

in the relaxation of cesium. A slight temperature dependence of the N_2^{14} disorientation cross section can also be seen.

A few concluding remarks can be made on the accuracy of the approximations leading to expressions (4) and (6). If higher order terms in Eq. (2) are indeed negligible, then in Fig. 4, $\ln[(I_0 - I)/I_0]$ at $t=0$ should be equal to 1.0. A departure from this value would indicate a defect in this approximation. We found that for cesium the values of this intercept ranged from 0.86 to 0.96. This is consistent with the work on sodium, reported by Anderson and Ramsey, but does not agree with the value of 0.70 reported by Bernheim for rubidium in helium. Any further attempt to measure the $t=0$ intercept of $\ln[(I_0 - I)/I_0]$ with sufficient accuracy to give information on the spatial distribution of aligned

alkali atoms would require the use of a shutter of much faster closing times. Such an experiment might be possible using a solid state shutter based on the Pockels effect.

ACKNOWLEDGMENTS

We wish to thank Professor H. Frauenfelder, Professor D. Alpert, and Mrs. J. Franz for several helpful and interesting discussions. Dr. G. Kane and Dr. J. Ehrman provided considerable assistance in the use of the computer. Special thanks go to G. Sandorfi, whose aid in the construction of the experimental apparatus and analysis of the data was invaluable. Finally, we are grateful to the Digital Computer Laboratory of the University of Illinois for their generous provision of computer time necessary for the reduction of the experimental data.

Calculation of Magnetic Hyperfine Constant of P^{31}

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The results of different kinds of calculations, which use the concept of spin polarization, all predict a negative sign of the magnetic hyperfine constant of the 4S ground state of P^{31} in contradiction with the sign deduced by Lambert and Pipkin from an optical pumping experiment. This result means that either an error in experimental sign has been made or that the first serious breakdown of the exchange polarization model has been found.

I. INTRODUCTION

THE magnetic hyperfine interactions in S state and many other ions having nonzero spin have, in large part, become understood in terms of the spin or exchange polarization of the closed s shells. This polarization yields a net s -electron spin density at the nucleus which interacts with the nucleus via the Fermi contact term.¹ While various objections have been raised to this picture, a series of calculations has emerged involving single-substitution configuration-interaction²⁻⁵ (C.I.) perturbation,⁶ and so-called spin-

polarized Hartree-Fock^{5,7-9} (SPHF) methods.^{2,10} One feature of the results is that, with one possible exception

Soc. (London) **A230**, 169 (1955); and R. K. Nesbet, *Phys. Rev.* **118**, 681 (1960).

⁴ N. Bessis, H. Lefebvre-Brion, and C. M. Moser, *Phys. Rev.* **124**, 1124 (1961); **128**, 213 (1962).

⁵ N. Bessis, H. Lefebvre-Brion, and C. M. Moser, *Phys. Rev.* **130**, 1441 (1963).

⁶ For example, see R. M. Sternheimer, *Phys. Rev.* **86**, 316 (1952), and M. Cohen, D. A. Goodings, and V. Heine, *Proc. Phys. Soc. (London)* **73**, 811 (1959).

⁷ R. E. Watson and A. J. Freeman, *Phys. Rev.* **123**, 2027 (1961).

⁸ For example, see L. M. Sachs, *Phys. Rev.* **117**, 1504 (1960), and D. A. Goodings, *ibid.* **123**, 1706 (1961).

⁹ Such calculations have, by common usage, been called "unrestricted Hartree-Fock." As there are other restrictions associated with conventional Hartree-Fock theory (e.g., See Ref. 10) which are not relaxed in such calculations it seems more appropriate to term these "spin-polarized Hartree-Fock" thus indicating the actual restriction being relaxed—the restriction of common radial behavior of orbitals differing only in spin quantum number.

¹⁰ For a review and a more complete list of references, see A. J.

* Supported by the U. S. Air Force Office of Scientific Research.

¹ E. Fermi, *Z. Phys.* **60**, 320 (1930).

² For a discussion of the relation between single-substitution configuration-interaction and Hartree-Fock theory, see R. K. Nesbet, *Proc. Roy. Soc. (London)* **A230**, 312 (1955).

³ For example, see E. Fermi and E. Segrè, *Z. Physik* **82**, 729 (1933); A. Abragam, J. Horowitz, and M. H. L. Pryce, *Proc. Roy.*

TABLE I. Total energies, hyperfine constants A , and individual s -shell contributions to A for atomic P as predicted by various configuration-interaction and spin-polarized Hartree-Fock calculations (see text for their definition).

	Configuration interaction	SPHF calculation I (utilizes same basic set as the C. I. results)	SPHF calculation II	Other SPHF calculations	Exp.
Total energy	-340.7164 a.u.	-340.7164 a.u.	-340.7188 a.u.	-340.7184 to -340.7187 a.u.	
1s shell contribution to A	-122 Mc/sec	-212 Mc/sec	-195 Mc/sec	-207 to -211 Mc/sec	
2s shell contribution to A	+94	+148	+138	+144 to +145	
3s shell contribution to A	-103	-12	-51	-1 to -9	
Total A	-132	-77	-107	-71 to -74	+55
A after spin projection of SPHF results		-46	-65	-42 to -44	

(mentioned later), they always reproduce the sign of the experimental hyperfine interaction, and are often in fair (normally accidental) numerical agreement as well.

In the present paper we discuss the case of atomic $P[(3p)^3,^4S]$ for which there are experimental hyperfine data¹¹ and for which we have obtained configuration interaction plus a series of SPHF results. Experiment and theory are found to yield results of the same magnitude but of differing sign. This result means that either an error in experimental sign has been made or that the first serious breakdown in the ability of the exchange polarization model to understand experimental fact has been found. As exchange polarization is currently invoked in the discussion of a wide variety of experimental results, this matter is of some interest.

II. HYPERFINE EFFECTS, EXCHANGE POLARIZATION, AND THE SPHF AND CONFIGURATION INTERACTION METHODS

We will not discuss details of either the exchange polarization model or of the computational methods for this has been done extensively elsewhere^{2-10,12-14}; however, a number of comments are necessary.

In atomic phosphorus one has an S -state atom consisting of closed $1s$, $2s$, $2p$, and $3s$ shells and a half-filled $3p$ shell. The $3p$ shell, being spherical, provides neither spin dipolar nor orbital magnetic hyperfine interactions. Thus, in the conventional one-electron view, one would expect no hyperfine interaction to be observed. A rather substantial hyperfine interaction is observed here, just as it is for similar S -state ions such as N, Mn^{2+} , and Gd^{3+} . Since the early work of Fermi and Segrè,³ such cases have been interpreted as arising from an exchange polarization of the closed s shells by the valence shell. The magnitude and sign of the resulting s -electron spin density at the nucleus depends, in

detail, on the radial behavior of the valence shell relative to the various closed s shells. In general, different s shells make contributions of differing sign to the spin density and in turn to the contact term, as we shall see for the case of P. At times an almost complete cancellation of terms occurs, and it has been in such a case that calculations have failed to reproduce the experimental sign. This failure occurred for the neutral $3d^n4s^2$ iron series atoms; here, however, the matter has been complicated by odd, and for several atoms, doubtful experimental data. These iron series atoms represent the one example, prior to P, where theory perhaps (but less obviously) breaks down.¹⁵

It has been shown^{4,12,13} that formal connections exist between single-substitution C.I. and SPHF theory. The conventional SPHF approach is very straightforward to apply if one possesses Hartree-Fock computational machinery but it suffers from the fact that the resulting many-electron wave functions are not proper spin eigenfunctions. There has been considerable discussion as to whether this does⁵ or does not^{4,13,14} adversely affect one's prediction of hyperfine effects. We will report values of the contact term computed for both these improper spin functions and for the spin projections of these functions. The C.I. functions are of proper symmetry. Questions of wave-function spin symmetry will be of minor interest to us here as they are expected to affect the magnitude, but not the sign, of one's predictions.

III. RESULTS

Results for the C.I. and two of the SPHF calculations appear in Table I. The calculations utilized standard analytic methods¹⁶ and one of the SPHF results (calculation I) was obtained with the basis set used in the C.I. calculation while the other (calculation II) is the best (in the sense of best total energy) of the SPHF calculations. Also appearing are the ranges of values of the listed quantities indicated by three other SPHF

Freeman and R. E. Watson in *Treatise on Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published).

¹¹ R. H. Lambert and F. M. Pipkin, *Phys. Rev.* **128**, 198 (1962).

¹² R. Lefebvre, *Cahiers Phys.* **381**, 1 (1959).

¹³ W. Marshall, *Proc. Phys. Soc. (London)* **A78**, 113 (1961).

¹⁴ V. Heine, *Czech. J. Phys.* **13**, 619 (1963).

¹⁵ And here, perhaps, one should merely view the experimental and theoretical contact terms as essentially zero valued.

¹⁶ For example, see Ref. 7 for discussion and further references.

calculations yielding total energies which are within 0.0004 au of the energy of calculation II. The C.I. result was obtained with the perturbation methods applied previously to B, O, N,⁴ and F.⁵ C.I. calculations involving fuller basis sets, yielding energies in closer agreement with that of result II, were not attempted because previous experience indicated that no substantial change in the character of the results would occur. Listed in the table are total energies and individual shell contributions to the hyperfine constant A (defined as in Lambert and Pipkin¹¹). For the SPHF calculations we also estimate the result for A after projecting out¹⁷ the components of improper symmetry appearing in the SPHF functions. These were obtained by assuming A to equal $S/(S+1)$ or the unprojected value [cf. Ref. (5) for the discussion of this].

One important feature of the results is the variation in sign of individual shell contributions to A . The $1s$ and $3s$ shells make negative contributions, while the $2s$ shell is positive. The sign of the results seems to be largely determined by the competition between the $1s$ and $2s$ shell contributions with the $1s$ always dominating. The smaller $3s$ term then serves to enhance the magnitude of the already negative A . In viewing the individual shell contributions, one must remember that these also arise from taking a difference of large quantities, namely, the difference in spin-up and spin-down s -electron behavior. Therefore, what appears to be a severe variation in the contribution of a particular shell to A represents in fact but a very small variation in the over-all behavior of that shell. We believe the results indicate that the exchange polarization, whatever the improved details of a calculation, predicts a negative A for P. The agreement between experimental and theoretical absolute magnitude is reasonable.

Finally, the most important feature of the results is the consistent difference in sign with the experimentally reported¹¹ value for A of +55 Mc/sec. If the experimental sign is correct, we may have in P a case where the model of exchange polarization breaks down. We should note that the sign of the contact term in P has implications beyond the present disagreement between theory and experiment. There exist Knight-shift data¹⁸ for Si in V_3Si which can be reasonably understood only if one assumes a core polarization contact term which has the same sign as is obtained in the present P calcu-

lations. Since Si and P are neighbors in the periodic table, one would anticipate a common sign for their core polarization terms, as is typical for ions in the same row of the periodic table. The sign reversal implied by the Lambert and Pipkin result would require therefore a new interpretation of the Knight shifts in the interesting V_3X compounds.

IV. DISCUSSION

Berggren and Wood¹⁹ have raised serious questions as to the role played by exchange polarization, asserting that it has little or no role in the hyperfine interaction for atomic Li[($1s$)²($2s$),² S]. Their observations were based on evaluating the contact term for the James and Coolidge²⁰ wave function, a wave function which introduces interelectronic correlation effects by the explicit use of interelectronic coordinates. Their contact term agreed well with experiment largely due to $2s$ - $1s$ shell nonorthogonality and from this they concluded that spin polarization, which wasn't obviously present, plays almost no role. Subsequent investigators have obtained better wave functions in the sense of better total energies: One of these yields a contact term in substantial disagreement²¹ with experiment; another yields agreement²² with experiment. These suggest that the Berggren and Wood contact term was perhaps in fortuitous agreement with experiment. In any case, the nonorthogonality terms, between the open $2s$ and a closed s shell, which led to their agreement with experiment, do not occur (to the same order at least) when the open valence shell is made up of p electrons as we have for P.

If exchange polarization is to be a useful model for understanding hyperfine interactions in atoms, molecules, and solids, it must reproduce the sign and order of magnitude of experiment for such a comparatively simple system as P. However, one should not expect detailed quantitative agreement if relativistic and correlation corrections are omitted. Both will be far more complicated than the case of Li discussed above for not only is P much larger, but the correlation effects contributing to a magnetic hyperfine interaction are of higher order.

¹⁹ K. F. Berggren and R. F. Wood, Phys. Rev. **130**, 198 (1963).

²⁰ H. M. James and A. S. Coolidge, Phys. Rev. **49**, 688 (1936).

²¹ The wave function appears in A. W. Weiss, Phys. Rev. **122**, 1826 (1961), the resulting hyperfine interaction in J. Martin and A. W. Weiss, J. Chem. Phys. (to be published).

²² The wave function appears in E. A. Burke, Phys. Rev. **130**, 1871 (1963); the resulting contact term has yet to be published by E. A. Burke.

¹⁷ For example, see P. O. Löwdin, Phys. Rev. **97**, 1509 (1955).

¹⁸ A. M. Clogston and V. Jaccarino, Phys. Rev. **121**, 1357 (1961).