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Exchange Polarization Effects in Hyperfine Structure

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Exchange polarization of core electrons by outer unpaired electrons has been calculated for 10 different atomic configurations of Li, Na, K, F, Cl, Be, B, and N in the unrestricted Hartree-Fock (UHF) approximation. Numerical integration techniques were used and accurate conventional Hartree-Fock (HF) wave functions were also obtained for these configurations. The theory of atomic hyperfine structure in the UHF approximation is developed and the HF and UHF calculated values of the hyperfine coupling constants are compared with available experimental data. The importance of core polarization in solid state problems is briefly mentioned with particular attention to color centers. Finally, unsuccessful attempts to calculate core polarization by perturbation expansion methods are discussed.

1. INTRODUCTION

In atoms in which one or more electrons belonging to outer shells are unpaired with respect to their spin direction, core electrons with spin parallel to that of the unpaired electrons experience stronger total exchange forces than core electrons of opposite spin. This exchange polarization of the core electrons or "core polarization" results in nonzero values of the quantities,

$$\rho_{ns}=|\psi_{ns\uparrow}(0)|^2-|\psi_{ns\downarrow}(0)|^2, \qquad (1)$$

for each pair of s electrons in the atomic core, and these contribute to the Fermi contact term of the hyperfine interaction. The importance of such contributions has been recognized in the theory of atomic hyperfine structure,[1-4] in the Knight shift in metals,[5] and in hyperfine fields in ferromagnetic materials.[6-8]

In this paper are described the results of investigations of exchange polarization in atoms by the unrestricted Hartree-Fock (UHF) method in which electrons of the same n and l but different m_s are allowed to have different radial wave functions.[2,9,10] The method of calculation is described in the next section, followed in Sec. 3 by presentation and discussion of the results. The theory of atomic hyperfine structure is developed in Sec. 4, and the calculated results are compared with available experimental data. In Sec. 5, the importance of core polarization in solid state physics is briefly discussed. Finally, Sec. 6 describes an unsuccessful attempt to calculate core polarization by perturbation expansion methods, the reasons for its failure being of interest in connection with the general problem of perturbation expansions for core wave functions.

2. METHOD OF CALCULATION

The UHF calculations, the results of which are given in the next section, were performed by numerical integration methods on EDSAC 2, the electronic computer of the Mathematical Laboratory at Cambridge. The method used to form and solve the self-consistent field equations is similar to that described at length by Hartree[11] except in a number of modifications appropriate to a high-speed computer. These are described in some detail elsewhere.[12]

In order to obtain core polarization values accurate to about three significant figures, it was necessary to calculate the individual wave functions to an accuracy of six significant figures over their entire range. This is because the differences ρ_{ns} are less than 1% of $|\psi_{ns\uparrow}(0)|^2$ or $|\psi_{ns\downarrow}(0)|^2$ and because in a number of atoms a rather large cancellation takes place among the ρ_{ns} from different shells (see Sec. 3). Clearly six-figure accuracy for a single one-electron wave function in the HF or UHF approximations is physically meaningless. Nevertheless, some significance can be attached to the calculated values of ρ_{ns} in spite of the neglect of correlation effects because it is known from free electron theory that at electron densities such as occur in the cores of atoms, correlation effects are much smaller than exchange effects, particularly differences between electrons of opposite spin.

Among the 11 UHF calculations reported here one can safely impose the conditions that the nondiagonal $\lambda_{nl\uparrow,n'l\uparrow}$'s and $\lambda_{nl\downarrow,n'l\downarrow}$'s[11-13] are zero except for chlorine and the ^2P term of sodium. In both these calculations they were also taken to be zero. The error resulting from this simplification is thought to be negligible because the values of orthogonality integrals in these

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[1] R. Sternheimer, Phys. Rev. **86**, 316 (1952).

[2] G. W. Pratt, Phys. Rev. **102**, 1303 (1956).

[3] V. Heine, Phys. Rev. **107**, 1002 (1957).

[4] S. M. Blinder, Bull. Am. Phys. Soc. **5**, 14 (1960).

[5] M. H. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. (London) **73**, 811 (1959).

[6] W. Marshall, Phys. Rev. **110**, 1280 (1958).

[7] D. A. Goodings and V. Heine, Phys. Rev. Letters **5**, 370 (1960).

[8] A. J. Freeman and R. E. Watson, Phys. Rev. Letters **5**, 498 (1960).

[9] J. H. Wood and G. W. Pratt, Phys. Rev. **107**, 995 (1957).

[10] R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1125 (1960); **120**, 1134 (1960).

[11] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

[12] D. A. Goodings, thesis, Cambridge University, 1960 (unpublished).

[13] R. E. Watson, Technical Report No. 12, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (unpublished).

two cases were not very different from those in the other calculations.

There is a practical difficulty in doing Hartree-Fock calculations by numerical integration procedures which should be mentioned. For some wave functions, particularly those belonging to inner shells, the non-linear exchange term is so large at large r that it overpowers the other terms in the equation, with the result that the inward integration from large r fails to get started properly. No very systematic way was developed for dealing with this troublesome situation. However, at the expense of a great deal of computer time, the tails of the wave functions were extended out until the orthogonality integrals indicated that no significant error remained.

Another disadvantage of the numerical integration method is that it is much slower than the analytic techniques used extensively by Watson[13] and others. Nevertheless, in its favor is the ability to produce accurate solutions avoiding the difficulty of choosing sets of basis functions and assessing the error resulting from their being incomplete. For example, in their Ni^{2+} calculation Watson and Freeman[10] remark that the basis set used would not allow for "subtle wave function behavior" either very close to the nucleus or in the outer part of the ion. In fact there is only one "d function" in their basis set which is suitable for describing the exponential behavior of the Ni^{2+} $3d$ function at large r. Watson and Freeman do not estimate how much error in their core polarization value is likely to arise from this defect, and presumably such an estimate is difficult to make without a very thorough examination of the basis set. The discussion in Sec. 6 supports the contention that accurate results depend on the basis set having been chosen very carefully. Unfortunately the present series of calculations does not provide a comparison between the methods.[14]

Finally, attention should be drawn to the important fact that the total UHF wave function, Ψ_{UHF}, is not an eigenfunction of $\mathbf{S}^2$. A detailed discussion of this failing has been given recently by Marshall[15] who has shown that, provided certain exchange integrals are small, the UHF results for core polarization can be expected to be accurate to a good approximation. The relevant exchange integrals have not yet been evaluated for any particular case. However, from comparison with experiment one can guess that the UHF estimate of core polarization is likely to be accurate to within about 25% in most cases, although exceptions are likely to occur which can be recognized only by detailed study.

TABLE I. Core polarization results from UHF calculations (atomic units).

Atom	Term	ρ_{1s}	ρ_{2s}	ρ_{3s}	$\lvert\psi_{cp}(0)\rvert^2$	$\lvert\psi_A(0)\rvert^2$
Li	^2S	0.0609			0.0609	0.2247
Li	^2P	−0.0184			−0.0184	−0.0184
Be	^3P	0.0938			0.0938	0.7237
B	^2P	−0.0913	0.1085		0.0172	0.0172
N	^4S	−0.7418	0.9301		0.1883	0.1883
F	^2P	−0.5076	0.6411		0.1335	0.1335
Na	^2S	0.0463	0.0745		0.1208	0.6469
Na	^2P	−0.0098	0.0143		0.0045	0.0045
Cl	^2P	−0.211	0.113	0.132	0.034	0.034
K	^2S	0.0340	0.0409	0.0880	0.1629	0.8542

3. CORE POLARIZATION RESULTS AND DISCUSSION

Let us suppose that in any given atom the unpaired electrons always have spin ↑. This assumption leads to unambiguous definitions for ρ_{ns} and the following:

$$|\psi_A(0)|^2=\sum_i\left[\pm|\psi_i(0)|^2\right], \tag{2}$$

$$|\psi_{cp}(0)|^2=\sum_{ns\text{ pairs}}\rho_{ns}, \tag{3}$$

$$\langle np\uparrow|r^{-3}|np\uparrow\rangle=\int_0^\infty\left[P^2(np\uparrow;r)/r^3\right]dr, \tag{4}$$

$$\langle np\downarrow|r^{-3}|np\downarrow\rangle=\int_0^\infty\left[P^2(np\downarrow;r)/r^3\right]dr. \tag{5}$$

The summation in (2) is over all electrons in the atom or ion with the plus sign taken for electrons with spin ↑, the minus sign for electrons with spin ↓. The importance of having defined these quantities and ρ_{ns} for configurations with unpaired electron spins ↑ will be seen later. In the HF case, the quantity corresponding to (4) and (5) is $\langle np|r^{-3}|np\rangle$. When it is immaterial whether the HF or UHF case is being referred to, the general symbol $\langle r^{-3}\rangle$ will be used for this matrix element.

The HF and UHF calculations have been carried out for 10 different atomic configurations. The results relating to core polarization and atomic hyperfine structure are given in Tables I and II. Normalized wave functions and other data are fully recorded elsewhere.[12]

There are a number of interesting features about the results in Table I. Most obvious is the large cancellation among the ρ_{ns}'s which exists in many cases. Although known to be unsatisfactory (see Sec. 6), perturbation expansions for ρ_{ns} and $\rho_{n's}$ can be made to show rather crudely the origin of this effect.[5] The expansions, although unreliable, also offer some explanation of why no explicit cancellation is visible for the ^2S terms of the alkali atoms. For, the term which cancels in the expansion of ρ_{1s} has a value of only 5% of ρ_{1s} for sodium compared with 50% of ρ_{1s} in the case of fluorine.

Undoubtedly the most striking feature of Table I is that when the unpaired electrons are of s type, all

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[14] Although the present investigation included Fe $3d^64s^2$, comparison of the HF calculation with similar calculations by R. E. Watson, Phys. Rev. **119**, 1934 (1960) and by D. Mayers (unpublished) revealed an error in the angular coefficients in the $3d$ radial equation. A similar error exists in the UHF calculation reported earlier[7] which might cause the calculated value of H_{core} to be in error by perhaps 20%. I am grateful to Dr. Watson and Dr. Mayers for drawing my attention to this mistake.

[15] W. Marshall, Proc. Phys. Soc. (London) (to be published).

TABLE II. Calculated hyperfine structure parameters.

Atom	Term	$\lvert\psi_A(0)\rvert^2$ HF case	$\lvert\psi_A(0)\rvert^2$ UHF case	$\langle np\lvert r^{-3}\rvert np\rangle$ HF case	$\langle np\uparrow\lvert r^{-3}\rvert np\uparrow\rangle$ UHF case	$\langle np\downarrow\lvert r^{-3}\rvert np\downarrow\rangle$ UHF case
Li	^2S	0.1637	0.2247			
Li	^2P	0	−0.0184	0.05856	0.05861	
Be	^3P	0.6296	0.7237	0.2952	0.2951	
B	^2P	0	0.0172	0.7756	0.7819	
N	^4S	0	0.1883			
F	^2P	0	0.1335	7.544	7.706	7.309
Na	^2S	0.5667	0.6469			
Na	^2P	0	0.0045	0.1675	0.1675	
Cl	^2P	0	0.034	6.679	6.783	6.526
K	^2S	0.6879	0.8542			

ρ_{ns}'s are positive, whereas for unpaired electrons of p or d type ρ_{ns}'s for inner levels are negative, becoming positive for outer levels. This latter observation was used in considering metallic iron,[7] for it was reasoned that if the atomic $3d$ functions were to be slightly expanded, ρ_{3s} would behave more like an "inner" level, i.e., decrease, as was found to be the case. However, the reason why exchange polarization by s electrons is basically different from p or d electrons is not very well understood. An explanation in terms of "exchange (difference) potentials"[5] is unclear.

Another observation drawn from Table I is that the ratio ρ_{1s}/ρ_{2s} in boron, nitrogen, and fluorine is very nearly the same. This provides a rough means of estimating core polarization in other atoms with an incomplete $2p$ shell. Likewise, the ratios which the ρ_{ns} bear to one another are remarkably similar for different elements in the iron series.

4. CORE POLARIZATION IN ATOMIC HYPERFINE STRUCTURE

4.1. Theory in the HF and UHF Approximations

The hyperfine interaction between the electrons and the nucleus of an atom has two parts; the dipole-dipole interaction between the magnetic moment of the nucleus and the orbital and spin magnetic moments of the electrons outside the nucleus,

$$\mathcal{H}_{\text{dipolar}}=\frac{2\mu_n\mu_B}{I\hbar^2}\sum_i\left[\frac{\mathbf{l}_i-\mathbf{s}_i}{r_i^3}+3\frac{(\mathbf{s}_i\cdot\mathbf{r}_i)\mathbf{r}_i}{r_i^5}\right]\cdot\mathbf{I}; \tag{6}$$

and the Fermi contact term arising from electrons penetrating inside the nucleus,

$$\mathcal{H}_{\text{contact}}=\frac{16\pi}{3}\frac{\mu_n\mu_B}{I\hbar^2}\sum_i\left[\mathbf{s}_i\lvert\psi_i(0)\rvert^2\right]\cdot\mathbf{I}. \tag{7}$$

Here μ_n is the nuclear magnetic moment and I is the nuclear spin. The contribution of each interaction to the hyperfine coupling constant is conveniently found by considering the state $\lvert J, M_J=J\rangle$. Using the Wigner transformation to the $\lvert M_LM_S\rangle$ representation, and noting that the operator $\sum_i s_{iz}\lvert\psi_i(0)\rvert^2$ is diagonal in M_S, one obtains

$$a_c=\frac{16\pi}{3}\frac{\mu_n\mu_B}{IJ\hbar}\sum_{M_LM_S}(LSM_LM_S\lvert JJ)^2 \times\langle M_LM_S\lvert\sum_i s_{iz}\lvert\psi_i(0)\rvert^2\rvert M_LM_S\rangle, \tag{8}$$

$$a_d=\frac{2\mu_n\mu_B}{IJ\hbar}\sum_{M_LM_S}\sum_{M_L'M_S'}(LSM_LM_S\lvert JJ) \times(LSM_L'M_S'\lvert JJ)\left\langle M_LM_S\left\lvert\sum_i\left[\frac{l_{iz}-s_{iz}}{r_i^3}+3\frac{(\mathbf{s}_i\cdot\mathbf{r}_i)z_i}{r_i^5}\right]\right\rvert M_L'M_S'\right\rangle. \tag{9}$$

Now let us suppose that the electronic configuration and the term of the atom in question are specified, i.e., n and l quantum numbers for all the one-electron states and total L and S quantum numbers are known. Then for the particular J level under consideration, one can assign m and m_s quantum numbers to the one-electron states in such a way that $M_L+M_S=J$, and from these states one can form a determinantal wavefunction $\Psi(M_LM_S)$ of HF or UHF type. In general there will be more than one way of assigning m and m_s values to satisfy $M_L+M_S=J$, each way giving rise to a separate determinant. Thus in the HF or UHF approximation, the states $\lvert M_LM_S\rangle$ appearing in (8) and (9) are determinants found in this way.

The matrix elements in (8) and (9) are easily worked out using the theorem for linear one-electron operators.[16] For the particularly simple and important case $J=L+S$ where the summations in (8) and (9) only have one term, one obtains

$$a_c=\frac{16\pi}{3}\frac{\mu_n\mu_B}{IJ}\sum_i m_{s_i}\lvert\psi_i(0)\rvert^2, \tag{10}$$

$$a_d=\frac{2\mu_n\mu_B}{IJ}\sum_i\left[(m_i-\sigma_{l_im_i}m_{s_i})\langle n_ip_i\lvert r^{-3}\rvert n_ip_i\rangle\right], \tag{11}$$

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[16] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935).

TABLE III. Angular integrals σ_{lm}.

l	0	1	1	2	2	2	3	3	3	3
m	0	±1	0	±2	±1	0	±3	±2	±1	0
σ_{lm}	0	2/5	−4/5	4/7	−2/7	−4/7	10/15	0	−6/15	−8/15

where

$$\sigma_{lm}=\int_0^{2\pi}\int_0^{\pi}|Y_{lm}(\theta,\phi)|^2(1-3\cos^2\theta)\sin\theta d\theta d\phi. \quad (12)$$

Values of σ_{lm} up to $l=3$ are given in Table III. For an HF determinantal wave function it is easy to see that closed shells give no contribution to a since the m_i add to zero in (11) and spin pairs cancel each other exactly in (10) and (11). However, in the UHF case, closed shells (in fact, owing to spherical symmetry, closed sub-shells) still give a zero contribution to a_d, but it is possible to obtain an important contribution to a from core polarization.

A number of different cases will now be discussed.

4.2. The Alkali Atoms

In the alkali atoms the core is polarized by exchange with the valence electron. For the ^2S ground state the valence electron is of s type and a is simply,

$$a=\frac{16\pi}{3}\frac{\mu_n\mu_B}{I}|\psi_A(0)|^2. \quad (13)$$

For the HF case $|\psi_A(0)|^2$ is the valence electron $|\psi_{ns}(0)|^2$, while the UHF case contains in addition the core polarization contribution. It should be noted that it is immaterial whether the valence electron has spin ↑ or ↓ provided $|\psi_A(0)|^2$ is defined according to the convention of Sec. 3.

The HFS constants obtained from the HF and UHF calculations for the ^2S ground states of Li, Na, and K are given in Table IV where they are compared with the experimental values of Kusch and Taub.[17] The percentages in brackets refer to the experimental values. Here and elsewhere only the most important isotope of each element is used for comparison. Also included in the table for comparison are the results of a configuration interaction calculation by Nesbet[18] and a number of calculations based on empirical potentials.[19–21]

TABLE IV. The hfs constants for the ^2S term of the alkali atoms (Mc/sec).

	Li^7	Na^{23}	K^{39}
a_{expt}	401.786	885.80	230.862
a_{HF}	284 (71%)	669 (76%)	143 (62%)
a_{UHF}	390 (97%)	764 (86%)	178 (77%)
Configuration interaction calculation:			
Nesbet[18]	397 (98.8%)		
Calculations from empirical potentials:			
Jones and Schiff[19]	246 (61%)	623 (70%)	
Kohn[20]	387 (96%)		
Kjeldaas and Kohn[21]		808 (91%)	

The UHF calculation for lithium is in excellent agreement with a similar calculation by Sachs[22] who used analytic wave functions. Sachs also reports the result of projecting unwanted symmetry components out of the UHF wave function. However, Marshall[15] has shown that this procedure is misleading as the projection scheme not only removes components of undesired symmetry but also greatly reduces components of desired symmetry.

It can be seen that including core polarization gives substantial improvement (10–25%) in the value of $|\psi_A(0)|^2$ over the HF case. We also note that the agreement of the UHF results with experiment becomes progressively worse in going from lithium to potassium indicating that the error due to neglecting correlation, mainly in the value of $|\psi_{ns}(0)|^2$ for the valence electron, becomes more important for heavy atoms.

Let us now consider the ^2P terms in which the valence electron is of p type. In the $J=\frac{1}{2}$ level the state $|J=\frac{1}{2}, M_J=\frac{1}{2}\rangle$ is composed of the two determinantal states $|M_L=1\, M_S=-\frac{1}{2}\rangle$ and $|M_L=0, M_S=\frac{1}{2}\rangle$. The first determinant is made up of closed shells and the one-electron state $(np1\downarrow)$ while the second has closed shells and the state $(np0\uparrow)$. It can be seen from (9) that these determinants will be mixed by the terms $s_{i+}r_{i-}$ and $s_{i-}r_{i+}$ in the dipolar operator. But although the unpaired spins are oppositely directed in these determinants, the defining of $\langle np\uparrow|r^{-3}|np\uparrow\rangle$ and $\langle np\downarrow|r^{-3}|np\downarrow\rangle$ for configurations in which the unpaired spins are ↑ means that no term of the form $\langle np\uparrow|r^{-3}|np\downarrow\rangle$ appears in the expression for $(a_{d1/2})_{\text{UHF}}$. One obtains

$$(a_{1/2})_{\text{UHF}}=\frac{16}{3}\frac{\mu_n\mu_B}{I}\left[\langle np\uparrow|r^{-3}|np\uparrow\rangle-\frac{\pi}{3}|\psi_A(0)|^2\right]. \quad (14)$$

TABLE V. The hfs constants for the ^2P term of Li and Na (Mc/sec).

	Li^7		Na^{23}	
$(a_{3/2})_{\text{expt}}$	not measured		18.5	
$(a_{1/2})_{\text{expt}}$	not measured		94.45	
	HF case	UHF case	HF case	UHF case
$a_{c3/2}$	0	−10.7	0	1.7
$a_{d3/2}$	6.5	6.5	12.6	12.6
$a_{3/2}$	6.5	−4.2	12.6	14.3
$a_{c1/2}$	0	10.7	0	−1.7
$a_{d1/2}$	32.3	32.4	63.0	63.0
$a_{1/2}$	32.3	43.1	63.0	61.3

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[17] P. Kusch and H. Taub, Phys. Rev. **75**, 1477 (1949).

[18] R. K. Nesbet, Phys. Rev. **118**, 681 (1960).

[19] H. Jones and B. Schiff, Proc. Phys. Soc. (London) **A67**, 217 (1954).

[20] W. Kohn, Phys. Rev. **96**, 590 (1954).

[21] T. Kjeldaas and W. Kohn, Phys. Rev. **101**, 66 (1956).

[22] L. M. Sachs, Phys. Rev. **117**, 1504 (1960).

TABLE VI. $\langle np\uparrow|r^{-3}|np\uparrow\rangle$ and $|\psi_A(0)|^2$ from experiment.

$n^{2S+1}L$	$(a_{3/2})_{\text{expt}}$ (Mc/sec)	$(a_{1/2})_{\text{expt}}$ (Mc/sec)	$\langle np\uparrow\|r^{-3}\|np\uparrow\rangle$ (atomic units)	$\|\psi_A(0)\|^2$ (atomic units)
3^2P of Na	18.5 ± 0.6	94.45 ± 0.5	0.251 ± 0.002	-0.0008 ± 0.0015
4^2P of K	5.70 ± 0.3	28.85 ± 0.3	0.434 ± 0.008	-0.0009 ± 0.0044
5^2P of K	1.97 ± 0.1	8.99 ± 0.15	0.138 ± 0.003	0.0021 ± 0.0016

For the $J=\frac{3}{2}$ level, (10) and (11) can be used directly giving,

$$(a_{3/2})_{\text{UHF}}=\frac{16}{15}\frac{\mu_n\mu_B}{I}\left[\langle np\uparrow|r^{-3}|np\uparrow\rangle+\frac{5\pi}{3}|\psi_A(0)|^2\right]. \quad (15)$$

The HF expressions are of course readily obtained from (14) and (15) by making radial functions the same for both spin states.

Of interest is the fact that $(a_{c1/2})_{\text{UHF}}=-(a_{c3/2})_{\text{UHF}}$. This is a consequence of the sum rule,

$$\sum_J \langle JM_J|\text{Op}|JM_J\rangle=\sum_{M_LM_S}\delta_{M_L+M_S,M_J}\times\langle M_LM_S|\text{Op}|M_LM_S\rangle, \quad (16)$$

which holds for any operator Op diagonal in the $|M_LM_S\rangle$ representation. Since $\sum_i s_{iz}|\psi_i(0)|^2$ is such an operator, the result follows from the fact that for $M_J=\frac{1}{2}$ the matrix elements on the right-hand side cancel exactly, the unpaired electron having opposite spin in the two cases.

Values of $a_{1/2}$ and $a_{3/2}$ from the HF and UHF calculations are given in Table V along with the experimental results for sodium.[23,24] To understand why the agreement with experiment is not very good, the following analysis is helpful.

If both the $n^2P_{1/2}$ and $n^2P_{3/2}$ states have been measured, Eqs. (14) and (15) can be solved for $\langle np\uparrow|r^{-3}|np\uparrow\rangle$ and $|\psi_A(0)|^2$. The resulting values for the lowest ^2P state of sodium and for the two lowest ^2P states of potassium are given in Table VI along with the experimental values.[25–27] It can be seen that for experimental data comparable in accuracy to that given in the table, this procedure is likely to yield a value of $\langle np\uparrow|r^{-3}|np\uparrow\rangle$ accurate to within about 2%. However, core polarization values estimated in this way are highly dependent on the accuracy of the experimental data and consequently are of little value. For example, no significance can be attached to the negative signs obtained for the first two values in the table.

The reason for the poor agreement with experiment of the calculated a_J's of sodium is now clear. The calculated value $\langle 3p\uparrow|r^{-3}|3p\uparrow\rangle=0.168$ is only 67% of the value in Table VI. This is due to neglecting correlation, the inclusion of which would most affect the outer p shell, of relatively low electron density, making it more compact. Because of this and the indication that the calculated $|\psi_A(0)|^2=0.0044$ for sodium is too large, one cannot place much confidence in the UHF prediction that $a_{3/2}$ is negative for lithium.

4.3. Halogen Atoms

The ^2P ground term of a halogen atom is characterized by a hole in the outer p shell. To avoid confusion we shall refer not to the hole but to the unpaired p electron (assumed to have spin $\uparrow$) as polarizing the core electrons by exchange. A development similar to that which led to (14) and (15) gives,

$$(a_{1/2})_{\text{UHF}}=\frac{16}{3}\frac{\mu_n\mu_B}{I}\left[\frac{7}{10}\langle np\downarrow|r^{-3}|np\downarrow\rangle+\frac{3}{10}\langle np\uparrow|r^{-3}|np\uparrow\rangle-\frac{\pi}{3}|\psi_A(0)|^2\right], \quad (17)$$

$$(a_{3/2})_{\text{UHF}}=\frac{16}{15}\frac{\mu_n\mu_B}{I}\left[\langle np\downarrow|r^{-3}|np\downarrow\rangle+\frac{5\pi}{3}|\psi_A(0)|^2\right]. \quad (18)$$

The calculated HF and UHF values of the different hfs constants for F^{19} and Cl^{35} are given in Table VII along with available experimental data.[28–30] The meas-

TABLE VII. The hfs constants for the ^2P term of F and Cl (Mc/sec).[a]

	$J=\frac{1}{2}$ state		$J=\frac{3}{2}$ state	
	F^{19}	Cl^{35}	F^{19}	Cl^{35}
Experimental data:				
a_c	···	···	149 ± 3	···
a_d	···	···	2010.0	···
a	···	1037.19	···	205.29
Calculated values:				
a_{HF}	10 086	930.0 (90%)	2017 (100%)	186.0 (91%)
$(a_c)_{\text{UHF}}$	−187	−5.0	187 (126%)	5.0
$(a_d)_{\text{UHF}}$	9931	919.4	1954 (97%)	181.7
a_{UHF}	9744	914.4 (88%)	2141	186.7 (91%)

[a] Note: percentages in brackets refer to the experimental values.

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[23] M. L. Perl, I. I. Rabi, and B. Senitzky, Phys. Rev. **98**, 611 (1955).

[24] J. M. Dodd and R. W. N. Kinnear, Proc. Phys. Soc. (London) **75**, 51 (1960).

[25] P. Buck and I. I. Rabi, Phys. Rev. **107**, 1291 (1957).

[26] G. J. Ritter and G. W. Series, Proc. Roy. Soc. (London) **A238**, 473 (1957).

[27] W. N. Fox and G. W. Series, Proc. Phys. Soc. (London) **77**, 1141 (1961).

[28] H. E. Radford, V. W. Hughes, and V. Beltran-Lopez, Bull. Am. Phys. Soc. **5**, 272 (1960).

[29] L. Davis, B. T. Feld, C. W. Zabel, and J. R. Zacharias, Phys. Rev. **76**, 1076 (1949).

[30] J. G. King and V. Jaccarino, Phys. Rev. **84**, 852 (1951).

TABLE VIII. Hfs constants for $^3P_2$ state of Be and $^2P_{1/2}$ state of B (Mc/sec).

	Be^9			B^{11}	
$(a_2)_{\mathrm{expt}}$	124.63		$(a_{1/2})_{\mathrm{expt}}$	366.08	
Calculated values	HF case	UHF case	Calculated values	HF case	UHF case
a_{c2}	-98.8	-113.5	$a_{c1/2}$	0	-8.2
a_{d2}	-8.8	-8.8	$a_{d1/2}$	353.6	356.5
a_2	-107.6	-122.3	$a_{1/2}$	353.6	348.3
% of experiment	86%	98%	% of experiment	97%	95%

urement of $a_{c3/2}$ for fluorine by Radford *et al.*,[28] is of particular interest as it is the most direct measurement of core polarization available at the present time. The UHF calculation gives a value which is 25% larger. This may be partly due to neglecting the perturbing effect of the neighboring $^2P_{1/2}$ level on the $^2P_{3/2}$ level, as mentioned by Radford *et al.* However, it seems likely that the main source of error is the incorrect symmetry of the UHF determinantal wave function.

Again it should be noted that the agreement with experiment is less good for chlorine than for fluorine. The $3p$ shell of chlorine has a larger mean radius and therefore a lower electron density. Thus, in accordance with work on free-electron gases, correlation effects are expected to be more important in this case.

It is of interest that the first attempt to calculate the effect of exchange polarization was made for chlorine by Sternheimer[1] who employed a perturbation expansion approach for the dipolar part only of the hyperfine interaction. He obtained corrections to $\langle r^{-3}\rangle$ of $+1\%$ and -6% for the $^2P_{1/2}$ and $^2P_{3/2}$ states, respectively, compared with -1% and -2%, respectively, given by the present calculation (omitting the contact term).

4.4. Beryllium, Boron, and Nitrogen

The ground state (^4S term) of nitrogen can show no hyperfine structure in the HF approximation, but one would expect a large exchange polarization effect to account for the observed splittings. Accordingly, a UHF calculation was carried out. The resulting value of $|\psi_A(0)|^2$, however, was found to be almost twice the value expected from the experimental hfs data. In attempting to explain this puzzle, UHF calculations were carried out for boron and the ^3P term of beryllium. It is convenient to discuss these latter calculations first.

Having estimates of core polarization for the ^2P and ^2S terms of lithium, it is of interest to make from them an estimate for the ^3P term of beryllium in which both a $2s$ and a $2p$ electron lie outside the $1s$ core with their spins in the same direction.

Assuming that exchange polarization from the s and p electrons is additive, and also that the fractional change $\rho_{1s}/|\psi_{1s}(0)|$ due to a single unpaired $2s$ or $2p$ electron is the same in both lithium and beryllium, one obtains for beryllium the estimate $\rho_{1s}=0.106$. As the UHF calculation gives a value $\rho_{1s}=0.094$ these assumptions appear to be quite reasonable. The calculated HF and UHF values of a_2 obtained from (10) and (11) with $J=2$ are compared in Table VIII with the experimental value of Lurio and Blachman.[31] The result of including core polarization in a_c is to increase a_2 by 12% giving good agreement with experiment.

The $^2P_{1/2}$ ground state of boron has been measured by Lew and Title.[32] The calculated values of $a_{1/2}$, obtained from (14) with $n=2$, are compared with the experimental values in Table VIII. One can see that in the UHF case the negative core polarization contribution is partly compensated for by the increase in $\langle r^{-3}\rangle$ over the HF case.

Let us now use the UHF results for boron to make a rough estimate of $|\psi_A(0)|^2$ for the ^4S term of nitrogen in which there are three unpaired $2p$ electrons outside the $1s$ and $2s$ core. The reasonableness of our estimate of ρ_{1s} for beryllium from the ^2S and ^2P terms of lithium gives support to the simple picture that the fractional change in $\rho_{1s}/|\psi_{1s}(0)|$ and $\rho_{2s}/|\psi_{2s}(0)|$ for nitrogen is about three times that in boron. This leads to an estimate of $|\psi_A(0)|^2=0.32$ for nitrogen. However, this method of estimating rather badly upsets the ratio ρ_{1s}/ρ_{2s} which in Sec. 3 was noted to be very nearly constant for the UHF calculations of B, N, and F. Owing to the large cancellation between ρ_{1s} and ρ_{2s} it might be preferable to keep this ratio constant. This gives an estimate of $|\psi_A(0)|^2=0.16$.

The fact that the first estimate of $|\psi_A(0)|^2$ is twice the second shows that one has little hope of estimating it very closely by such rough methods. Nevertheless, from the way in which they were obtained, the values of 0.32 and 0.16 represent rough upper and lower bounds and one might expect the value of $|\psi_A(0)|^2$ to lie somewhere between them. The UHF calculation for nitrogen gives $|\psi_A(0)|^2=0.188$ and therefore appears to be satisfactory in the sense that it is reasonably consistent with the UHF calculations for boron and fluorine.

However, as mentioned earlier, the UHF value of $|\psi_A(0)|^2$ is almost twice the experimental result of Anderson *et al.*[33] From (10) the UHF expression is

$$a_{3/2}=\frac{16\pi}{9}\frac{\mu_n\mu_B}{I}|\psi_A(0)|^2. \tag{19}$$

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[31] A. Lurio and A. G. Blachman, Bull. Am. Phys. Soc. **5**, 344 (1960).

[32] H. Lew and R. S. Title, Can. J. Phys. **38**, 868 (1960).

[33] L. W. Anderson, F. M. Pipkin, and J. C. Baird, Phys. Rev. **116**, 87 (1959).

TABLE IX. Hfs constant for the ${}^4S_{3/2}$ state of N^{14} (Mc/sec).

	Contribution from ρ_{1s}	Contribution from ρ_{2s}	$a_{3/2}$
Experiment			10.4509
UHF calculation	-79.8	100.0	20.2
Das and Mukherjee[34]	-36.4	43.7	7.3
Blinder[4]	(negative)	(positive)	-10.07
Configuration interaction[35]			8.5

The calculated value is compared with experiment in Table IX. Also included in the table are the results of a variational calculation by Das and Mukherjee[34] which gave a reasonable result, and a perturbation calculation by Blinder.[4] Blinder appears to have expanded ρ_{1s} and ρ_{2s} in terms of the HF 1*s* and 2*s* eigenfunctions. However, for reasons referred to in Sec. 6, this procedure is generally unreliable, and thus it is not particularly surprising that this calculation gave the wrong sign for *a*.

The large UHF result remains puzzling. One would expect the hyperfine structure of this state of nitrogen to be a very direct measurement of the exchange polarization phenomenon. It appears, therefore, that the UHF wave function is inadequate for this case, and that to obtain a fairly good value, one must perform a proper configuration interaction calculation retaining the ${}^4S$ symmetry. Such a calculation has been recently reported by Bessis-Mazloum and Lefebvre-Brion.[35] Including only the two configurations $(1s)^2(2s)(2p)^3(3s)$ and $(1s)(2s)^2(2p)^3(3s)$, they obtained $a=8.5$ Mc/sec, in good agreement with experiment. Since the configuration interaction approach is in general rather slowly convergent, and because of reasons referred to in Sec. 6 regarding the use of eigenfunction expansions for describing core perturbations, one would not have expected good agreement in this particular case.

4.5. Iron Series and Higher Transition Series

The importance of core polarization in transition series elements should be briefly mentioned. This was first revealed in the iron series by Abragam *et al.*[36] who analyzed the experimental hfs data by the method used in constructing Table VI. The UHF calculation for iron of the present investigation, reported previously,[7,14] gave a value of $|\psi_{cp}(0)|^2$ for Fe^{2+} about 25% larger than that expected from the analysis of Abragam *et al.*

Comparably large core polarization effects are also expected in higher transition series such as the rare earths. For europium with a half-filled 4*f* shell Sandars and Woodgate[37] have found negative values for the hfs constants of the $(4f)^7(6s)^2\,{}^8S_{7/2}$ ground state. They state that admixture of ${}^6P_{7/2}$ and ${}^6D_{7/2}$ states are of the wrong sign to explain the experimental results and conclude that the dominant factor is exchange polarization of the *s* core electrons. A similar explanation is likely to hold for the $(5f)^7(7s)^2\,{}^8S_{7/2}$ ground state of americium recently measured by Marrus *et al.*[38]

5. CORE POLARIZATION IN SOLIDS

Although the present paper is mainly concerned with exchange polarization in free atoms, the importance of the effect in solids should be briefly mentioned.

A great deal of attention has been given recently to the study of hyperfine fields in ferromagnetic materials.[6] It is plausible that the large negative effective magnetic field acting at the nuclei of Fe, Co, and Ni is predominantly due to the contact interaction of core *s* electrons exchange polarized by the ferromagnetic *d* electrons. Estimates of core polarization from UHF calculations for atomic iron are not quite large enough to account for the experimental results.[7,8,14]

Exchange polarization can also make an important contribution to the Knight shift in metals, because, in a magnetic field, the excess of conduction electrons with spin ↑ over those with spin ↓ polarizes the core electrons.[5] In cases where the Knight shift is found to be negative,[39,40] a negative core polarization contribution must predominate over the contribution from the conduction electrons.

Finally, it should be mentioned that in analyzing electron spin resonance data for color centers, account should be taken of exchange polarization of neighboring ion cores by the electrons or holes associated with the center. Känzig and Woodruff[41] describe the hole associated with a *V* center or *H* center by an LCAO (linear combination of atomic orbitals) approach,

$$\psi=\sum_i \phi_i=\sum_i (\zeta_i\phi_{p_i}+\eta_i\phi_{s_i}), \tag{20}$$

where ϕ_{p_i} and ϕ_{s_i} are atomic orbitals from the *i*th halogen ion. Values of ζ_i and η_i obtained from the experimental data lead to values of $\sum_i (\zeta_i^2+\eta_i^2)$ between 1.5 and 2.0 for LiF and KCl owing to the neglect of overlap in their model. It is interesting, however, that when exchange polarization is included, without changing the model in any other respect, the values of $\sum_i (\zeta_i^2+\eta_i^2)$ are reduced by 20% for LiF and 5% for KCl.

6. CORE POLARIZATION CALCULATED BY PERTURBATION EXPANSION METHODS

As the ratios $\rho_{ns}/|\psi_{ns}(0)|^2$ are generally about 1% or less, one would think it should be possible to calcu-

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[34] T. P. Das and A. Mukherjee, Bull. Am. Phys. Soc. **5**, 241 (1960).

[35] N. Bessis-Mazloum and H. Lefebvre-Brion, Compt. rend. **251**, 648 (1960).

[36] A. Abragam, J. Horowitz, and M. H. L. Pryce, Proc. Roy. Soc. (London) **A230**, 169 (1955). The sign of χ for neutral Cu is incorrectly given as negative by Abragam *et al.*

[37] P. G. H. Sandars and G. K. Woodgate, Proc. Roy. Soc. (London) **A257**, 269 (1960).

[38] R. Marrus, W. A. Nierenberg, and J. Winocur, Phys. Rev. **120**, 1429 (1960).

[39] T. J. Rowland, J. Phys. Chem. Solids **7**, 95 (1958).

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

[41] W. Känzig and T. O. Woodruff, J. Phys. Chem. Solids **5**, 268 (1958); **9**, 70 (1959).

late core polarization by perturbation methods. However, it is clear at the outset that the large cancellation among the *ns* levels which exists for many atoms affects the accuracy required in the calculation of individual ρ_{ns} values. Roughly speaking, in order that $|\psi_A(0)|^2$ will be accurate to within about 50% the perturbation expansion must be capable of calculating each ρ_{ns} to within about 10% of the UHF value.

Preliminary hand calculations for lithium and sodium by perturbation expansion methods have been described previously.[5] A slightly different description follows which is exactly equivalent but has the advantage of showing more clearly the approximations which are involved.

The radial wave equations for the UHF functions $P(ns\uparrow;r)$ and $P(ns\downarrow;r)$ can be subtracted and the resulting expression simplified by making the following approximations:

$$V(ns\uparrow;r)P(ns\uparrow;r)-V(ns\downarrow;r)P(ns\downarrow;r)\\ =V(ns;r)[P(ns\uparrow;r)-P(ns\downarrow;r)], \quad (21)$$

$$E_{ns\uparrow}P(ns\uparrow;r)-E_{ns\downarrow}P(ns\downarrow;r)\\ =E_{ns}[P(ns\uparrow;r)-P(ns\downarrow;r)]+\Delta EP(ns;r), \quad (22)$$

$$X(ns\uparrow;r)-X(ns\downarrow;r)=\xi(ns;r). \quad (23)$$

Here $V(ns\uparrow;r)$ and $V(ns\downarrow;r)$ are the UHF central field potentials and $V(ns;r)$ is the corresponding HF potential; E_{ns} is the HF one-electron energy (negative and in rydbergs), $\Delta E=E_{ns\uparrow}-E_{ns\downarrow}$; and $\xi(ns;r)$ is the exchange term from unpaired spins computed from HF wave functions. With these approximations the "difference equation" becomes:

$$\left\{\frac{d^2}{dr^2}+\frac{2V(ns;r)}{r}+E_{ns}\right\}[P(ns\uparrow;r)-P(ns\downarrow;r)]\\ +2\frac{\xi(ns;r)}{r}+\Delta EP(ns;r)=0. \quad (24)$$

$P(ns\uparrow;r)-P(ns\downarrow;r)$ is now expanded in terms of an orthonormal set of basis functions $Q_k(r)$, each orthogonal to $P(ns;r)$;

$$P(ns\uparrow;r)-P(ns\downarrow;r)=\textstyle\sum_k \alpha_k Q_k(r). \quad (25)$$

By substituting, in (24), multiplying by $Q_k(r)$, and integrating over r one obtains a secular equation for the coefficients α_k involving only E_{ns} and integrals of the various $Q_k(r)$ and the HF functions $V(ns;r)$ and $\xi(ns;r)$. The order of the secular equation is, of course, equal to the number of $Q_k(r)$ included in the expansion. Then if $\lim_{r\to 0}[P(ns;r)/r]=A_{ns}$ and $\lim_{r\to 0}[Q_k(r)/r]=q_k$, solving the secular equation for the α_k gives,

$$\rho_{ns}=(A_{ns}/2\pi)(\textstyle\sum_k \alpha_k q_k). \quad (26)$$

TABLE X. Perturbation calculation of ρ_{1s} using the expansion functions (27).

Number of $Q_k(r)$	2	3	4	5	6	7	8
Li	95%	88%	84%	82.4%	81.9%		
Na	97%	89%	83%	80%	78.7%	78.3%	
F	80%	99%	87%	93%	91.2%	92.4%	
Cl	88%	78%	87%	76%	87%	78%	86%

The $Q_k(r)$ of (25) are so far unspecified beyond their being orthogonal to $P(ns;r)$ and orthonormal among themselves. Near the nucleus they vary with r as r^{l+1} with $l\geqslant 0$. Since $Q_k(r)$ with $l\geqslant 1$ do not contribute to ρ_{ns} as given by (26) one might reasonably suppose that all such functions can be omitted from (25). (It will be seen that the present work leads us to question this assumption.) An obvious choice of functions fulfilling the requirements are the bound eigenfunctions $P(n's;r)$ with $n'\neq n$, but for the reasons given previously[5] these are entirely unsatisfactory. A much better set of functions for perturbations on core wave functions is

$$Q_k(r)=P(n's;r) \quad \text{for} \quad k=n'<n,$$

$$Q_k(r)=q_k(1+c_{k1}r+c_{k2}r^2+\cdots+c_{kk}r^k)re^{-\epsilon r} \quad (27)\\ \text{for} \quad k\geqslant n.$$

The constants c_{ki} are chosen so that $Q_k(r)$ is orthogonal to $P(ns;r)$ and to $Q_1(r)\cdots Q_{k-1}(r)$, and q_k is chosen so as to normalize $Q_k(r)$. We also set $\epsilon=(-E_{ns})^{\frac{1}{2}}$ so that the exponential falls off in roughly the same way as $P(ns;r)$.[42] It should be remarked that the function $P(ns;r)$ was not included in the expansion (25) as it can be shown to give a contribution to ρ_{ns} which is of second order in the small quantities α_k.

The results (as a percentage of the UHF value) of calculations of ρ_{1s} using the set (27) are set out in Table X for different numbers of expansions functions. Unexpectedly, the convergence of the expansion turned out to be rather bad, particularly for chlorine. A possible explanation suggested by closer study is that adding successive $Q_k(r)$ to the expansion improved the shape over the tail region with little regard for the fit near the origin. It was therefore reasoned that if the $Q_k(r)$ have the "correct" form $q_k r(1-Zr)$ near the nucleus, then improvement in the tail region would be automatically accompanied by improvement in the value of ρ_{ns}. However, calculations of ρ_{1s} with the basis set,

$$Q_k(r)=P(n's;r) \quad \text{for} \quad k=n'<n,$$

$$Q_k(r)=q_k[1-(Z-\epsilon)r+c_{k2}r^2+\cdots+c_{k,k+1}r^{k+1}]re^{-\epsilon r}\\ \text{for} \quad k\geqslant n, \quad (28)$$

gave results almost exactly the same as those obtained with (27).

Of greater concern than the convergence characteristics of either (27) or (28) are the values eventually converged upon, the result for chlorine lying well outside the range of accuracy necessary to give $|\psi_A(0)|^2$

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[42] S. F. Boys, G. B. Cook, C. M. Reeves, and I. Shavitt, Nature **178**, 1207 (1956).

to within 50%. This could be caused by the perturbation approximations (21)–(23) or by incompleteness of the basis set. On careful examination it was found that the largest error due to approximations arises from omitting the first order term $[V(ns\uparrow;r)-V(ns\downarrow;r)]P(ns;r)$ from the right-hand side of (21). When included by an iterative procedure it altered the values of ρ_{1s} for Na, F, and Cl by only 2–4%. (For Li a sizeable 10% improvement occurred, but this seems reasonable for a structure having only three electrons. Comparable changes might be expected for the outer s levels of the other atoms.) One is led to conclude that the poor results obtained are due to incompleteness of the set of expansion functions (27) or (28).

Although it is impossible to assess the completeness in any rigorous way as functions varying near the nucleus as r^{l+1} with $l\geqslant 1$ have not been included among the $Q_k(r)$, nevertheless by examining the quantities,

$$S_N=(\sum_{k=1}^{N}\alpha_k^2)\bigg/\int_0^\infty [P(1s\uparrow;r)-P(1s\downarrow;r)]^2dr, \quad (29)$$

two important points emerge. First the "completeness" expressed by S_N is a little improved by having more than the first two $Q_k(r)$ in the expansion. Furthermore, as one might expect, there is a marked correlation between the values of S_8 and the values of the ratio of the expansion calculation ρ_{1s} to the UHF value. Both these points support the conclusion that in the present problem, and presumably in other problems involving perturbations on core wave functions, one should include functions which vary near the nucleus as r^{l+1} with $l\geqslant 1$, even though such functions cannot contribute to ρ_{ns}.

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