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The Spin Polarized Hartree-Fock Method
and the Contribution of Core Polarization to Hyperfine Fields of 4d Ions

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A study has been made of the contribution of core polarization to observed hyperfine fields, H_c , of 4d ions using the spin-polarized Hartree-Fock (SPHF) method. As a starting basis we used analytic restricted Hartree-Fock solutions obtained previously. Results obtained for the 6S state ions Mo^+ , Tc^{2+} , and Ru^{3+} and for Pd^{2+} and Pd^{3+} , show that H_c is large and negative and is due almost entirely to the negative 2s and 4s contributions; the small 3s contribution is positive. While the individual s-shell contributions vary with ion, H_c per spin is constant (to within 5%), unlike the much cruder constancy noted earlier for the 3d ions. Detailed comparisons are made with earlier results for the 3d ions. H_c per unpaired spin is found to be ~ -375 kG per unpaired spin, in very good agreement with experiments on Pd metal, e.g., from Knight shift measurements, Seitchik et al find that H_c per spin is -345 ± 10 kG per unpaired spin.

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The Spin Polarized Hartree-Fock (SPHF) method has had perhaps its greatest success in accounting for the large negative hyperfine fields observed in the metals and ionic compounds of the 3d elements.⁽¹⁾ This has been all the more remarkable in view of the fact that (1) the experimental data were taken on solids, while the calculations were done for free ions and (2) the SPHF method is known to be only approximate and the calculations rely on the numerical differencing of large numbers to yield a final result which is many times smaller. For other than the 3d ions the SPHF results have had varying success in reproducing experiment and in one case (P), at least, has given the wrong sign.⁽²⁾ Because of the interest in predictions of the SPHF method when applied to heavier elements and because of the availability of experimental data for the 4d ions, we undertook to investigate the contribution of core polarization of the core electrons to the hyperfine fields in these systems. We here report some results of these investigations and compare these with the limited data available. Good agreement with experiment is found.

In the SPHF method, one of the restrictions associated with the conventional or restricted Hartree-Fock (RHF) method is relaxed, namely, the requirement that electrons in the same nl quantum shell have the same radial function for both spins. As is now well known, this results in a net spin density, at the nucleus for each closed s shell, with the resulting hyperfine field H_c just the superposition of contributions from all the s electron shells, i.e.,

$$H_c = (8\pi/3) g\mu_o S \sum_{ns} \left\{ |\psi_{ns\uparrow}(0)|^2 - |\psi_{ns\downarrow}(0)|^2 \right\} \quad (1)$$

where S is the total spin of the ion in question.

The present SPHF calculations were done using the analytic restricted Hartree-Fock wave functions determined previously.⁽³⁾ Results were obtained using SCF techniques and programs described elsewhere.⁽⁴⁾ Here we concentrate mainly on results and refer the reader to earlier publications for descriptive details about methods and techniques.⁽¹⁾

A convenient measure of the hyperfine field, introduced by Abragam et al⁽⁵⁾, is just the quantity

$$\chi = 4\pi/2S \sum_{ns} \left\{ |\psi_{ns\uparrow}(0)|^2 - |\psi_{ns\downarrow}(0)|^2 \right\} \quad (2)$$

With χ given in atomic units (a.u.), H_c is found in gauss by using the conversion factor $1 \text{ a.u.} = 4.21 \times 10^4 \text{ gauss}$. The minus sign indicates that the hyperfine field is found to be negative or antiparallel to the net spin moment on the ion. For the 3d ions Abragam, Horowitz and Pryce⁽⁵⁾ noted a crude constancy for χ ($\approx -3 \text{ a.u.}$). SPHF calculations⁽⁶⁾ subsequently yielded consistent results but showed a distinct, though small, tendency for χ to increase in magnitude with increasing Z . On careful examination of more modern and more extensive experimental data, Geschwind⁽⁷⁾ observed that χ does increase with Z (by $\sim 25\%$ on going from the $3d^3$ to the $3d^8$ configuration). The SPHF indication of this trend before the fact represents one of the striking successes of the formalism to date. In reporting our results we shall make comparisons in terms of χ and seek (and, in fact, find a remarkable) constancy with varying atomic number and ionicity.

As an example of our results we list in Table I the net individual s-electron shell contributions, $|\psi_{ns\uparrow}(0)|^2 - |\psi_{ns\downarrow}(0)|^2$, to the hyperfine field in Pd^{2+} in its ground state configuration ($4d^8, {}^3F$). It is clear that the dominant contributions come from the 2s and 4s shell electrons which are both negative. The negative 1s

and positive 3s contributions are each very small; their algebraic sum is entirely negligible. The resulting χ value, -8.90 a.u. or -375 kG per unpaired spin is large and approximately three times that obtained for the 3d ions.

Table I also emphasizes the striking difference between the 3d ion results and that obtained for the representative case of Pd^{2+} . For the 3d ions, the 2s contribution was largest and negative, the 3s positive and about 1/2 the 2s value and the 1s was negligibly small and negative. [For comparison, we show in Table II results obtained earlier⁽⁶⁾ for Mn.] These results were previously understood in terms of the attractive nature of the exchange force and the position of the positive 3d spin density relative to the wave functions of the 1s, 2s and 3s shells. The fact that the two dominant contributions to H_c in the 4d ions are both the same sign, unlike the 3d case, arises because of the different spatial relationship between the different parts of the 4d wave function (which, unlike the 3d orbital, is noded) and the s electron wave functions. As in the 3d case, the 1s and 2s contributions are negative (due to the inner loop of the 4d function), but the 3s which remains positive (as expected) has been greatly reduced. For the 4d ions, the 4s contribution is negative and large, unlike the counterpart case of the 3s electrons in the 3d ions. [For the 3d neutral atoms, the 4s contribution was found to be positive and large. While no neutral 4d atom calculations were performed, one expects, ⁽⁶⁾ by extrapolation from the 4s behavior in the 3d case, that the 5s contribution will be positive.] These results appear to be consistent with the simple ideas of exchange as previously described.^(1, 6)

Table III gives values of χ for a number of the other ions for which results have been obtained. What is most striking about these results is their near constancy - to within 5% - unlike the more familiar results for the 3d ions. This

greater constancy is most certainly due to the fact that the dominant 2s and 4s contributions have the same sign. In this way the sensitive differencing problem, and hence the greater uncertainty in the final result found for the 3d case, is avoided. One other feature of the results listed in Table III should be noted. Again, unlike the case of the 3d ions, we find a strong constancy independent of the degree of ionicity--at least for the +1, +2 and +3 ions shown here-- and independent of Z for given ionicity. Such a constancy was observed in neither computation nor experiment for the 3d ions. One 3d constancy⁽⁷⁾ was observed which deserves mention. In a given crystalline environment χ would be independent of ionicity for a given $3d^n$ configuration (eg. for V^{2+} , Cr^{3+} and Mn^{4+} in sixfold oxygen coordination). Since χ is known to be sensitive to covalent effects⁽⁸⁾ and since there is considerable evidence of varying covalency [e.g., from g factors] for such sequences of ions, the observation of this constancy implies that χ varies systematically for the free ion sequences. The 3d SPHF calculations have not yielded the appropriate variation.

Finally, it is interesting to compare these results with experiment. Unfortunately, very little is known experimentally about H_c or χ in these ions. One case which has been worked out recently is that ~~in~~^{of} Pd metal. Using NMR to measure the Knight shift and the ^{measured} magnetic susceptibility, Seitchik et al⁽⁹⁾ determined that H_c per unpaired spin (or χ) = -345 ± 10 kG/unpaired spin. This result is in remarkable agreement with our calculated value (either for Pd^{2+} alone or for some average value of the results shown in Table III). This agreement is quite surprising in view of the complex experimental analysis involved and the uncertainties inherent in the SPHF method. Whether this result is fortuitous awaits further experimental results which will allow more detailed comparisons to be made.

TABLE I Contributions of the s Electrons to a Resulting χ in $\text{Pd}^{2+}(4d^8, {}^3F)$

<u>Electron Shell</u>	<u>$\psi_{\uparrow}(o) ^2 - \psi_{\downarrow}(o) ^2$</u>
1s	-0.65
2s	-7.29
3s	+0.90
4s	-10.76
Total $\chi = -8.90$	

TABLE II Contributions⁽⁶⁾ of the s electrons in $\text{Mn}(3d^5 4s^2)$.

<u>Electron Shell</u>	<u>$\psi_{\uparrow}(o) ^2 - \psi_{\downarrow}(o) ^2$</u>
1s	-0.03
2s	-6.63
3s	+3.23
4s	+2.89

TABLE III χ Values for Some 4d Ions.

<u>Ion</u>	<u>χ (in a.u.)</u>
$\text{Mo}^+ (4d^5)$	-8.75
$\text{Tc}^{2+} (4d^5)$	-8.81
$\text{Ru}^{3+} (4d^5)$	-8.58
$\text{Pd}^{2+} (4d^8)$	-8.90
$\text{Pd}^{3+} (4d^7)$	-8.62

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