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Unrestricted Hartree-Fock Method: Electron Densities and Magnetic Form Factors for Spin Polarized Ni^{++}

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The effect of relaxing the restrictions associated with the Hartree-Fock method are discussed with particular emphasis on that constraint which requires common radial behavior for wave functions with all quantum numbers except m_s (spin direction) in common. Results of such a "spin polarized" Hartree-Fock self-consistent field calculation are reported for the Ni^{+2} ion and related to earlier calculations of Wood and Pratt, and Heine. Emphasis is placed on a consideration of the effects on the electron density and on x-ray and magnetic form factors. As is discussed, spin polarization of the 3*d* shell and the core results in an interesting effect on the magnetic form factor for this case. The calculation suggests that one would obtain a magnetic form factor which is measurably expanded (hence, a contracted charge distribution) in comparison with that appropriate for any single 3*d* electron. Also presented are results of calculations of several hyperfine parameters which are in rough agreement with experiment.

I. INTRODUCTION

THE Hartree-Fock formalism, as conventionally applied to multielectron systems, has a number of restrictions associated with it which play an important role in the shell description of atoms. The effect of relaxing these restrictions has recently been of some interest. Emphasis has been placed on studying the constraint requiring common radial behavior for wave functions with all quantum numbers except m_s (spin direction) in common.[1–9] Estimates of some of the effects of relaxing this restriction for iron series atoms[10,11] have been made, but of necessity these calculations have had to be crude.

In this paper we are reporting a self-consistent field "spin polarized" Hartree-Fock calculation for the free Ni^{+2} ion. We have several purposes in mind with this calculation. First, it is interesting to observe what is predicted by this model of an atom and to see how these predictions compare with those of the conventional "restricted" Hartree-Fock formalism and with experiment. Secondly, the calculation serves to calibrate a forthcoming "spin polarized" Hartree-Fock calculation for a Ni^{+2} ion in a crude cubic field similar to that used in an earlier calculation[12] for Mn^{+2}. The Ni^{+2} ion was chosen for the two calculations because of its almost filled 3*d* shell which contains both paired electrons and a net spin. Discussions of results will emphasize effects on the charge density and on x-ray and magnetic form factors. As will be seen from the results the "spin polarized" formalism leads to an interesting effect on the magnetic form factor for this case. Some results of calculations of the hyperfine structure parameters are also presented.

In the next section we briefly review the Hartree-Fock formalism and then go on to discuss these matters at some length, for while most readers are aware of the restrictions, we believe that there is, in practice, a strong tendency to overlook the implications of either the retention or the relaxation of these restraints. Section III contains a brief review of the Wood and Pratt[10] and the Heine[11] calculations which are predecessors to our calculation. This is followed by a description of the calculation, Sec. IV, and a discussion of the results, Sec. V.

II. THE HARTREE-FOCK FORMALISM

As is well known, the Hartree-Fock formalism consists of approximating a true many-electron wave function by a single (or on occasion a linear combination of) Slater determinant(s). A Slater determinant for an

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[1] References 2 through 9 represent only a very incomplete listing of discussions of this topic.

[2] J. C. Slater, Phys. Rev. **82**, 538 (1951).

[3] P. O. Löwdin, *Proceedings Nikko Symposium Molecular Physics* (Maruzen, Tokyo, 1954), p. 13; Phys. Rev. **97**, 1509 (1955); Revs. Modern Phys. **32**, 328 (1960).

[4] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

[5] R. K. Nesbet, Revs. Modern Phys. (to be published).

[6] R. Lefebvre, Compt. rend. **237**, 1158 (1953).

[7] J. A. Pople and R. K. Nesbet, J. Chem. Phys. **22**, 571 (1954).

[8] G. Berthier, J. chim. phys. **51**, 363 (1954).

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

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

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

[12] For Mn^{+2} in a cubic field see R. E. Watson, Phys. Rev. **117**, 742 (1960) (there is an error in this calculation, details are available from the author); for Ni^{+2} in a cubic field see R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1134 (1960).

N electron system takes the form:

$$\Psi=(N!)^{-\frac{1}{2}}\begin{vmatrix}\psi_1(x_1)\psi_2(x_1)\cdots\psi_n(x_1)\\ \psi_1(x_2)\psi_2(x_2)\cdots\\ \cdots\\ \cdots\\ \psi_1(x_n)\psi_2(x_n)\cdots\psi_n(x_n)\end{vmatrix}, \qquad (1)$$

the x_i's denote electron space and spin coordinates and $(N!)^{-\frac{1}{2}}$ is the normalization constant if the one-electron ψ_i's are orthonormal. Since such a determinant is unaffected by replacement of ψ_k by $\psi_k+C\psi_j$, for any constant C, it is no restriction to assume the ψ_i's orthogonal.

For a Hamiltonian consisting only of kinetic and electrostatic interaction terms,[13] the total energy for a single determinant function is:

$$\begin{aligned}E=&\sum_{i=1}^{N}\int\psi_i(x)^*K_{\rm op}\psi_i(x)d\tau\\ &+\sum_{i=1}^{N}\sum_{j<i}\int\int|\psi_i(x_1)|^2\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}|\psi_j(x_2)|^2d\tau_1d\tau_2\\ &-\sum_{i=1}^{N}\sum_{\substack{j<i\\ \parallel\,\text{spin}}}\int\int\psi_i(x_1)^*\psi_j(x_2)^*\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\\ &\qquad\times\psi_i(x_2)\psi_j(x_1)d\tau_1d\tau_2,\end{aligned} \qquad (2)$$

where $K_{\rm op}$ is the one-electron kinetic+nuclear potential energy operator. The integrations are over space coordinates (the integration over spin having been carried out). The final terms, called exchange terms, only appear for ψ_i, ψ_j pairs of parallel spin.[14] Application of the variational principle to E by varying an individual ψ_i leads to a Hartree-Fock equation which in its integrated form would be:

$$\begin{aligned}\epsilon_i\int|\psi_i(x)|^2d\tau=&\int\psi_i(x)^*K_{\rm op}\psi_i(x)d\tau\\ &+\sum_{j=1}^{N}\int\int|\psi_i(x_1)|^2\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\\ &\qquad\times|\psi_j(x_2)|^2d\tau_1d\tau_2\\ &+\sum_{\substack{j=1\\ \parallel\,\text{spin}}}^{N}\int\int\psi_i(x_i)^*\psi_j(x_2)^*\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\\ &\qquad\times\psi_i(x_2)\psi_j(x_1)d\tau_1d\tau_2.\end{aligned} \qquad (3)$$

Again the second sum is limited to one-electron states of parallel spin. ϵ_i is the one-electron energy and is, in fact, a Lagrange multiplier present for the purpose of obtaining a normalized ψ_i. The terms $i=j$ are included, for the integral in one sum cancels that in the other, since there are advantages in including such terms in the calculations.

In practice, the Hartree-Fock formalism, briefly sketched above, is further modified by the addition of restrictions which have the advantage of simplifying the job of solving the equations but which also have profound effects on the final form of the wave functions (and therefore on matrix elements involving them). We will here discuss the constraints for the case of an atomic system since this will be of interest to us. The extension of the restrictions to molecular and crystalline systems should then be apparent. Three restrictions are normally incorporated into Hartree-Fock calculations and a fourth often appears in analysis of experimental data based on assuming Hartree-Fock descriptions of electronic systems. We will first consider the three associated with conventional Hartree-Fock calculations. (i) The spacial part of a ψ_i is assumed to be separable into a radial and an angular part, i.e.:

$$\psi_i(r_1\theta_1\phi_1\sigma)=[U_i(r)/r]S_i(\theta\phi)\mathcal{S}_i(\sigma), \qquad (4)$$

where $\mathcal{S}_i(\sigma)$ is a spin function with a spin quantum number, m_s, of $\pm\frac{1}{2}$. In practice $S_i(\theta,\phi)$ is normally chosen to be a spherical harmonic, $Y_l^m(\theta,\phi)$,[15] or in other words, ψ_i is assumed to be an eigenfunction for a spherical environment (in which a spacial function is separable). Since only atomic S states are exactly spherical, this represents a real restraint on the Hartree-Fock formalism. The assumption of separability is, however, often used for cases involving potentials other than those which are spherical or nearly spherical [in this case the $S_i(\theta,\phi)$'s become something other than spherical harmonics]. This assumption is often less justifiable and an example will be discussed briefly in another paper.[16] This restriction implies that the $S_i(\theta,\phi)$'s be assigned before the application of the variation principle to Eq. (2) and that only the $U_i(r)$'s are to be obtained variationally. In this way the Hartree-Fock equations change from three-dimensional to one-dimensional equations, thus greatly simplifying their solution. Of greater importance is the fact that this restriction leads to the use of the one-electron quantum numbers n, l, and m_l for other than exactly spherical atoms. It must be emphasized that the use of n, l, and m_l for non-spherical atoms (which is necessary for the shell structure description of an atom) requires the introduction of a restriction to the Hartree-Fock formalism. (ii) Assuming (i), $U_i(r)$ is constrained to be independent of the m_l value associated with ψ_i. This is not a restriction for

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[13] See P.-O. Löwdin, Technical Note No. 27, Quantum Chemistry Group, Uppsala University, Uppsala, Sweden, June 1, 1959 (unpublished) for a discussion of the H.-F. scheme in which spin-orbit terms are explicitly included.

[14] For details and a fuller discussion see D. R. Hartree, *The Calculations of Atomic Structure* (John Wiley & Sons, New York, 1957).

[15] See E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1953), for definitions and phase conventions.

[16] R. E. Watson and A. J. Freeman, reference 12; also see G. F. Koster, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, January 15, 1960 (unpublished), and to be published.

the case of a spherical atom. (iii) $U_i(r)$ is likewise constrained to be independent of m_s. This is not a constraint for ions where the total ion spin quantum number S is a good quantum number and equals zero.

These last two restrictions imply a single $U_i(r)$ for any shell (i.e., n and l value) and in turn a separate Hartree-Fock equation per shell rather than a separate equation per electron. The reduction in the number of equations is of course important when solving them. In practice, the "restricted" Hartree-Fock equation for a shell is an average of the Hartree-Fock equations derived for the separate occupied ψ_i's of that shell.[14] Further, the introduction of (ii) and (iii) is not always compatible with the requirement of orthogonal ψ_i's. Keeping orthogonal ψ_i's then requires the introduction of "off-diagonal Lagrange multipliers"[17] which represent real constraints for certain types of atomic systems.

Of greater importance than the reduction in the magnitude of a computation, is the fact that the relaxation of any of the above restraints leads to the collapse of the conventional shell structure formalism. In other words, the relaxation of constraints leads to the partial abandonment of a very successful description of atomic systems. Atomic lithium is a simple example of what occurs. The Li ground state is a ^2S, $(1s)^2 2s$ configuration single determinant in conventional notation, with the closed $1s$ shell making a ^1S contribution to the atom's symmetry. Due to the fact that one $1s\psi_i$ has an exchange interaction with the $2s$ and the other does not, the relaxation of (iii) leads to differing U_{1s}'s and to a single determinant of the form, $[1s\uparrow 1s'\downarrow 2s\uparrow]$, (here arrows denote spin and the prime differing U_{1s}'s). The $1s$ shell is no longer "closed," i.e., it no longer makes a ^1S contribution, and the determinant no longer has total spin (S) as a good quantum number.[18] Two additional determinantal functions can be constructed from the $U_i(r)$'s, namely $[1s\downarrow 1s'\uparrow 2s\uparrow]$ and $[1s\uparrow 1s'\uparrow 2s\downarrow]$.[19] One ^4S and two ^2S states can be constructed by linear combination[20] of three determinants. The expression for the total energy and the Hartree-Fock equations for the multideterminant states are much more complicated than those for the single determinant restricted Hartree-Fock case.[21]

While the Hartree-Fock equations for the three electron unrestricted symmetrized case can be solved, the number of determinants and the corresponding complexity of the resultant integro-differential equations increases rapidly with systems involving increasing numbers of electrons. Therefore, for systems involving more than a few electrons, these complications have been avoided by relaxing constraints on the one-electron functions of the restricted Hartree-Fock determinantal function and applying the variation principle to the *single* determinant alone. For lithium, the variational principle is applied to the determinant $[1s\uparrow 1s'\downarrow 2s\uparrow]$, yielding a many-electron function which is predominantly ^2S but with a small amount of ^4S character mixed in; this "unrestricted" function would have a lower energy[9] than the original restricted Hartree-Fock function since a constraint has been removed. The Wood and Pratt[10] calculations for atomic Fe and Heine's[11] for Mn are examples of this approach where only restriction (iii) has been relaxed.

Going from the traditional restricted Hartree-Fock formalism to a less restricted but still unsymmetrized form leads to a very small change ($\sim 0.001\%$) in the total energy.[22] Despite this small energy change the accompanying changes in the one-electron functions are of importance. Examples of areas where the effect is appreciable are: fine structure, quadrupole polarization of electronic charge,[23] the interaction of ions with a crystalline environment,[12] and the prediction of neutron magnetic form factors.[24]

A fourth restriction is often added when the Hartree-Fock formalism is used to parameterize experimental results. It is best described by the use of examples. (iv) In the case of a many-electron state which is to be ionized by the removal of an electron associated with a particular ψ_j it is assumed that the other ψ_i's are unperturbed by the removal of electron j. This assumption leads to Koopman's theorem[25] which states that the ionization energy is simply the one-electron energy of the jth electron (ϵ_j) as given by Eq. (3). In the slightly different case where the jth electron is not actually removed from the system but ψ_j is replaced by ψ_k it is assumed, or rather the restriction is made, that the other ψ_i's are unperturbed. Using Koopmans' theorem we discover that the difference in energy between the two many-electron states is simply $\epsilon_k - \epsilon_j$. This type of restriction underlies the normal energy band description of a solid.[26]

A version of restriction (iv) is also used for the set of states belonging to a single configuration (assignment of n and l values to the ψ_i's). Here it is assumed that the

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[17] R. E. Watson, Ph.D. thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1959 (unpublished).

[18] This statement breaks down if $U_{1s'}$ can be expressed as a linear combination of U_{1s} and U_{2s}, i.e., if the U_i's are not linearly independent.

[19] If U_{1s} and $U_{1s'}$ are constrained to be the same, the first of these is identical except for sign, with the earlier determinant and the last is zero valued (since a determinant with two identical columns is zero valued). This is an example of the Pauli exclusion principle which is built into wave functions of the determinantal form.

[20] Projection operators are conveniently used for constructing such properly symmetrized states, see R. Fieschi and P.-O. Löwdin, Technical Note No. 4, Quantum Chemistry Group, Uppsala University, Uppsala, Sweden, September, 1957 (unpublished).

[21] For a fuller discussion of Li see R. K. Nesbet and R. E. Watson, Ann. Phys. **9**, 260 (1960).

[22] For the example of lithium, see reference 21.

[23] As in the work of R. Sternheimer and others. For a review article see M. H. Cohen and F. Reif, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957), Vol. 5, p. 322.

[24] A. J. Freeman and R. E. Watson, Phys. Rev. **118**, 1168 (1960).

[25] T. Koopman, Physica **1**, 104 (1933).

[26] For example, see J. Callaway, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1958), Vol. 7, p. 99.

$U_i(r)$ for any shell is the same for all states of the configuration. This assumes that the other restrictions (i to iii) are already in force and leads to the Racah parameterization[27] of atomic multiplet spectra in terms of a limited number of Slater F^k and G^k integrals of the form;

$$F^k(i,j)=\int_0^\infty\int_0^\infty |U_i(r)|^2|U_j(r')|^2\frac{r_<^k}{r_>^{k+1}}drdr', \quad (5)$$

and

$$G^k(i,j)=\int_0^\infty\int_0^\infty U_i(r)^*U_j(r')^*\frac{r_<^k}{r_>^{k+1}}U_i(r')U_j(r)drdr', \quad (6)$$

where $r_<$ denotes the r of lesser magnitude. For the case of a $3d^n$ iron series ion (with just the $3d$ shell unfilled) the multiplet spectrum is parameterized in terms of a $F^2(3d,3d)$ and a $F^4(3d,3d)$. This formalism has been extended to the case of an ion in a crystalline environment[28] where the F^k's are augmented by a crystalline field splitting parameter Dq. For an iron series ion Dq takes the form:

$$Dq\sim\int_0^\infty |U_{3d}(r)|^2V_c(r)dr, \quad (7)$$

where $V_c(r)$ is the field due to the crystalline environment. The case of an ion in a crystalline environment will be discussed at length elsewhere.[29]

Restriction (iv) has been frequently applied with great success due to a remarkable cancellation of the errors associated with its use in the Hartree-Fock formalism and not because of some basic validity of the restriction. The remainder of this section will be used to present two examples which illustrate this point.

Restricted Hartree-Fock calculations have been carried out for a number of iron series atoms and ions[30]; among these are calculations for the neutral iron $3d^8$, ^3F and singly ionized iron $3d^7$, ^4F states. The one-electron nuclear potential+kinetic energy integrals [the K integrals of Eq. (2)] differ for the two states, the differences being 0.051 ry for the $3d$, 0.125 for the $3p$, and 0.275 for the $3d$. This leads to a 2.77-ry variation in the K integrals associated with the occupied U_{3s}, U_{3p}, and U_{3d} which, if we assume (iv), do not vary at all. The measured ionization energy is 0.2994 ry or one-ninth of the energy variation associated with the above K integrals, yet the calculated one-electron energy (ϵ_{3d}, $m_l=0$) of the electron being removed is 0.3359 ry, in reasonable agreement with experiment. Further examples of the good agreement between observed ionization energies and one-electron energies will be found elsewhere.[31]

The fitting of experimental free ion multiplet spectra with F^k's treated as parameters, has been fairly successful while fits for ions in crystalline environments have been very successful. The greater success of the latter may be due to a parametrization scheme which for this case fits fewer spectral lines with more parameters. In the case of the free ions of the iron series there are appreciable and systematic differences between the F^k's obtained from experiment and those obtained from Hartree-Fock calculations.[32] Inspection of those cases where the Racah equations and experiment disagree as to the order of multiplet states, suggests that the F^k discrepancies are due to the experimental F^k's not being strict F^k integrals. This suggests that effects outside of the restricted Hartree-Fock formalism appreciably affect the multiplet spectra.

III. EARLIER IRON SERIES SPIN POLARIZED CALCULATIONS

Wood and Pratt[10] did a self-consistent field Hartree-Fock calculation for the neutral Fe, $4s^23d^6$ free atom where $U_i(r)$'s for electrons of different spin in a shell were allowed to differ, i.e., restrictions (iii) of the previous section was relaxed, leading to an "unsymmetrized" determinantal function. We would describe their calculation as a "spin polarized"[33] calculation and it should be noted that restrictions (i) and (ii) were still in force. For computational reasons these authors did not handle exchange exactly but instead used the Slater $\rho^{\frac{1}{3}}$ (charge density to the one-third power) exchange potential.[34] As they indicated, this introduced errors in regions of low charge density, i.e., near the nucleus and for large radii. Since a conventional restricted Hartree-Fock calculation has recently been done for the $4s^23d^6$ ground state of neutral Fe[35] a brief comparison of results seems desirable. The one-electron energies for the two calculations are listed in Table I. In making comparisons it should be noted that the restricted Hartree-Fock one-electron energies are established to about 0.01 ry. The table indicates that the

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[27] While a number of the multiplet spectra equations had been obtained previously (e.g., see Condon and Shortley[15]) the classic papers are those of G. Racah, Phys. Rev. **61**, 186 (1942); **62**, 438 (1942); **63**, 367 (1943).

[28] For example, see W. Moffitt and C. J. Ballhausen, Ann. Rev. Phys. Chem. **7**, 107 (1956); W. Low, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Suppl. 2.

[29] A. J. Freeman and R. E. Watson, Phys. Rev. **120**, 1254 (1960).

[30] R. E. Watson, Technical Report No. 12, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts, June 15, 1959 (unpublished), and Phys. Rev. **118**, 1036 (1960).

[31] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, New York, 1960), Vol. 1, and reference 30.

[32] See Fig. 2 of reference 30.

[33] There is some question of terminology with reference to such calculations. Originally these have been referred to as "unrestricted Hartree-Fock calculations" by Slater and his group. We are inclined to call such a calculation a *spin polarized* calculation, reserving the term *unrestricted* Hartree-Fock for the case where the restrictions (ii), (iii), and perhaps (i) are relaxed. Löwdin and collaborators refer to a solution properly symmetrized prior to the variational calculation as an *extended* Hartree-Fock scheme.

[34] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[35] R. E. Watson, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, April 15, 1960 (unpublished); and Phys. Rev. **119**, 1934 (1960).

inaccuracy of the potential (used by Wood and Pratt) near the nucleus had a large effect on $U_{1s}(r)$ and its one-electron energy with resulting repercussions on the other $U_i(r)$'s. The Wood and Pratt wave functions are in fact better than their energies would indicate, e.g., they yield x-ray scattering factors which are in fair agreement with those computed for the restricted Hartree-Fock function.[36]

Heine[11] did a calculation for Mn^{++} and Mn in which he used the results of an existing Cu calculation to supply a Coulomb potential and added a $\rho^{\frac{1}{3}}$ exchange potential due to the unfilled 3*d* shell. He solved for functions of the 2*s*, 3*s*, and 4*s* shells (no 1*s*) in this potential, i.e., it was not a self-consistent field calculation. His purpose was to obtain an estimate of the Fermi[37] contact hyperfine interaction parameter

$$\chi=(4\pi/S)\langle\textstyle\sum_k \delta(r_k)m_{sk}\rangle_{S_z=S}, \tag{8}$$

where S is the ion's total spin, the index k ranges over electron coordinates, and the $S_z=S$ indicates that the term is to be evaluated for an ion in the state where $M_S=S$. The bracket $\langle\ \rangle$ is the net spin density (wave function density weighted by m_s values) at the nucleus. For the iron series doubly ionized ion ground states the experimental χ is roughly a constant with a value of ~ -3 in atomic units.[37] Heine obtained a value for χ of -3.3 for Mn^{+2} (and a similarly good value for Mn) and Wood and Pratt obtained -2.4 for Fe^{+2}.

TABLE I. Comparison of the one-electron energies (ϵ_i's) of the Wood and Pratt[a] spin polarized Hartree-Fock calculations for neutral $[(3d\uparrow)^5(3d\downarrow)^3(4s)^2]$ Fe with the restricted Hartree-Fock values of Watson.[b]

	Wood and Pratt one-electron energies		Restricted Hartree-Fock one-electron energies
	Spin↑	Spin↓	
1*s*	−584.5 ry	−584.2 ry	−522.7 ry
2*s*	−61.08	−60.40	−63.84
3*s*	−7.463	−6.930	−8.308
4*s*	−0.532	−0.428	−0.510
2*p*	−53.16	−52.65	−54.79
3*p*	−5.061	−4.540	−5.455
3*d*	−1.122	−0.664	−1.271

[a] See reference 10.
[b] See reference 35.

IV. DESCRIPTION OF THE CALCULATION

The calculation has been done using self-consistent field analytic techniques.[38] Normalized analytic one-electron radial functions $[U_i(r)\text{'s}]$ are obtained as solutions of the Hartree-Fock radial equations. The $U_i(r)$'s have the form:

$$U_i(r)=\textstyle\sum_j C_{ij}R_j(r) \tag{9}$$

their normalization condition is:

$$\int_0^\infty |U_i(r)|^2dr=1, \tag{10}$$

and the basis functions are of the form,

$$R_j(r)=N_jr^{l+A_j+1}e^{-Z_jr}. \tag{11}$$

The l is the one-electron angular momentum appropriate for the one-electron function of which $U_i(r)$ is the radial part. The N_j is a normalization constant and is expressible in terms of the other parameters, i.e.;

$$N_j=\left\{\frac{(2Z_j)^{2l+2A_j+3}}{(2l+2A_j+2)!}\right\}^{\frac{1}{2}}. \tag{12}$$

It should be noted that the eigenvectors (C_{ij}'s) are defined in terms of normalized R_j's. A set of R_j's is supplied for each l value for which Hartree-Fock solutions are to be obtained. $U_i(r)$'s of a common l value are constructed from a common set of R_j's.

The strength of the analytic procedure lies in the fact that the necessary integrals are obtained analytically and the Hartree-Fock self-consistent procedure becomes a process of matrix manipulation and diagonalization. This process can be more rapidly and accurately carried out on a computer than can the conventional numerical methods of solving Hartree-Fock equations. The limitation of the analytic approach lies in the fact that we must use less than complete sets of basis functions. Thus we cannot obtain exact solutions. Associated with the approach is the problem of choosing sets of basis functions (R_j's). We have used the set employed in an earlier restricted Hartree-Fock calculation[30] for Ni^{+2}. The set of R_i's (or rather their Z_j's, N_j's ,and A_j's) appear in Table II. The size of this set represents an uneasy compromise between the choice of a large set which would allow accurate wave-function construction and a small one which would retain the advantages of wave functions of analytic form. Inspection of the basis set used here suggests that it would not allow for subtle wave-function behavior either very close to the

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[36] A J. Freeman and R. E. Watson, Acta. Cryst. (to be published).

[37] See A. Abragram, J. Horowitz, and M. H. L. Pryce, Proc. Roy. Soc. (London) **A230**, 169 (1955).

[38] The analytic approach to solving Hartree-Fock equations has been developed by many workers. C. A. Coulson [Proc. Cambridge Phil. Soc. **34**, 204 (1938)] appears to have been the first to have used an expansion technique in a molecular problem, while C. C. J. Roothaan [Revs. Modern Phys. **23**, 69 (1951)] presented the approach in a particularly desirable form for closed-shell molecules. Nesbet, with his symmetry and equivalence restrictions, extended the method to nonclosed shells and emphasized its use for atomic cases [see reference 4 and also Quarterly Progress Reports No. 15, January, 1955, p. 10; No. 16, April, 1955, p. 38 and p. 41; No. 18, October, 1955, p. 4, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts (unpublished)]. Nesbet's approach was modified in the course of calculations by Allen, R. E. Watson, and R. K. Nesbet (e.g., the modified restricted Hartree-Fock calculations of reference 21). Recently C. C. J. Roothaan [Revs. Modern Phys. **32**, 179 (1960)] has extended his formalism to cover the nonclosed shell case for the conventional restricted Hartree-Fock method where nonzero off-diagonal Lagrange multipliers occur. The iron series ions with just a nonclosed 3*d* shell do not require his formalism.

Table II. Parameters (A_j, Z_j, and N_j) which define the basis set (R_j's).

	j	A_j	Z_j	N_j
R_j's used for the construction of s functions ($l=0$)	1	0	29.2991	317.18411
	2	1	25.9035	3943.3516
	3	1	13.3851	756.87370
	4	2	12.4174	2844.7630
	5	2	7.4187	468.90632
	6	2	4.4208	76.593477
p functions ($l=1$)	7	0	18.2297	1638.3933
	8	0	11.0602	469.76085
	9	1	10.1407	1400.1563
	10	1	6.1124	238.05644
	11	1	3.7142	41.635831
d functions ($l=2$)	12	0	2.3154	7.9639743
	13	0	4.5232	82.984888
	14	0	8.5025	755.70446
	15	0	15.0077	5521.2606

nucleus or in the outer part of the ion, i.e., the "tails" of the U_{3s}, U_{3p}, and (to a slight extent) U_{3d}. We estimate that a maximum error on the order of 0.01 ry is produced in the one-electron energies due to the limited basis set.

The unsymmetrized spin polarized Hartree-Fock equations were derived by taking the single determinant restricted Hartree-Fock description of $\mathrm{Ni}^{+2}(3d)^8$, ^3F ($M_S=+1$, $M_L=+3$) and applying the variational principle as described by Hartree,[14] to functions of one spin in a shell separately from those of the other. This yielded two Hartree-Fock equations per electron shell or one per "subshell." Due to our initial M_S choice, we filled the $3d$ subshell of plus spin leaving three electrons ($m_l=2$, 1, and 0) in the subshell of negative spin. As noted in Sec. 2, the function ceases to be a pure ^3F state as soon as the set of $U_i(r)$'s for a given l and m_s value are different (strictly speaking linearly independent) from those of $-m_s$. The wave function to be described in the following section is thus predominantly but not identically a ^3F state.

V. RESULTS

A. Eigenvectors and Eigenvalues

The eigenvectors (C_{ij}'s) appear in Table III. Table IV contains the one-electron nuclear potential+kinetic energies (K_i's), the one-electron energies (ϵ_i's), the Slater $F^k(3d,3d)$ integrals[39] and the total energy. The same quantities obtained for the earlier restricted Hartree-Fock calculation[30] for Ni are included for comparison. These quantities are accurately evaluated for the functions defined in Table III (for spin polarized calculation) and elsewhere[40] (for the restricted case). The first fact to observe is the very small total energy improvement of 0.003 ry, an effect which is one two-hundredth the size of some of the energy differences between ϵ_i's and K_i's of differing spin. It should also be noted that the averages (weighted, in the $3d$ case, by the numbers of electrons of spin up and down) of the spin polarized ϵ_i's and K_i's are in good agreement with the restricted Hartree-Fock values. The two $U_{3d}(r)$'s and their differing $F^k(3d,3d)$'s cannot be easily related to the $\mathrm{Ni}^{+2}(3d)^8$ multiplet spectrum for several reasons. First, one should consider the effect of relaxing restriction (ii) as well as (iii). This should lead to additional $F^k(3d,3d)$ differences. In comparison with what follows, this is a minor consideration. Secondly, if one does Hartree-Fock calculations for different multiplet states of the same configuration, one obtains $F^k(3d,3d)$'s and other *integrals* which show differences which are of the

Table III. The eigenvectors (C_{ij}'s) defining the spin polarized Hartree-Fock radial functions (U_i's) in terms of the basis functions (R_j's). The arrows denote the spin values ($m_s=\pm\frac{1}{2}$) associated with the U_i's, note that $M_S=+1$.

$j=$	1	2	3	4	5	6
$i=1s\uparrow$	0.91714999	0.10098404	−0.00162370	0.00128502	−0.00023301	−0.00000102
$1s\downarrow$	0.91715289	0.10098632	−0.00162971	0.00127521	−0.00023253	−0.00000193
$2s\uparrow$	−0.28036141	−0.16394354	0.68524057	0.45154710	0.03649725	−0.00117615
$2s\downarrow$	−0.28070223	−0.16432674	0.68672005	0.45224966	0.03397806	−0.00125708
$3s\uparrow$	0.10582698	0.05066751	−0.22364005	−0.41109321	0.39772722	0.82649480
$3s\downarrow$	0.10526667	0.05113588	−0.22496994	−0.40579286	0.39306664	0.82902639
$j=$	7	8	9	10	11	
$i=2p\uparrow$	0.14685634	0.84377484	0.02080950	0.02110774	−0.00275806	
$2p\downarrow$	0.14663382	0.84676890	0.01871883	0.01919158	−0.00296159	
$3p\uparrow$	−0.04762232	−0.33693859	−0.05352594	0.57699250	0.57721481	
$3p\downarrow$	−0.04538758	−0.33927573	−0.04406725	0.56238492	0.58690628	
$j=$	12	13	14	15		
$i=3d\uparrow$	0.41980857	0.55308983	0.17064442	0.00464008		
$3d\downarrow$	0.44168992	0.53276300	0.17258038	0.00387780		

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[39] Considerations of space make it desirable to omit the other F^k and G^k integrals; they have been computed and are available to interested persons.

[40] See p. 228 of the technical report, reference 30.

same order of magnitude as the $F^k(3d,3d)$ differences of Table IV. Lastly, there are systematic discrepancies that occur between theoretical and "experimental" $F^k(3d,3d)$ values.[32] We believe that these discrepancies are due to many-electron (correlation) effects which are outside of the scope of the Hartree-Fock, F^k type of description of an atom.

B. Charge Densities and Form Factors

Table IV also gives information concerning the radial behavior of the $U_i(r)$'s since K_i's of larger magnitude indicate relatively contracted $U_i(r)$'s. We see that the $U_i(r)$'s of the majority (plus) spin have converged [relative to the minority spin $U_i(r)$'s] upon each other. The convergence is *not* in toward the nucleus. The $U_{1s\uparrow}$, $U_{2s\uparrow}$, and $U_{2p\uparrow}$ are relatively expanded and the $U_{3s\uparrow}$, $U_{3p\uparrow}$, and $U_{3d\uparrow}$ are contracted. This is illustrated by Fig. 1 which represents the net radial spin density of the argon-like core, i.e.:

$$\rho_A(r) \equiv \sum_{i=\text{argon core}} 2(m_s)[U_i(r)]^2 = \sum_{\text{spin}\uparrow}[U_i(r)]^2 - \sum_{\text{spin}\downarrow}[U_i(r)]^2. \quad (13)$$

TABLE IV. The one-electron nuclear potential+kinetic energies (K_i's), the one-electron energies (ϵ_i's), the $F^k(3d,3d)$'s and the total energies for the spin polarized and restricted Hartree-Fock calculations for Ni^{+2}.

	Spin polarized calculation note that $M_S=+1$ spin↑	spin↓	Restricted calculation
K_{1s}	−783.7034 ry	−783.7036 ry	−783.7034 ry
K_{2s}	−192.2294	−192.2906	−192.2601
K_{3s}	−74.4584	−74.3875	−74.4227
K_{2p}	−190.8927	−190.9840	−190.9385
K_{3p}	−70.6687	−70.4770	−70.5733
K_{3d}	−59.9826	−59.4111	−59.7662
ϵ_{1s}	−612.6471	−612.6482	−612.6486
ϵ_{2s}	−77.2961	−77.1474	−77.2227
ϵ_{3s}	−11.3540	−10.9642	−11.1595
ϵ_{2p}	−67.3493	−67.2063	−67.2787
ϵ_{3p}	−8.2001	−7.7245	−7.9627
ϵ_{3d}	−2.8984	−2.7046	−2.8251
$F^0(3d,3d)$	1.98160	1.95021	1.96965
$F^2(3d,3d)$	0.91619	0.89725	0.90896
$F^4(3d,3d)$	0.56986	0.55716	0.56501
Total energy	−3012.0449		−3012.0422

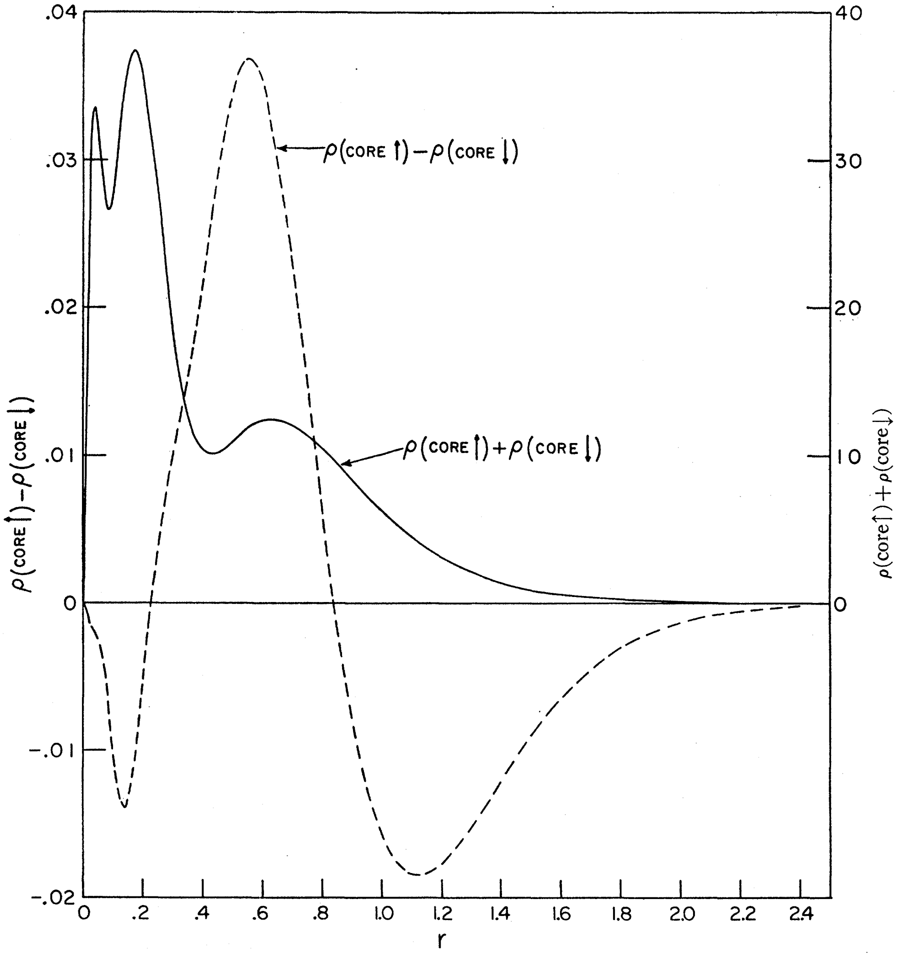

FIG. 1. The net radial spin density of the argon-like core ρ_A, i.e., $[\rho(\text{core}\uparrow)-\rho(\text{core}\downarrow)]$, and the argon core radial charge density $[\rho(\text{core}\uparrow)+\rho(\text{core}\downarrow)]$ for spin polarized Ni^{+2}.

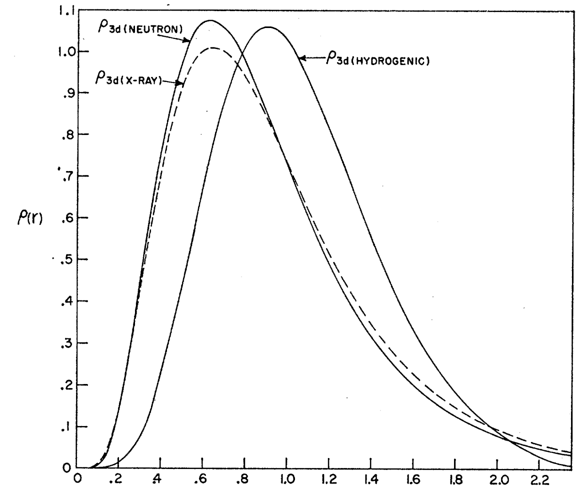

FIG. 2. Spin polarized $3d$ charge density, $\rho_{3d(\text{x ray})}$; spin density, $\rho_{3d(\text{neutron})}$; and a hydrogenic $3d$ charge density, $\rho_{3d(\text{hydrogenic})}$ for Ni^{+2}.

Negative values indicate regions where a negative spin is associated with the charge distribution. The electron spin density of the "closed" argon-like core is small; this is best indicated by the argon core radial charge density [insert a plus sign in the right-hand side of Eq. (13)] which also appears in Fig. 1.

Instead of discussing the behavior of the two $U_{3d}(r)$'s, we will discuss the electron densities that yield the one-electron spherical scattering factors appropriate for x-ray and neutron diffraction, i.e., the ρ's that appear in

$$f_{3d}(k)=\int_0^\infty \rho_{3d}(r)\frac{\sin kr}{kr}dr, \tag{14}$$

where k is the familiar $4\pi\sin\theta/\lambda$. The one-electron $3d$ charge density "seen" by x rays is the average of the $[U_{3d}(r)]^2$'s or:

$$\rho_{3d(\text{x ray})}\equiv\tfrac{1}{8}\{5[U_{3d\uparrow}(r)]^2+[U_{3d\downarrow}(r)]^2\}, \tag{15}$$

while that "seen" by neutrons is the ion's spin density divided by the number of unpaired spins:

$$\rho_{3d(\text{neutron})}\equiv\tfrac{1}{2}\{5[U_{3d\uparrow}(r)]^2-3[U_{3d\downarrow}(r)]^2+\rho_A\}, \tag{16a}$$

or

$$\rho_{3d(\text{neutron})}=[U_{3d\uparrow}(r)]^2 +\tfrac{1}{2}\{3([U_{3d\uparrow}(r)]^2-[U_{3d\downarrow}(r)]^2)+\rho_A\}, \tag{16b}$$

where ρ_A is the argon core contribution as defined in Eq. (13). The two densities are identical for a restricted Hartree-Fock function, i.e., the second term on the right-hand side of Eq. (16b) equals zero. The spin polarized $\rho(r)$'s appear in Fig. 2 along with that for a hydrogenic function[41] yielding almost the same multiplet spectrum [i.e., it is chosen so that its $F^2(3d,3d)$ agrees with the restricted Hartree-Fock $F^2(3d,3d)$]. We see that a hydrogenic $3d$ function is not a good approximation to the Hartree-Fock function. The difference between $\rho_{3d(\text{neutron})}$ and $\rho_{3d(\text{x ray})}$ is primarily a matter of shape—they cannot be brought into agreement simply by scaling. This is typical of what we have observed in the past of $3d$ function behavior, i.e., when separate restricted Hartree-Fock calculations have been done for two states of the same iron series element (e.g., for two stages of ionization, for two different configurations and the same stage of ionization, for two multiplet states of the same configuration, or for an ion with and without an external environment) variation in $U_{3d}(r)$ and $[U_{3d}(r)]^2$ has been primarily a matter of shape and not scaling. The $U_{3d}(r)$'s have also tended to be quite different than hydrogenic. Stern[42] and Wood[43] have observed a similar behavior for the set of $3d$ functions obtained in energy band calculations for metallic iron. Scaling is unimportant because the *bulk* of a $3d$ function is relatively unperturbed by the various environments (and/or symmetry requirements). The variations primarily consist of adding or subtracting charge to the $3d$ tail, subject to the requirement of $U_{3d}(r)$ normalization. While the above observations are based solely on theoretical calculations, they do suggest that it is inappropriate either to approximate iron series $U_{3d}(r)$'s by hydrogenic functions or to describe $U_{3d}(r)$ variations by scaling alone.

Since scattering factors rather than charge densities, enter in diffraction experiments, it is desirable to inspect these. A number of scattering factors, (spherical part only) appear in Table V. Included are one-electron $3d\uparrow$, $3d\downarrow$, $3d$(x ray), and $3d$(neutron) (i.e., magnetic) form factors. Argon core and total ion (x-ray) scattering factors are also tabulated. Comparison with the results[44] for the restricted Hartree-Fock Ni^{+2} function shows agreement between argon core and total ion scattering factors of better than 0.01 e.u., with the spin polarized results always lying higher. If one restricts inspection to values of $\sin\theta/\lambda$ of 1.0 A^{-1} or less, the argon core agreement is to 0.004 e.u. and the total ion's to 0.006 e.u. The restricted f_{3d} and the spin polarized $f_{3d(\text{x ray})}$ agree to 0.0003 e.u. with the latter lying higher. These differences are small, indicating that the restricted and spin polarized charge densities are almost identical, with the latter very slightly contracted (indicated by expanded or higher scattering factors) in comparison with the former. The difference, however, between $f_{3d(\text{x ray})}$ and $f_{3d(\text{neutron})}$ is small but measurable, i.e., current neutron diffraction techniques can readily distinguish form factor effects of this size. Equation (16) suggests that $f_{3d(\text{neutron})}$ may be interpreted as $f_{3d\uparrow}$ plus contributions from the spin polarized electron dis-

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[41] Hydrogenic functions and their form factors are included in our discussion since it has been a fairly common practice to compare measured neutron form factors with hydrogenic form factors [such as those of L. Pauling and J. Sherman, Z. Krist. **A81**, 1 (1932)].

[42] F. Stern, Phys. Rev. **116**, 1399 (1959).

[43] J. H. Wood, Phys. Rev. **117**, 714 (1960).

[44] Appearing in part in R. E. Watson and A. J. Freeman, Acta Cryst. (to be published).

TABLE V. Form factors for spin polarized Ni^{++} in e.u.

$(\sin\theta/\lambda)$ (A^{-1})	$f_{3d\uparrow}$	$f_{3d\downarrow}$	$f_{3d(\text{x ray})}$	$f_{3d(\text{neutron})}$	$f_{\text{argon core}}$	$f_{\text{total ion}}$
0	1.0000	1.0000	1.0000	1.0000	18.00	26.00
0.05	0.9797	0.9790	0.9795	0.9809	17.89	25.72
0.10	0.9224	0.9198	0.9214	0.9268	17.56	24.93
0.15	0.8368	0.8317	0.8349	0.8456	17.04	23.72
0.20	0.7345	0.7270	0.7316	0.7476	16.36	22.21
0.25	0.6266	0.6173	0.6231	0.6432	15.56	20.54
0.30	0.5219	0.5116	0.5180	0.5404	14.69	18.84
0.35	0.4258	0.4155	0.4219	0.4448	13.80	17.18
0.40	0.3411	0.3314	0.3375	0.3593	12.91	15.61
0.45	0.2686	0.2601	0.2654	0.2851	12.07	14.19
0.50	0.2080	0.2008	0.2053	0.2221	11.28	12.92
0.60	0.1177	0.1133	0.1160	0.1267	9.92	10.84
0.70	0.0600	0.0578	0.0591	0.0645	8.85	9.33
0.80	0.0249	0.0242	0.0246	0.0262	8.05	8.24
0.90	0.0048	0.0048	0.0048	0.0039	7.44	7.48
1.00	−0.0060	−0.0056	−0.0058	−0.0079	6.95	6.91
1.10	−0.0111	−0.0105	−0.0108	−0.0133	6.55	6.46
1.20	−0.0127	−0.0122	−0.0125	−0.0149	6.19	6.09
1.30	−0.0124	−0.0119	−0.0122	−0.0144	5.84	5.74
1.40	−0.0112	−0.0108	−0.0111	−0.0129	5.51	5.42
1.50	−0.0099	−0.0096	−0.0098	−0.0113	5.17	5.09

tribution of the "paired" 3*d* electrons and the argon core. Inspection of Table V shows that $f_{3d\uparrow}$ lies closer to $f_{3d(\text{x ray})}$ than to $f_{3d(\text{neutron})}$. Further study shows that the contribution from the "paired" 3*d* electrons is the principle cause of the $f_{3d(\text{x ray})}-f_{3d(\text{neutron})}$ differences. The observations outlined above suggest that the interpretation of an experimentally obtained neutron magnetic form factor, in terms of a single, unfilled shell wave function, must be done with care. This calculation suggests that for Ni^{+2}, one would obtain a magnetic form factor which is measurably *expanded* (hence a contracted charge distribution) in comparison with that appropriate for *any* of the 3*d* electrons.

Before leaving this topic we should mention the widely investigated case of Mn^{+2}. Here all the 3*d* electrons are of parallel spin, and only the argon core is available for spin polarization effects. Since the argon core contribution to the magnetic scattering is small, and since there is *no* polarized 3*d* contribution, one would expect $f_{3d(\text{x ray})}$ and $f_{3d(\text{neutron})}$ to be in substantial agreement and in turn that a measured $f_{3d(\text{neutron})}$ can be better relied upon for direct information about 3*d* electron behavior.

C. Hyperfine Parameters

Let us now consider the Fermi contact term χ [see Eq. (8)] which occurs in an $\mathbf{S}\cdot\mathbf{I}$ ($\mathbf{I}$ being the nuclear spin) hyperfine interaction.[45] Only *s* functions provide nonzero contributions at $r=0$ and in the restricted Hartree-Fock formalism their contribution is zero. Since the common Ni isotopes have zero nuclear spin, we must obtain a value of χ from other doubly ionized iron series ions. As has been noted, χ has a roughly constant experimental value of −3 a.u. for these ions. The spin polarized Ni^{+2} 1*s*, 2*s*, and 3*s* shells make contributions of −0.27, −9.62, and +5.95, respectively, for a χ of −3.94 a.u. We note a competition of terms quite consistent with Fig. 1 and the earlier discussion of wave function behavior. This sort of behavior is in qualitative agreement with the results of Marshall[46] and Wood and Pratt.[10] The latter obtained a relatively greater 1*s* contribution; this may have been due to their use of a $\rho^{\frac{1}{3}}$ exchange potential. The spin polarized χ's represent substantially better agreement with experiment than do earlier configuration interaction estimates, of Abragam, Horowitz and Pryce.[37] In closing the discussion of χ, it should be noted that while the earlier spin polarized calculations suffered from poor exchange potentials (and lack of self-consistency in Heine's case), the present calculation relies on a basis set which *may* supply too little variational freedom close to the nucleus. This will be investigated in the near future.

There is another hyperfine parameter involving the interaction of electron spin and angular momentum with the nuclear spin which may be discussed. If one assumes a restricted Hartree-Fock function, this parameter is proportional to $\langle r^{-3}\rangle$ where:

$$\langle r^{-3}\rangle \equiv \int_0^\infty \frac{[U_{3d}(r)]^2}{r^3}dr. \tag{17}$$

Abragam, Horowitz, and Pryce[37] report experimental $\langle r^{-3}\rangle$ values for free neutral atoms and for doubly ionized ions in salts. It is our experience[35,36,24] that the neutral atom 4*s* electrons perturb a $U_{3d}(r)$ *less* than does a crystalline environment, and therefore we will rely on the neutral atom $\langle r^{-3}\rangle$'s. Interpolating Abragam, Horowitz and Pryce's data (since $I=0$ for Ni), we obtain $\langle r^{-3}\rangle_{\exp}=6.3$ e.u. The spin polarized $U_{3d\uparrow}$ and $U_{3d\downarrow}$ yield calculated values of 7.15 and 6.99 e.u., respec-

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[45] It should be noted that the charge densities making up χ are $[U_i(r)/r]^2$ and not $[U_i(r)]^2$ [see Eq. (4)].

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

tively. The analysis leading to the $\langle r^{-3}\rangle_{\text{exp}}$ was based on the assumption of a restricted Hartree-Fock function. Inspection of the spin density in Fig. 1 suggests that there are additional sources to this hyperfine term and that we should not expect detailed agreement in $\langle r^{-3}\rangle$'s. We have not investigated this particular aspect of the problem.

VI. CONCLUSION

We have been investigating the effect of relaxing one of the restrictions associated with the conventional restricted Hartree-Fock formalism. The particular restriction in question, (iii), requires common $U_i(r)$'s for electrons of differing m_s value. Relaxation of this constraint in a calculation for Ni^{+2} has led to measurable effects in the electron spin distribution of that ion. A Fermi contact hyperfine parameter was obtained which, in common with earlier calculations, is in fair agreement with experiment. Of perhaps greater importance is the effect on the magnetic form factor which represents an electronic spin distribution measurably different from that of either of the $3d$ electron types. This suggests that experimentally determined magnetic form factors for an ion like Ni^{+2}, can perhaps be misleading if interpreted as arising directly from a single $3d$ charge distribution. This difficulty is most likely to occur for an ion with an almost filled shell, where the "paired" electrons of that shell can be spin polarized so as to make a contribution to the magnetic scattering.

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Crystalline Field and Spin Polarization Effects on Electron Densities and Magnetic Form Factors

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The combined effects of spin (or exchange) polarization and an external crystalline field on charge densities, x-ray and magnetic form factors, and hyperfine parameters are investigated following the analytic Hartree-Fock self-consistent field approach. The crystalline field was represented by a crude cubic field arising from an octahedral array of point charges surrounding the central ion—in this case Ni^{+2}. In the strong field approximation the atomic $3d$ electrons are "split" by the crystalline field and the spinpolarization effect, resulting in a description of these electrons by a set of three distinct orbitals (each having different radial distributions and called $t_{2g}\uparrow$, $t_{2g}\downarrow$ and $e_g\uparrow$). The ion's spin density leads to a Fermi contact hyperfine term in better agreement with experiment than the value reported in an earlier spin polarized calculation for the free Ni^{+2} ion and a magnetic form factor whose Fourier transform resembles none of the individual $3d$ charge distributions.

I. INTRODUCTION

In earlier investigations we have considered several factors affecting charge densities and measured magnetic form factors[1–3] of iron series ions. An external crystalline field was shown to produce two effects on the $3d$ charge density for an ion like Mn^{++} and hence on its magnetic form factor as well: (1) an expansion of the $3d$ charge density from its free ion value and (2) a "splitting" of the doubly degenerate (e_g) and triply degenerate (t_{2g}) cubic functions from their common free ion value, resulting in two different radial charge densities. The expansion effect, as suggested by experimental $F^k(3d,3d)$ integrals was shown[2] to be compatible with neutron diffraction data.[4] The splitting effect led to the prediction that a half-closed shell ion, like Mn^{++}

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[1] R. E. Watson, Phys. Rev. **117**, 742 (1960). There is an error associated with this calculation; an erratum is available from the author.

[2] A. J. Freeman and R. E. Watson, Phys. Rev. **118**, 1168 (1960), and J. Appl. Phys. **31**, 374S (1960).

[3] R. E. Watson and A. J. Freeman, preceding paper [Phys. Rev. **120**, 1125 (1960)], henceforth denoted as I.

[4] J. M. Hastings, N. Elliot, and L. M. Corliss, Phys. Rev. **115**, 13 (1959).