphasized in recent years.[1-3] Inadequate knowledge of the precise role played by the distortions of core electrons is a major reason for the present inadequate quantitative understanding of hyperfine interactions. For example, there is currently great interest in the role these polarizations (called antishielding) play in experimental estimates of the nuclear quadrupole moment (Q) of the excited state of Fe^{57}, the isotope which plays such a prominent role in Mössbauer experiments. These estimates, involving theoretical calculations, for the Fe^{2+} and Fe^{3+} ions have yielded[4-8] rather differing values for this moment.

Following the pioneering work of Sternheimer[1,2] on magnetic dipole and electric quadrupole polarizations (or antishielding effects) of closed shells, theoretical investigations have traditionally started with conventional Hartree or Hartree-Fock wave functions (where closed shells are inert and spherical). One then

adds the distorting potential (due, generally, to aspherical valence electrons or sources outside the ion) as a perturbation and applies perturbation theory techniques to estimate the antishielding effects. In a recent publication,[9] we presented a method for calculating, within the framework of the unrestricted Hartree-Fock (UHF) formalism, the antishielding associated with magnetic and electric effects. By way of illustrating the method, emphasis was placed on the calculation of the Sternheimer quadrupole antishielding factor for the case of a closed-shell ion in an external crystal field gradient. In addition it was shown that, in its natural handling of orthogonalization, self-consistency, and exchange, this new scheme offers certain advantages over the perturbation-variation approaches.

In this paper we shall use the UHF method to study the antishielding of the magnetic dipole and electric quadrupole interactions associated with the aspherical valence electrons of ions. We shall see that in addition to closed-shell antishielding, there exist repercussions within the open shell which are significant for hyperfine interactions. Results of specific computations for the free Fe^{2+} ion and the Cl atom are given and comparisons are made with earlier perturbation theory results. Fe^{2+} was chosen because of the experimental interest already noted; Cl was chosen because Sternheimer's early work was concerned with this ion. Magnetic dipole and electric quadrupole antishielding results will be discussed for both ions along with an estimate of Q for Fe^{57m}. Estimates of Q^{4-8} have either involved the Fe^{2+} ion where one normally ignores the effect of the crystalline environment and concentrates on the quadrupole interaction (and induced antishielding)

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[1] R. M. Sternheimer and H. M. Foley, Phys. Rev. **92**, 1460 (1953); H. M. Foley, R. M. Sternheimer, and D. Tycko, *ibid.* **93**, 734 (1954); R. M. Sternheimer, *ibid.* **96**, 951 (1954); R. M. Sternheimer and H. M. Foley, *ibid.* **102**, 731 (1956).

[2] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950); **84**, 244 (1954); **86**, 316 (1952); **95**, 736 (1954); **105**, 158 (1957).

[3] See, for example, A. J. Freeman and R. E. Watson, in *Treatise on Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published). R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961) and references therein.

[4] S. De Benedetti, G. Lang, and R. Ingalls, Phys. Rev. Letters **6**, 60 (1961).

[5] G. Burns, Phys. Rev. **124**, 524 (1961).

[6] C. E. Johnson, W. Marshall, and G. J. Perlow, Phys. Rev. **126**, 1503 (1962); A. Abragam and F. Boutron, Compt. Rend. **252**, 2404 (1961).

[7] R. Ingalls, Phys. Rev. **128**, 1155 (1962).

[8] R. M. Sternheimer, Phys. Rev. **130**, 1423 (1960).

[9] R. E. Watson and A. J. Freeman, Phys. Rev. **131**, 26 (1963), henceforth, denoted as I.

due to the unfilled $3d$ shell, or they involve the spherical Fe^{3+} ion, and estimates of the crystal field gradient and the antishielding associated with it. We will see that the trend observed by Ingalls,[7] i.e., that successive improved computations have led to a closing of the gap between the estimates of Q based on the Fe^{2+} or Fe^{3+} results, is continued with the present investigation. Finally, the serious symmetry problem which is associated with this, as well as with many other polarization investigations applied either to atoms or solids, is discussed.

II. STERNHEIMER ANTISHIELDING AND THE UNRESTRICTED HARTREE-FOCK METHOD FOR OPEN SHELL IONS

It was shown previously[9] that the contribution of closed atomic shells to hyperfine interactions could be determined within the Hartree-Fock formalism, provided one relaxed several restrictions generally associated with the conventional (restricted) Hartree-Fock (RHF) description of open shell ions.[3,10] In RHF theory, one requires that a one-electron H-F space-orbital (ψ_i) be separable into a product of a radial function times a spherical harmonic;

$$\psi_i(\mathbf{r}) = [U_i(r)/r] Y_{m_i}{}^{l_i}(\theta,\phi) \qquad (1)$$

and that $U_i(r)$ be independent of the m_s and m_l quantum numbers associated with $\psi_i(\mathbf{r})$ [i.e., that there be one $U_i(r)$ per shell]. These restrictions assume a *spherical* H-F potential whose exchange terms are identical for electrons of either m_s value and lead to the conventional shell structure description of an ion where closed shells are "closed" in the sense of having inert ^1S character. In this conventional description, one obtains the familiar expressions for the orbital, spin magnetic dipole, and electric quadrupole hyperfine interactions. For an ion with a single open (non-s) shell these may be written as

$$H_{L \cdot I} = (\mu/I)\langle r^{-3} \rangle \sum_i \mathbf{l} \cdot \mathbf{I}, \qquad (2)$$

$$H_{SD} = (\mu/I)\langle r^{-3} \rangle \sum_i \{3(\mathbf{s}_i \cdot \mathbf{r}_i/r_i)(\mathbf{I} \cdot \mathbf{r}_i/r_i) - \mathbf{s}_i \cdot \mathbf{I}\}, \qquad (3)$$

$$H_Q = [e^2 Q/2I(I-1)]\langle r^{-3} \rangle \times \sum_i [I(I+1) - 3(\mathbf{I} \cdot \mathbf{r}_i/r_i)^2], \qquad (4)$$

respectively, where I and μ are the nuclear spin and magnetic moment and the operators inside the sums involve angular and spin, but not radial, coordinates of the *open* shell only. The radial dependence for the shell appears in the term

$$\langle r^{-3} \rangle = \int_0^\infty [U_i(r)]^2 r^{-3} dr, \qquad (5)$$

which is, of course, identical for the three interactions since there is but a single function per shell.

So much for the conventional H-F description of the hyperfine interactions. Let us now discuss the predictions based on the UHF approach where the restrictions mentioned above (i.e., the separability, m_l, and m_s restrictions) are relaxed. The open shell of an ion which has nonzero hyperfine interactions given by Eqs. (2) to (4) contributes an aspherical term of $Y_0{}^2(\theta,\phi)$ symmetry to the Hartree-Fock potential which, by definition, has been omitted from the RHF equations for the ion's closed shells. Including this term (within the UHF formalism) induces small aspherical distortions of $Y_0{}^2(\theta,\phi)$ symmetry within these shells. (Using perturbation techniques, Sternheimer[2] pioneered in investigating the contribution of these distortions to H_Q.) These polarization effects can be incorporated in Eq. (4) if we replace the $\langle r^{-3} \rangle$ *integral* by an effective *parameter* $\langle r^{-3} \rangle_Q$ where

$$\langle r^{-3} \rangle_Q = \langle r^{-3} \rangle (1 - R_Q). \qquad (6)$$

R_Q is a Sternheimer antishielding factor much like the external field antishielding factor, γ_∞, and is also made up of "radial" and "angular" antishielding contributions (see I for a discussion of these).

Consider now the case of the H_{SD} interaction. The open shell makes a contribution to the Hartree-Fock potential which is not only aspherical but has different exchange terms for electrons differing in m_s. The contribution, when included in the H-F equations, induces closed shell (spin-polarized[3] aspherical) distortions which, in turn, contribute to an $\langle r^{-3} \rangle_{SD}$ parameter.

Closed shells may also contribute to a $\langle r^{-3} \rangle_{LI}$ parameter, but unlike the cases of $\langle r^{-3} \rangle_Q$ and $\langle r^{-3} \rangle_{SD}$ the pertinent distortions are entirely due to aspherical exchange potential terms. An aspherical Coulomb potential produces identical distortions in a pair of orbitals which differ only in the sign of their m_l quantum number, whereas an aspherical exchange potential may affect the pair differently. As contributions to $\langle r^{-3} \rangle_{LI}$ only occur when the spatial functions of these electron orbital pairs are different,[11] Coulomb distortions cannot contribute to this interaction.

The mechanisms sketched (briefly) above leading to closed shell contributions to the $\langle r^{-3} \rangle$ parameters, differ for the three cases, and this implies that the effective $\langle r^{-3} \rangle$ values also differ. The extent of any such differences is of some interest if only because Q is never observed directly by experiment, but requires an estimate of the electric quadrupole field. In the case of free ion data this is commonly done by equating $\langle r^{-3} \rangle_Q$ with an experimentally known $\langle r^{-3} \rangle_{SD}$ or $\langle r^{-3} \rangle_{LI}$. Sternheimer concluded from his computations that the

[10] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961); see R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955), for the pioneering investigation into the symmetry properties of Hartree-Fock orbitals which are appropriate to the aspherical UHF problem of interest here.

[11] Other, of course, than differences simply associated with differing $Y_l{}^{m_l}(\theta,\Phi)$. In the case of radial antishielding, the contribution to $\langle r^{-3} \rangle_{LI}$ comes from differing radial behavior, hence, differing $\langle r^{-3} \rangle$ integrals for the pair.

three $\langle r^{-3}\rangle_{\rm eff}$'s are almost identical, although they each differ by as much as thirty percent from the $\langle r^{-3}\rangle$ integral. Recently, Harvey[12] has obtained separate experimental values of $\langle r^{-3}\rangle_{LI}$ and $\langle r^{-3}\rangle_{SD}$ for atomic oxygen and fluorine and found that in each case the two effective $\langle r^{-3}\rangle$ values differ by about 10%. Bessis et al.[13] have done a configuration interaction estimate of the radial antishielding for the open $2p$ shell of oxygen and find similar deviations in the $\langle r^{-3}\rangle_{\rm eff}$ values which are smaller than those found by Harvey. These differences which are greater than Sternheimer's work predicted, suggest that considerably more must be known about free-ion antishielding for large ions before values of $\langle r^{-3}\rangle_Q$ are known to better than 10%.

III. DESCRIPTION OF THE CALCULATIONS

Sternheimer obtained estimates of free-ion anti-shielding by numerical integration of the perturbation equations. Ingalls[7] solved the analytic-variation version[14] of the same equations in his estimate of $\langle r^{-3}\rangle_Q$ for Fe^{2+}. We have used the self-consistent field UHF methods described in I where a separate H-F radial equation is solved for each electron orbital; these solutions yield the "radial" contribution to the antishielding. As previously stated, this approach naturally and properly deals with self-consistency, exchange, and orthogonality—problems which beset the perturbation-variation calculations.[15] Orbitals of mixed angular character have not been obtained and as a result (see I) angular antishielding has not been included. While these angular terms play a minor role in external field antishielding (γ_∞), their effect is not negligible, relative to radial antishielding, in the case of free ions with aspherical valence electrons. The inclusion of angular effects, however, would have considerably complicated the computations and in view of the symmetry problem, discussed in Sec. V, such an effort did not seem warranted. We shall rely on Ingall's estimate of the angular antishielding contribution to the Fe^{2+} $\langle r^{-3}\rangle_Q$, the one case where detailed quantitative results will be of interest to us. Other than this, we shall use the radial antishielding results to gain some information on how and why the magnetic dipole and electric quadrupole $\langle r^{-3}\rangle$ values differ.

The analytic H-F methods[16,17] applied in I have

[12] J. S. M. Harvey, Ph.D. thesis, Oxford University, 1962 (unpublished); we are grateful to P. G. H. Sandars for informing us of this work.

[13] N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. 128, 213 (1962).

[14] T. P. Das and R. Bersohn, Phys. Rev. 102, 733 (1956).

[15] See Ingalls (Ref. 7) for an example of orthogonalization effects within the analytic variational approach, Ref. 14.

[16] R. E. Watson, Technical Report No. 12, Solid-State and Molecular Theory Group, MIT, 1959 (unpublished).

[17] For details on the analytic approach see C. A. Coulson, Proc. Cambridge Phil. Soc. 34, 204 (1938); C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951); and R. K. Nesbet, Rev. Mod. Phys. (to be published).

been used here employing basis sets obtained for previously reported[1,16] RHF functions. In the course of the investigation several calculations with a second larger basis set were done for Fe^{2+}. The resulting RHF function is superior to those appearing in the literature and is tabulated in Appendix I. The improved basis set had, however, little effect on the $\langle r^{-3}\rangle_{\rm eff}$ values; for this reason, the results appearing in the body of this paper are those which were obtained with the smaller basis set.

Calculations will be reported for ions with $L=M_L$ and $S=M_S$; the m_l and m_s RHF restrictions have been relaxed, yielding one radial function per H-F one-electron orbital. As already indicated, this gives the radial contribution to the three $\langle r^{-3}\rangle_{\rm eff}$ values, and the spin-polarized s shell Fermi-contact term contributions[3] as well.

A second set of calculations was done where only the m_l restriction was relaxed, i.e., orbitals differing only in m_s quantum numbers were constrained to have the same radial behavior. Such calculations yield closed shell $\langle r^{-3}\rangle_Q$ and $\langle r^{-3}\rangle_{LI}$ contributions but nothing for the spin-dependent hyperfine terms. While this set of calculations yields no new results, it was undertaken in order to shed some light on the first set of calculations and on some of the problems associated with the RHF formalism. These matters are discussed in Appendix II; only the first set (m_l+m_s UHF) of results is discussed in the following section.

IV. RESULTS

A. Neutral Chlorine Atom

The Cl m_l+m_s UHF calculation was done for the ion in the $3p^5$, ^2P ($M_L=1$, $M_S=\frac{1}{2}$) state. The resulting radial antishielding contributions to the $\langle r^{-3}\rangle_{\rm eff}$ values are listed in Table I; contributions from subshells of differing m_s are listed separately. One may interpret the total $\langle r^{-3}\rangle_{\rm eff}$ values as being associated either with the five occupied $3p$ electrons or with the $3p$ hole.[18] Angular antishielding has, of course, been omitted and it is expected that it will at least reduce $\langle r^{-3}\rangle_Q$, thereby

TABLE I. Radial distortion contributions to the $\langle r^{-3}\rangle_{\rm eff}$ hyperfine parameters (in a.u.) as obtained by the present calculations for the Cl $^2P_{3/2}$ state.

Subshell	Contributions to		
	$\langle r^{-3}\rangle_Q$	$\langle r^{-3}\rangle_{SD}$	$\langle r^{-3}\rangle_{LI}$
$2p^3\downarrow$	0.88	0.88	0.69
$2p^3\uparrow$	0.12	-0.12	0
$3p^3\uparrow$	-0.22	0.22	0
$3p^2\downarrow$	6.36	6.36	6.35
Total	7.13	7.34	7.03
$\langle r^{-3}\rangle_{\rm RHF}=6.50$ a.u.			

[18] In this case one must reverse the signs of Eqs. (2) to (4) and limit the sums to the hole.

bringing it closer to the RHF $\langle r^{-3} \rangle$ value. Neglecting these angular terms we see that the three $\langle r^{-3} \rangle_{\text{eff}}$ values differ by less than 5%, though their disagreement with the RHF value is somewhat greater. The subshells of spin antiparallel to that of the unfilled subshell make zero valued contributions to $\langle r^{-3} \rangle_{LI}$ as was expected (see Sec. II). Not so expected is the relatively large role played by the $2p^3 \downarrow$ subshell in $\langle r^{-3} \rangle_Q$ and $\langle r^{-3} \rangle_{SD}$. This is not due to an exchange interaction between subshells but instead to the behavior of that $2p$ orbital having m_l and m_s in common with the $3p$ hole, a matter which is discussed in Appendix II. The deviation between the RHF $\langle r^{-3} \rangle$ and $\langle r^{-3} \rangle_{\text{eff}}$ values would be even greater if it were not for the open $3p^2 \downarrow$ subshell; these electrons have radial functions which are more diffuse than their RHF counterpart. This effect is reflected in the $\langle r^{-3} \rangle$ integrals for its orbitals (which are 6.352 and 6.345 a.u. for m_l equal to 0 and +1, respectively) and is due to exchange effects. We shall see that the same effect occurs for Fe^{2+} later on in this section at which time this matter will be discussed in more detail.

The spin polarized H-F formalism (m_s UHF) also yields a nonzero Fermi contact term arising from the ion's s shells.[3] This term is isotropic (in the sense of being independent of the M_L quantum number) and is of the form

$$H_c = (\mu/I)\mathbf{I} \cdot \sum_I s8\pi/3 |\psi_i(0)|^2, \qquad (7)$$

where the sum is over all the s electrons and $|\Psi_i(0)|^2$ is the s-electron density at the nucleus. The contribution from this term can be incorporated into one of the magnetic $\langle r^{-3} \rangle_{\text{eff}}$'s. For example, in the present case the $1s$, $2s$, and $3s$ shells make contributions of -2.08, $+0.78$, and $+1.14$, for a total of -0.16 a.u. to $\langle r^{-3} \rangle_{LI}$. These calculations yield a small contact term contribution to the magnetic hyperfine interaction because of the almost complete cancellation between shells.[19]

Sternheimer's original free-ion investigations[2] were for neutral Cl, but, unfortunately, lack of wave functions necessitated his using Cl⁻ H-F orbitals[20]; since this affects his numerical results, detailed comparisons will not be made. His calculations were done for specific J states with orbital and spin dipolar terms merged to yield a single R_{mag} defined as in Eq. (6); these results, translated into $\langle r^{-3} \rangle_{\text{eff}}$ values, are given in Table II. The radial antishielding is considerably larger than that obtained in the present calculation (c.f., Table I); the angular terms vary in sign for the magnetic and electric quadrupolar cases. The s shell spin polarization

TABLE II. Antishielding contributions to the $\langle r^{-3} \rangle_{\text{eff}}$ hyperfine parameters (in a.u.) obtained by a perturbation calculation for Cl $^2P_{3/2}$ using the $\langle r^{-3} \rangle_{\text{RHF}}$ of Table I and Sternheimer's R results.[2]

	$\langle r^{-3} \rangle_Q$	$\langle r^{-3} \rangle_{\text{mag}}$
$\langle r^{-3} \rangle_{\text{rad}}$	8.85	9.56
$\langle r^{-3} \rangle_{\text{ang}}$	0.26	−0.33
Fermi contact term contribution	0	−0.40
Total	9.11	8.83

yields a net antishielding which is similar to our results in both magnitude and sign but differs in that the $3s$ shell term has reversed sign and has joined the $1s$ in antishielding.[21]

B. Fe^{2+} Ion

The Fe^{2+} calculation was done for the ion in the $3d^6$, ^4D ($M_L = 2$, $M_S = 2$), state; the resulting radial antishielding contributions are listed in Table III. Also listed are the perturbation-variation radial terms on which Ingall's based his estimates[7] of the quadrupole moment of Fe^{57m}. Again neglecting angular antishielding we can compare $\langle r^{-3} \rangle_{\text{eff}}$ values. We find a somewhat different behavior than was seen for Cl. The three effective $\langle r^{-3} \rangle$ values are all smaller than the RHF value (and this trend would probably be furthered by the inclusion of the angular terms) with $\langle r^{-3} \rangle_Q$ almost in agreement with $\langle r^{-3} \rangle_{\text{RHF}}$ and the magnetic terms some ten percent smaller. The variation between these $\langle r^{-3} \rangle_{\text{eff}}$ values is greater than that for Cl and suggests that the frequently used practice of equating $\langle r^{-3} \rangle_Q$ to an experimentally known magnetic $\langle r^{-3} \rangle_{\text{eff}}$ in the process of estimating the value of Q has, at best, a 10% accuracy associated with it. Again, it should be remarked that the extent of the agreement between $\langle r^{-3} \rangle_{\text{eff}}$'s is remarkable in view of their differing origins.

A nonzero core s electron contact term is also pre-

TABLE III. Radial distortion contributions to the $\langle r^{-3} \rangle$ hyperfine parameters (in a.u.) for Fe^{2+}, $^4D(M_L = 2, M_S = 1)$, obtained in the present calculations compared with the analytic perturbation theory[a] result for $\langle r^{-3} \rangle_Q$.

Subshell	\multicolumn{3}{c}{Contributions to}	Perturbation estimate[a] of
	$\langle r^{-3} \rangle_{SD}$	$\langle r^{-3} \rangle_{LI}$	$\langle r^{-3} \rangle_Q$	$\langle r^{-3} \rangle_Q$
$2p^3\uparrow$	−0.77	0	0.77	} 1.03
$2p^3\downarrow$	−0.37	−0.54	−0.37	
$3p^3\uparrow$	0.42	0	−0.42	} −0.37
$3p^3\downarrow$	0.34	0.35	0.34	
$3d^5\uparrow$	0.16	0	−0.16	−0.08
$3d\downarrow$	4.78	4.78	4.78	5.08
Total	4.55	4.59	4.93	5.66
$\langle r^{-3} \rangle_{\text{RHF}} = 5.08$ a.u.				

[19] This differencing is similar to that obtained in spin polarized calculations for iron series ions (see Ref. 3) except that (1) the cancellation is almost complete here and (2) the $2s$ contribution has the same sign as the $3s$ with the $1s$ shell dominating. These differences are associated with the fact that the $3p$ electrons, unlike the $3d$ shell, penetrate into the region of the $2s$ causing the reversal of the sign of the $2s$ term and an enhancement of the $1s$ shell effect.

[20] D. R. Hartree, Proc. Roy. Soc. (London) **A156**, 56 (1936).

[a] Obtained by using the $\langle r^{-3} \rangle_{\text{RHF}}$ of this table and Ingall's R results (see Ref. 7).

[21] See Table I of Sternheimer (Ref. 2) for a breakdown of the contact term contributions.

dicted by the calculation. As this is identical with that obtained previously in a spin polarized (m_s, but not m_l UHF) calculation[3] we refer the interested reader there for details. This term is an order of magnitude more important here than for Cl largely because of the reversal in sign of the $2s$ shell contribution.

Comparison of the present $\langle r^{-3}\rangle_Q$ estimates with those of Ingalls[7] show qualitative but not quantitative agreement for the individual $2p^6$, $3p^6$, and $3d^5$ shells, but whereas the perturbation-variation calculation yields a net radial (i.e., $R_Q<0$) antishielding, the present self-consistent field investigation has resulted in a net shielding ($R_Q>0$). This difference is in large part due to the sixth $3d$ electron in the UHF calculation which is more diffuse and has a smaller $\langle r^{-3}\rangle$ integral than its RHF counterpart. This is due to a feature of RHF theory, which we shall now examine briefly.

For the case of the $3d^6$ shell of Fe^{2+}, each of the five d electrons of majority-spin experience d-d exchange interactions among one another whereas the remaining electron does not. In order to obtain a single radial function per shell (i.e., the RHF scheme) one normally solves the *average* of the radial H-F equations derived for individual (occupied) electron orbitals of that shell. The result of this averaging process for Fe^{2+} is to include an average exchange term (i.e., five sixths of the majority spin term) in the single RHF radial equation for the shell. On the other hand, in UHF theory, where one solves the individual H-F equations for the different electrons in a shell, the electrons of majority spin undergo the full effect of their exchange interaction and, since exchange acts like an attractive potential, their radial functions contract; the sixth $3d$ electron, not influenced by a d-d exchange term, expands relative to the RHF result. A similar situation occurs in the $3p^5$ shell of Cl where there is an imbalance in p-p exchange between the $3p^3\uparrow$ and $3p^2\downarrow$ subshells. Similar shifts also occur in an ion's closed shells. Along with these considerations of exchange effects, detailed analyses of electron orbital shifts in an open shell must, of course, also include consideration of any aspherical Coulomb terms.

C. Nuclear Quadrupole Moment of Fe^{57m}

As already indicated, estimates of Q for Fe^{57m} have been made from Mössbauer data for the divalent and trivalent ions in crystals. In the latter case the ion is in a $3d^5$, ^6S state, and the source of the quadrupole interaction is the crystalline field itself. Burns[5] carried out a calculation of the crystal lattice sum for the field gradient, and using analytic methods[14] to estimate the Fe^{3+} ion's external field antishielding, (γ_∞), estimated Q to be $+0.46$ b. More recently, Sternheimer[8] has used his computationally superior numerical methods to re-evaluate γ_∞ and otherwise using Burns' results obtained a Q of $+0.28$ b. In treating the case of Fe^{2+}, it has been common practice to ignore the effects of the crystalline environment, and if one assumes

$\langle r^{-3}\rangle_Q=\langle r^{-3}\rangle_{RHF}$ one obtains[4,6] a Q of 0.1 b. Ingall's estimate of antishielding for Fe^{2+} leads to a Q of 0.15 b. If we take Ingall's analysis of the experiment, his estimate of angular antishielding (a contribution to $\langle r^{-3}\rangle_Q$ of -1.68 a.u.), and the present UHF estimate of radial effects, one obtains a Q of $+0.18$ b.

This series of investigations has converged on an estimated value of Q which lies between $+0.18$ and $+0.28$ b, and one is tempted to think of this convergence as real.[22] However, the deficiencies in the theoretical estimates are such that the convergence may in fact be fortuitous, with the true value of Q lying outside of this range. In the case of Fe^{3+}, the estimates rely on a crystal lattice sum which is not straightforward[23] and on a tight-binding model of an ion in an external crystal environment, which may not be adequate (see discussion in I). For Fe^{2+}, the analyses assume the ion to be essentially free, ignore the influence of the environment, and in addition rely on computations which are beset with the problems discussed in the following section.

V. THE SYMMETRY PROBLEM AND RELATIVISTIC AND CORRELATION EFFECTS

The wave functions obtained in the course of the above investigations differ from the true many-electron eigenfunctions in a number of ways: They are non-relativistic and, by definition, interelectronic correlation effects have been omitted. In addition, the distorted closed shells no longer have inert ^1S character, and hence, the single determinant H-F functions are eigenfunctions of neither L^2 nor S^2. Thus, there arises the question of whether this has significant repercussions on the prediction of hyperfine effects. Since the one-electron operators $\mathbf{l}_i$ and $\mathbf{s}_i$ are involved, one might expect an affirmative reply.

Relativistic effects do have significant repercussions on the innermost shells of ions such as Cl and Fe^{2+}. Recent spin-orbit coupling calculations[24] suggest these effects to be small for the open valence shells and are more important for[25] Cl than for Fe^{2+}. Closed shell contributions to an $\langle r^{-3}\rangle_{eff}$ come from differences in behavior of electrons in a given shell. The effect of

[22] We have subsequently obtained an SCF estimate of the Fe^{3+} γ_∞ which is in good agreement with that of Sternheimer (i.e., -10.3 versus his -10.18 for the radial antishielding terms). Details will appear in a future publication. Burns (private communication) and co-workers have done further experimental work on Fe^{3+}, the results of which promise to lead to a further lowering of the Fe^{3+} based estimate of the Fe^{57} moment, perhaps bringing it to a value as low or lower than 0.18 b.

[23] This involved, a lattice sum over ion point charges omitting, among other things, ion sums over induced dipole and quadrupole moments which E. Brun, S. Hafner, and F. Waldner, Compt. Rend. (Suisse) 34, 391 (1961)., have shown to be important.

[24] M. Blume and R. E. Watson, Proc. Roy. Soc. (London) A271, 565 (1963).

[25] Though Cl has a smaller Z value, its $3p$ shell penetrates closer to the nucleus than does the $3d$ and, therefore, it is reasonable that relativistic repercussions on the hyperfine interactions (which depend strongly on the innermost loop of the radial functions) are greater for this ion.

relativistic corrections on such differences has yet to be investigated, but they are expected to be small compared with the effects which follow.

The inclusion of correlation effects in a wave function is known[26] to be important for the evaluation of two-electron operators but not for one-electron operators. In other words, Hartree-Fock functions should do well in predicting the quantities of interest to us here. There remains the question of how well—a question which is still largely unanswered—although the variation of hyperfine fields obtained within the H-F formalism suggest not very well. Since the one-electron orbitals are given some freedom to avoid one another spatially, a small prescribed amount of correlation, in the conventional sense, is built into the wave functions discussed in this paper. However, this freedom is severely constrained by the single determinant H-F treatment which is used.[27] It is perhaps overoptimistic to assume, as is generally done, that correlation effects play a negligible (enhancing) role in hyperfine interactions.

The fact that a wave function is of improper (say L^2 or S^2) symmetry does not necessarily result in repercussions on the expectation value of a particular operator. Investigation for hyperfine interactions has been limited to discussions of the spin polarization of atomic Li. In this case, if one annihilates (e.g., by projection techniques[28]) those parts of the UHF wave functions which are of improper symmetry, one discovers a significant change in the predicted hyperfine interaction,[29] although arguments have been[30] advanced which suggest that the unsymmetrized calculations yield a good approximation. These arguments have not been extended, in a quantitative way,[31] to the spin polarization of larger systems (much less to the distortions of interest to us here).[31a] Their validity has not been universally accepted because they abandon the function of proper symmetry actually appearing in the UHF function, thus implying that a cancellation of terms is the source of the good approximation. In

any case, the role of the symmetry breakdown is not understood for the aspherical effects of interest to us here and until this breakdown is shown to be benign, aspherical ion antishielding results should be viewed and used with caution.

It should 'be pointed out that the symmetry failure is not unique to the problem at hand, but occurs in many treatments of polarization effects in solids and molecules. For example, the familiar Ruderman-Kittel-Kasuya-Yoshida[32] spin polarization of conduction electrons in metals yields a many-electron function for the solid which will, in general, not be an eigenfunction of S^2. The influence of the symmetry breakdown for these cases is even less understood than the one considered here.

VI. CONCLUSION

The UHF method developed in an earlier paper has been used to obtain estimates of the Sternheimer radial antishielding contributions to the magnetic and electric hyperfine interactions of Cl and Fe^{2+}. The results differ from those obtained by existing perturbation-variation methods, due, in large part, to the treatment of the open shell electrons. The imbalance of exchange effects, within an over half-filled open shell, yields appreciable shielding contributions (relative to RHF predictions) to the hyperfine interactions. The resulting estimate of the quadrupolar moment of Fe^{57} yields a further narrowing of the gap between ferrous and ferric ion results obtained previously, but this may be fortuitous.

As discussed in the preceding section, there are a number of uncertainties associated with such investigations whether done by the present UHF method or by the more classical perturbation methods. These include the matter of the breakdown of symmetry. If one is optimistic, one assumes the computational results to be meaningful and not outrageous quantitatively, and if one is pessimistic, the present calculations indicate the uncertainties *within* the Hartree-Fock formalism and its ability to predict observables.

[26] For a review see G. G. Hall, Rept. Progr. Phys. **22**, 1 (1959).

[27] The extreme in this type of correlation occurs in the open-shell treatment of He. See H. Shull and P.-O. Löwdin, J. Chem. Phys. **25**, 1035 (1956).

[28] See, for example, P. -O. Löwdin, in Proceedings of the Paris Symposium on Molecular Quantum Mechanics, 1958 (unpublished), Quantum Chemistry Group, Uppsala University, 1958 (unpublished); Phys. Rev. **97**, 1509 (1955).

[29] L. M. Sachs, Phys. Rev. **117**, 1504 (1960); the symmetrized (projected) contact term is incorrectly reported here and, in fact, is 643 Mc/sec.

[30] W. Marshall, Proc. Phys. Soc. (London) **78**, 113 (1961); N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. **124**, 1124 (1961); and V. Heine, Czech. J. Phys. (to be published).

[31] Although A. J. Freeman and R. E. Watson (unpublished) and Bessis *et al.* (Ref. 13) have found in several cases (nitrogen and oxygen) that the projected function gave a contact term in better agreement with experiment than the spin polarized function.

[31a] Recently, N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. **130**, 1441 (1963), have abandoned their perturbation theory argument (see Ref. 30) indicating that one should use the unprojected function. When dealing with the radial $2p$ shell contributions to the $\langle r^{-3} \rangle_{eff}$ values for F, they report unprojected and projected results and indicate a preference for the latter.

[32] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956); and K. Yosida, Phys. Rev. **106**, 893 (1957).

APPENDIX I. RHF RESULTS FOR Fe^{2+}

A conventional H-F Fe^{2+} wave function, superior to those in the literature, is tabulated here. Its accuracy is similar to previously reported[3,9] Cu^+ and Mn^{2+} functions. The three functions serve to calibrate an earlier series of iron series calculations[16] and comparisons will be made with the Fe^{2+} function of that set. The present functions, like those obtained earlier, are orthonormal analytic orbitals, $U_i(r)$ of the form

$$U_i(r) = \sum_j C_{ij} R_j(r), \qquad (A1)$$

TABLE IV. Parameters (A_j and Z_j) and combining coefficient (C_{ij}) defining the restricted Hartree-Fock orbitals for Fe^{2+} $3d^6$, ^5D.

j	A_j	Z_j	$C_{1s,j}$	$C_{2s,j}$	$C_{3s,j}$
1	0	27.1413	0.91915864	−0.27866007	0.10334212
2	1	23.7801	0.09952211	−0.16345682	0.05706128
3	1	12.0977	−0.00269429	0.72216581	−0.25959995
4	2	11.3466	0.00196258	0.41014795	−0.33397587
5	2	6.7361	−0.00039889	0.04161314	0.25831141
6	2	4.3218	0.00004638	−0.00575154	0.88370606
7	2	2.4412	−0.00000093	0.00124268	0.04280706

j	A_j	Z_j	$C_{2p,j}$	$C_{3p,j}$
8	0	16.7957	0.15386097	−0.04706333
9	0	10.0264	0.85084908	−0.33887362
10	1	9.3049	0.00554905	−0.02602768
11	1	5.4600	0.02569848	0.54181512
12	1	3.4914	−0.00943355	0.55672032
13	1	2.3160	0.00300917	0.03823291

j	A_j	Z_j	$C_{3d,j}$
14	0	1.8628	0.21136774
15	0	2.6928	0.37189040
16	0	4.6342	0.44343215
17	0	8.1233	0.11325634
18	0	13.9775	0.00655315

normalized such that

$$\int_0^\infty |U_i(r)|^2 dr = 1. \qquad (A2)$$

The basis functions, R_j, are of the form

$$R_j(r) = N_j r^{(l+A_j+1)} e^{-Z_j r}, \qquad (A3)$$

where N_j is a normalization constant and is expressible in terms of the other parameters, i.e.,

$$N_j = [(2Z_j)^{2l+2A_j+3}/(2l+2A_j+2)!]^{1/2}. \qquad (A4)$$

$U_i(r)$ of common l value are constructed from a common set of $R_j(r)$'s; the parameters defining the $U_i(r)$'s are listed in Table IV. The computed total energy for the ion is -1261.655 a.u. (1 a.u. = 2Ry) as compared with a previously obtained[16] value of $= 1261.652$ a.u. One-electron energies (ϵ_i's), one-electron kinetic plus nuclear potential energies (K_i's), Slater $F^k(3d,3d)$ integrals and several $\langle r^n \rangle_{3d}$ integrals are listed for both Fe^{2+} calculations in Table V. The K_i's, which omit the interelectronic terms contained in the ϵ_i's, provide the better criterion for wave-function variation. Comparison of these and the $3d$ integrals indicate that only slight changes have occurred in the orbitals. The $\langle r^{-3} \rangle$ integral, which is of particular interest in this paper, has changed by less than one tenth of one per cent. The Fe^{2+} UHF calculations discussed elsewhere in this paper were done with the smaller basis set of the earlier RHF calculation. In addition, some of these calculations were performed using the larger basis set and gave less than 1% change in the resulting $\langle r^{-3} \rangle_{eff}$ values.

APPENDIX II. ADDITIONAL UHF RESULTS FOR Fe^{2+} AND Cl

A number of UHF calculations were done in addition to those discussed in Sec. IV; as they shed some light on the results of that section and on the H-F method, we shall review them here. Let us consider the simpler case of Fe^{2+} first.

Two calculations were done for Fe^{2+} in its $M_L = 0$ state for which (a) no $\mathbf{L \cdot I}$ hyperfine interaction occurs and (b) the closed shell distortions make zero valued contributions to $\langle r^{-3} \rangle_{LI}$. First, an $(m_l + m_s)$ unrestricted calculation was done which yielded an $\langle r^{-3} \rangle_Q$ of 4.92 a.u. and a $\langle r^{-3} \rangle_{SD}$ of 4.54 a.u., in expected agreement (c.f. Sec. II) with the results of Sec. IV. Second, an m_l (but not m_s) unrestricted calculation was carried out which yielded zero-valued closed shell contributions to $\langle r^{-3} \rangle_{SD}$ and a $\langle r^{-3} \rangle_Q$ of 4.93 a.u., i.e., the same value as given by the less restricted calculations. Close agreement is

TABLE V. Restricted Hartree-Fock one-electron energies (ϵ_i), one-electron kinetic plus nuclear potential energies (K_i's) and assorted $3d$ integrals as obtained in the present and an earlier[a] calculation for Fe^{2+} ($3d^6, {}^5D$). Energies in a.u.

	Present calculations	Earlier calculations		Present calculations	Earlier calculations[a]
ϵ_{1s}	−262.046	−262.049	K_{1s}	−337.855	−337.855
ϵ_{2s}	−32.597	−32.601	K_{2s}	−82.690	−82.689
ϵ_{3s}	−4.830	−4.831	K_{3s}	−31.818	−31.807
ϵ_{2p}	−28.078	−28.083	K_{2p}	−82.021	−82.021
ϵ_{3p}	−3.410	−3.412	K_{3p}	−29.969	−29.966
ϵ_{3d}	−1.3171	−1.3187	K_{3d}	−25.143	−25.139
$F^0(3d,3d)$	0.8843	0.8841	$\langle r^{-3} \rangle_{3d}$	5.084	5.081
$F^2(3d,3d)$	0.4095	0.4094	$\langle r^2 \rangle_{3d}$	1.392	1.393
$F^4(3d,3d)$	0.2548	0.2548	$\langle r^4 \rangle_{3d}$	4.509	4.496

[a] See Ref. 16.

not surprising, for in this calculation we solve the *average* of the pair of equations for a pair of occupied orbitals differing only in m_s. Individual electron orbitals do not make the same $\langle r^{-3} \rangle_Q$ contribution as in the $m_l + m_s$ UHF case, but because of the averaging process, the pairs, taken together do.

Cl is more complicated because its open $(3p)$ shell electrons have orbital angular momenta, l, in common with a closed shell. In carrying out the averaging process involved in deriving the RHF equations, one averages over the six occupied $2p$ orbitals to obtain the $2p$ equation and over the five occupied $3p$ orbitals for the $3p$ equation. The different averaging results in different potential terms for the two radial H-F equations whose solution yields $2p$ and $3p$ orbitals which are not orthogonal (thereby violating one of the requirements implicit in the formalism). Orthogonality is normally restored[10] by the introduction of a Lagrange multiplier or by the use of Nesbet's symmetry and equivalence restrictions.[33] It must be emphasized that it is the averaging process, rather than anything implicit in the original H-F equations, which causes the non-orthogonality and the need for introducing a constraint to it. In the $(m_l + m_s)$ UHF approach, where a separate H-F equation is solved for each electron, orbital orthogonality occurs automatically for $2p$ and $3p$ orbitals having common m_l and m_s quantum numbers, as these are eigenfunctions of the same integro-differential equation. For the five pairs of orbitals occupying both shells, the H-F equations are solved subject to the self-consistent condition that there are two occupied eigenfunctions. The sixth $2p$ orbital, which is paired with the $3p$ hole, suffers no such constraint; the effect of this on its wave function is reflected in its $\langle r^{-3} \rangle$ integral which is listed, along with

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[33] See R. K. Nesbet, Ref. 10.

TABLE VI. Values of the $2p$ shell $\langle r^{-3} \rangle$ integrals in a.u. obtained from the $(m_l + m_s)$ UHF calculation for Cl $3p^5$ in which the $3p$ shell hole has quantum numbers $m_l = -1$ and $m_s = -\frac{1}{2}$.

m_l	m_s	$\langle r^{-3} \rangle_{2p}$
-1	$-\frac{1}{2}$	97.25
0	$-\frac{1}{2}$	98.03
1	$-\frac{1}{2}$	97.94
± 1	$\frac{1}{2}$	98.02
0	$\frac{1}{2}$	98.08

those for the other $2p$ electrons, in Table VI. (These results are taken from the calculation discussed in Sec. IV.)

Several other UHF calculations were done for Cl. First, an $(m_l + m_s)$ unrestricted calculation was done for Cl in its $M_L = 0$ state which resulted in $\langle r^{-3} \rangle_Q$ and $\langle r^{-3} \rangle_{SD}$ values of 7.13 and 7.33 a.u., respectively. Second, an m_l (but *not* m_s) unrestricted calculation was done for the same $M_L = 0$ state and yielded an appreciably different $\langle r^{-3} \rangle_Q$ of 6.38 a.u. Such a large effect comes about because we have reverted to the averaging of equations for orbital pairs differing in m_s, a procedure which, unlike Fe^{2+}, requires the introduction of a constraint to maintain orbital orthogonality. The nonorthogonality occurs between the pair of $2p$ orbitals having $m_l = 0$ and the single $3p$ electron having the same m_l (the other $3p$ being the hole). To overcome this, the version of the symmetry and equivalence restrictions used[10] in the RHF calculation was applied; the result was a greatly reduced anti-shielding contribution associated with the $2p$ shell. In general, abnormal shielding effects can be expected from orbitals in a closed shell having l, m_l, and m_s in common with an unfilled shell hole; these effects will be appreciably changed if a formalism, which is insufficiently unrestricted, is used.