current it is reasonable to assume either that several different types of particles are formed or that the same type of particle is adsorbed with a binding energy depending upon the type of adsorption site. On the basis of either assumption, we may picture the adsorbed particles as residing in adsorption traps of different energy depth. As the surface temperature is increased, those particles in the traps of least depth acquire sufficient energy to escape.[4] At higher temperatures the deeper traps are emptied. Because the desorbed particles have been shown to be positive ions, the desorbed particles must exist on the surface as ions or be readily ionized. If, as seems likely, the adsorbed particles are ions, the persistent surface potentials observed directly by Shaw[5] and Laznovsky[6] and indirectly by many others are readily explained. It is conceivable that ion desorption may have influenced the interpretation of so-called "flash filament" measurements which have been used by many investigators to evaluate vacuum conditions and to study adsorption of a gas.

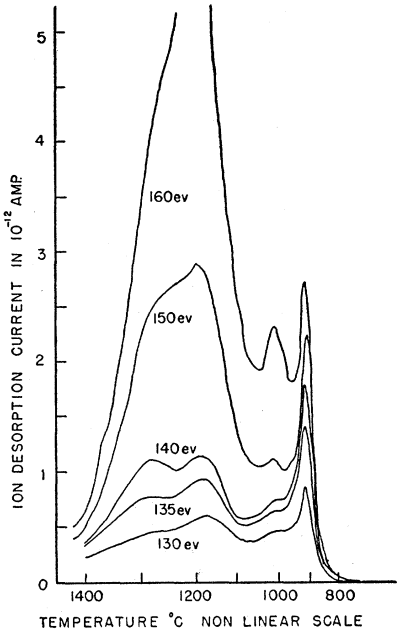

FIG. 1. Ion desorption current curves for various positive nitrogen ion bombarding energies. Curves were obtained by increasing the tungsten filament temperature at approximately 6 centigrade degrees per second after bombardment had ceased. Temperatures shown are approximate.

Preparations are now being made to try to detect ion desorption in other gases and from other surfaces, and to study the effects described above in more detail.

The writer is indebted to Mr. Donald Horne for taking most of the data described here.

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[4] The process assumed here is analogous to the trapping of electrons in phosphors. The glow curves obtained by warming certain phosphors after excitation are very similar in appearance to the ion desorption current curves we have obtained. See, for example, F. Urbach, *Solid Luminescent Materials*, edited by G. R. Fonda and F. Seitz (John Wiley and Sons, Inc., New York, 1948), p. 123.

[5] A. E. Shaw, Phys. Rev. 44, 1006 (1933).

[6] W. Laznovsky, Ph.D. thesis, University of Vienna, 1951 (unpublished). A copy of this thesis was kindly loaned to the writer by Dr. Richard Herzog.

PHYSICAL REVIEW VOLUME 107, NUMBER 4 AUGUST 15, 1957

Wave Functions and Energy Levels for Fe as Found by the Unrestricted Hartree-Fock Method*

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(Received April 26, 1957)

Results of a self-consistent field calculation using Slater's average exchange potential are given for atomic iron. The usual restriction of doubly filled orbitals in closed shells is dropped and orbitals, with the same n and l quantum numbers but different m_s are varied separately. This results in a separate set of radial wave functions for the two one-electron spin directions. The differences in these functions arise from an exchange polarization effect produced by the net spin of the Fe atom. Wave functions, one-electron energy parameters, net spin charge density, and electrostatic potential functions for each spin are given. A comparison is made between these results and those obtained by the Hartree method. The magnetic form factor found with these new Fe orbitals is shown to be in good agreement with experiment. The fine-structure splittings are also evaluated and found not to be in as good agreement as those calculated by the Hartree method. The hyperfine splitting of the Mn^{++} ion is estimated using the new orbitals and found to be in much better agreement than estimates based on a limited configuration interaction.

INTRODUCTION

THE usual formulation of a self-consistent field treatment of an atomic system consists of setting up a single determinant of one-electron functions each labeled by the quantum numbers n, l, m_l, and m_s. The expression for the average energy is varied with respect to these functions, but only orbitals with distinct n and l designations are varied independently. This is known as the restricted Hartree-Fock method.[1]

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* The research reported in this document was supported jointly by the Army, Navy, and Air Force under contract with the Massachusetts Institute of Technology.

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

The method is restricted in the sense that orbitals with the same n and l values but with different m_l or m_s are forced to have the same radial dependence. It has been shown[2] for an atom with net spin that if orbitals with the same n, l, and m_l values but with different m_s assignments are varied independently, that the resulting variational equations for orbitals of different m_s have a different form. This difference arises because of the net spin of the atom, there being a different exchange interaction for electrons with m_s of the same sign as the total M_s than for electrons with m_s of opposite sign to that of the total M_s. This effect is conveniently described as an exchange polarization, and the separate variation with regard to the different m_s values is known as the unrestricted Hartree-Fock method.

The unrestricted method as applied here is based on the use of a single determinant for the total state which is taken to be in the $3d^6\,4s^2$ configuration. Five of the six d-electrons are assigned α spin and each assumed to have the same radial dependence. The remaining d-electron is given β spin, an m_l value of 2 appropriate to the $^5D_4$ ground state of Fe, and its radial dependence is independent of the d-electrons with α spin. Since the radial functions now have a parametric spin dependence, the single determinant is no longer an eigenfunction of S^2. If the orbitals of the same n, l, and m_l but different m_s are nearly the same, the determinant will be a good approximation to such an eigenfunction. It is further to be noted that the exchange-polarization effect persists even when one carries through the full spin-degeneracy problem such that each spatial function has no particular spin association. For a more detailed explanation of this point the reader is referred to reference 2.

The primary purpose of the calculation reported here is to investigate an atom in which a large exchange polarization is expected and then to determine the physical consequences of this effect. To this end, the fine-structure splitting and the magnetic form factor of Fe have been evaluated. Since Fe has no nuclear magnetic moment, no comparison with hyperfine splittings is possible. However, using the one-electron functions found here, it is possible to approximate the charge density for each spin about an Mn^{++} ion and to estimate the hyperfine splitting. This is of particular interest as the Mn^{++} ion should show no hyperfine splitting if it were in the $3d^5$ configuration as described by the restricted Hartree-Fock method. Actually a large splitting is observed, and attempts to describe this splitting by limited configuration interaction calculations have been distinctly unsuccessful.[3] It has been pointed out in reference 2 that the effect of exchange polarization would lead to a nonvanishing spin density at the nucleus due to the s-electron orbitals with opposite spin association. The value obtained for this splitting by using the wave functions of the present calculation is in relatively good agreement with experiment.

METHOD OF SOLUTION

The total charge density of the chosen configuration is not spherically symmetric due to the presence of the single d-electron of β spin. Reduction to a central-field problem was accomplished by neglecting the angular dependence of this d-electron wave function. By the use of Slater's averaged exchange potential[4] the unrestricted Hartree-Fock equations are further reduced to a set of differential equations each containing but a single one-electron wave function explicitly and in which there is one potential in which all electrons of α spin are assumed to move and another potential for electrons of β spin.

Fock's equations are of the form[5]

$$H_1u_i(\sigma,r_1)+\left[\sum_{k=1}^{N} e^2\int\frac{u_k^*(r_2)u_k(r_2)}{r_{12}}dr_2 -3e^2\left\{\frac{3}{4\pi}\frac{N(\sigma,r_1)}{N(r_1)}\sum_{k=1}^{N}u_k^*(r_1)u_k(r_1)\right\}^{\frac{1}{3}}\right]\cdot u_i(\sigma,r_1)=E_iu_i(\sigma,r_1). \tag{1}$$

The term H_1 is the kinetic energy and the electrostatic energy arising from the electron-nucleus interaction of an electron at r_1. The factor $N(\sigma,r_1)/N(r_1)$ is the fraction of electrons of spin σ at r_1.

Equation (1) is reduced to a radial differential equation in the standard way for a central-field problem by setting

$$u(\sigma,r)=\frac{P_{n,l,\sigma}(r)}{r}Y_l^m(\theta,\phi). \tag{2}$$

The equation for $P_{n,l,\sigma}(r)$ in atomic units is

$$\frac{d^2P_{nl\sigma}(r)}{dr^2}+\left\{E_{nl\sigma}+\frac{2Z_p(r)}{r}+\frac{z(\sigma,r)}{r}-\frac{l(l+1)}{r^2}\right\}\times P_{nl\sigma}(r)=0. \tag{3}$$

The quantity $2Z_p(r)$ is r times the ordinary electrostatic potential set up by the nucleus of charge Z and all of the electrons. It is given by

$$2Z_p(r)=2Z-\sum_{\substack{\text{all}\\ \text{electrons}}}\left[\int_0^r P_{nl\sigma}{}^2(r')dr'+r\int_r^\infty\frac{P_{nl\sigma}{}^2(r')}{r'}dr'\right]. \tag{4}$$

The quantity $z(\sigma,r)$ of (3) is r times the averaged exchange potential for spin σ and is expressed in atomic

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

[3] Abragam, Horowitz, and Pryce, Proc. Roy. Soc. (London) **A230**, 169 (1955).

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

[5] G. W. Pratt, Jr., Phys. Rev. **88**, 1217 (1952).

units in terms of the radial functions as

$$z(\sigma,r)=6\left[\frac{3}{16\pi^2}\frac{N(\sigma,r)}{N(r)}\sum_{\substack{\text{all}\\ \text{electrons}}} rP_{nl\sigma}^{2}(r)\right]^{\frac{1}{3}}. \qquad (5)$$

The quantities $2Z_p(r)$ and $z(\sigma,r)$ are conveniently combined to define the function $W(\sigma,r)$ as

$$W(\sigma,r)=2Z_p(r)+z(\sigma,r). \qquad (6)$$

Self-consistency is determined with respect to the $W(\sigma,r)$ function.

The problem is solved by first estimating the initial $W_0(\sigma,r)$ function and using this in (3) to determine the corresponding set of one-electron functions $P_{n,l,\sigma}(r)$. Using this set, the final $W_1(\sigma,r)$ function is constructed for each spin by (6) and compared with the initial $W_0(\sigma,r)$. This is repeated until satisfactory agreement is found between the initial and final $W(\sigma,r)$ functions. Equation (3) was integrated on the International Business Machine 604 Calculating Punch using the Noumerov method described in reference 5.

The $W_0(\sigma,r)$ function was estimated in the following way. The $2Z_p(r)$ part was taken to be that determined by a previous self-consistent field investigation of Fe using the Hartree method by Manning and Goldberg.[6] In order to obtain the remaining $z(\sigma,r)$ contribution to $W_0(\sigma,r)$, the quantity $N(\sigma,r)/N(r)$ and the local electron density are required. The local density was calculated from reference 6, and for the first cycle $N(\sigma,r)/N(r)$ was taken as 15/26 for $\sigma=\alpha$ and 11/26 for $\sigma=\beta$.

The self-consistent procedure is apt not to converge if the $W_1(\sigma,r)$ function is used directly in (1) to determine a new set of $P_{n,l,\sigma}(r)$ functions. Therefore, a potential $W_2(\sigma,r)$ intermediate between $W_0(\sigma,r)$ and $W_1(\sigma,r)$ was employed in the second cycle. There being no criterion for selecting $W_2(\sigma,r)$, an arbitrary choice of

$$W_2(\sigma,r)=\tfrac{1}{2}\{W_0(\sigma,r)+W_1(\sigma,r)\}$$

was made. The result of the second cycle is a new set of radial functions from which the potential $W_3(\sigma,r)$ is found.

After completing the second cycle, one has sufficient information, i.e., $W_i(\sigma,r)$ with $i=0$, 1, 2, 3, to apply the interpolation method described in reference 5 to find the starting potential $W_4(\sigma,r)$ for the third cycle. This interpolation procedure was very successful in the case of Cu^+ and proved to be so in the present case. The potential $W_5(\sigma,r)$ found from the third cycle was satisfactorily consistent with $W_4(\sigma,r)$. The radial wave functions for each spin found in the third cycle were taken as final.

TABLE I. The 1*s* radial wave functions as determined by the Slater approximation and by the Hartree method (labeled MG).

r	$P_{1s}\alpha$	$P_{1s}\beta$	P_{1s}MG	r	$P_{1s}\alpha$	$P_{1s}\beta$	P_{1s}MG
0.000	0.000	0.000	0.000	0.120	1.264	1.263	1.457
0.002	0.549	0.549	0.495	0.140	0.861	0.861	1.026
0.004	1.047	1.048	0.939	0.160	0.577	0.577	0.709
0.006	1.495	1.495	1.337	0.180	0.381	0.381	0.485
0.008	1.895	1.895	1.693	0.200	0.250	0.249	0.326
0.010	2.251	2.252	2.009	0.220	0.162	0.162	0.219
0.012	2.568	2.568	2.289	0.240	0.105	0.104	0.145
0.014	2.848	2.848	2.536	0.260	0.067	0.067	0.095
0.016	3.094	3.094	2.752	0.280	0.043	0.042	0.062
0.018	3.310	3.310	2.940	0.300	0.027	0.027	0.040
0.020	3.486	3.486	3.102				
				0.350	0.008	0.007	0.015
0.025	3.731	3.731	3.409	0.400	0.002	0.000	0.005
0.030	3.853	3.853	3.596				
0.035	3.880	3.880	3.689				
0.040	3.836	3.836	3.708				
0.050	3.605	3.605	3.588				
0.060	3.266	3.265	3.336				
0.070	2.885	2.884	3.016				
0.080	2.502	2.501	2.672				
0.090	2.139	2.139	2.332				
0.100	1.810	1.810	2.012				

TABLE II. The 2*s* radial wave functions as determined by the Slater approximation and by the Hartree method (labeled MG).

r	$P_{2s}\alpha$	$P_{2s}\beta$	P_{2s}MG	r	$P_{2s}\alpha$	$P_{2s}\beta$	P_{2s}MG
0.000	0.000	0.000	0.000	0.220	−2.038	−2.039	−2.011
0.005	0.348	0.349	0.340	0.240	−2.022	−2.024	−2.008
0.010	0.608	0.609	0.594	0.260	−1.966	−1.967	−1.963
0.015	0.792	0.792	0.774	0.280	−1.880	−1.881	−1.888
0.020	0.911	0.912	0.893	0.300	−1.775	−1.775	−1.791
0.025	0.975	0.976	0.959	0.350	−1.470	−1.469	−1.502
0.030	0.995	0.996	0.982	0.400	−1.163	−1.161	−1.201
0.035	0.978	0.978	0.968	0.450	−0.892	−0.889	−0.931
0.040	0.930	0.931	0.925	0.500	−0.668	−0.666	−0.701
				0.550	−0.491	−0.489	−0.521
0.050	0.764	0.764	0.769	0.600	−0.357	−0.355	−0.379
0.060	0.535	0.535	0.551				
0.070	0.270	0.270	0.298	0.700	−0.182	−0.181	−0.195
0.080	−0.008	−0.009	0.029	0.800	−0.089	−0.088	−0.174
0.090	−0.287	−0.288	−0.242	0.900	−0.041	−0.040	−0.048
0.100	−0.556	−0.556	−0.504	1.000	−0.014	−0.014	−0.023
				1.100	−0.000	−0.000	−0.011
0.120	−1.036	−1.037	−0.978	1.200			−0.005
0.140	−1.421	−1.422	−1.362	1.300			−0.003
0.160	−1.705	−1.706	−1.649	1.400			−0.002
0.180	−1.893	−1.895	−1.846				
0.200	−2.000	−2.000	−1.962	1.600			0.000

TABLE III. The 2*p* radial wave functions as determined by the Slater approximation and by the Hartree method (labeled MG).

r	$P_{2p}\alpha$	$P_{2p}\beta$	P_{2p}MG	r	$P_{2p}\alpha$	$P_{2p}\beta$	P_{2p}MG
0.000	0.000	0.000	0.000	0.220	1.935	1.936	1.924
0.005	0.013	0.013	0.012	0.240	1.854	1.854	1.849
0.010	0.044	0.047	0.045	0.260	1.754	1.755	1.758
0.015	0.099	0.099	0.095	0.280	1.644	1.644	1.654
0.020	0.165	0.165	0.158	0.300	1.528	1.527	1.542
0.025	0.242	0.242	0.232	0.350	1.236	1.234	1.259
0.030	0.327	0.328	0.314	0.400	0.968	0.966	0.995
0.035	0.418	0.419	0.402	0.450	0.741	0.739	0.767
0.040	0.513	0.514	0.494	0.500	0.558	0.556	0.581
				0.550	0.414	0.412	0.433
0.050	0.709	0.710	0.683	0.600	0.304	0.302	0.319
0.060	0.903	0.904	0.872				
0.070	1.088	1.089	1.053	0.700	0.160	0.159	0.168
0.080	1.260	1.261	1.222	0.800	0.082	0.080	0.151
0.090	1.416	1.417	1.376	0.900	0.041	0.038	0.042
0.100	1.553	1.554	1.512	1.000	0.020	0.014	0.019
				1.100	0.008	0.000	0.009
0.120	1.770	1.771	1.729	1.200	0.000	0.000	0.004
0.140	1.914	1.915	1.876	1.300			0.001
0.160	1.992	1.993	1.958	1.400			0.000
0.180	2.014	2.015	1.987				
0.200	1.992	1.993	1.972				

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[6] M. F. Manning and L. Goldberg, Phys. Rev. **53**, 662 (1938).

TABLE IV. The *3s* radial wave functions as determined by the Slater approximation and by the Hartree method (labeled MG).

r	$P_{3s}\alpha$	$P_{3s}\beta$	P_{3s}MG	r	$P_{3s}\alpha$	$P_{3s}\beta$	P_{3s}MG
0.000	0.000	0.000	0.000	0.350	0.142	0.141	−0.063
0.005	0.133	0.132	0.130	0.400	0.453	0.448	0.367
0.010	0.232	0.230	0.227	0.450	0.719	0.711	0.634
0.015	0.302	0.299	0.295	0.500	0.928	0.919	0.850
0.020	0.347	0.343	0.340	0.550	1.080	1.070	1.013
0.025	0.371	0.366	0.364	0.600	1.179	1.169	1.125
0.030	0.377	0.372	0.371				
0.035	0.369	0.364	0.365	0.700	1.247	1.240	1.221
0.040	0.348	0.344	0.346	0.800	1.198	1.194	1.287
				0.900	1.084	1.085	1.103
0.050	0.279	0.276	0.282	1.000	0.943	0.948	0.977
0.060	0.186	0.184	0.195	1.100	0.798	0.806	0.841
0.070	0.080	0.079	0.093	1.200	0.662	0.672	0.710
0.080	−0.031	−0.031	−0.014	1.300	0.542	0.553	0.578
0.090	−0.141	−0.140	−0.120	1.400	0.438	0.450	0.487
0.100	−0.245	−0.242	−0.221				
				1.600	0.279	0.290	0.321
0.120	−0.424	−0.419	−0.399	1.800	0.173	0.183	0.207
0.140	−0.554	−0.548	−0.532	2.000	0.106	0.112	0.131
0.160	−0.634	−0.626	−0.617	2.200	0.063	0.067	0.082
0.180	−0.664	−0.656	−0.657	2.400	0.036	0.036	0.052
0.200	−0.652	−0.644	−0.655	2.600	0.018	0.015	0.032
0.220	−0.603	−0.595	−0.618	2.800	0.000	0.008	0.019
0.240	−0.525	−0.518	−0.553	3.000	0.000	0.000	0.012
0.260	−0.425	−0.420	−0.466	3.200			0.007
0.280	−0.310	−0.306	−0.362	3.400			0.005
0.300	−0.186	−0.183	−0.247	3.600			0.003

TABLE V. The *3p* radial wave functions as determined by the Slater approximation and by the Hartree method (labeled MG).

r	$P_{3p}\alpha$	$P_{3p}\beta$	P_{3p}MG	r	$P_{3p}\alpha$	$P_{3p}\beta$	P_{3p}MG
0.000	0.000	0.000	0.000	0.400	−0.556	−0.548	−0.462
0.005	0.005	0.005	0.004	0.450	−0.765	−0.754	−0.671
0.010	0.018	0.017	0.016	0.500	−0.928	−0.915	−0.840
0.015	0.037	0.037	0.035	0.550	−1.046	−1.032	−0.967
0.020	0.062	0.061	0.058	0.600	−1.124	−1.110	−1.056
0.025	0.091	0.090	0.085				
0.030	0.123	0.121	0.115	0.700	−1.181	−1.170	−1.137
0.035	0.157	0.154	0.146	0.800	−1.146	−1.139	−1.200
0.040	0.192	0.189	0.180	0.900	−1.058	−1.057	−1.061
				1.000	−0.945	−0.949	−0.966
0.050	0.264	0.259	0.248	1.100	−0.825	−0.833	−0.859
0.060	0.334	0.328	0.315	1.200	−0.707	−0.719	−0.751
0.070	0.399	0.392	0.378	1.300	−0.599	−0.613	−0.641
0.080	0.457	0.450	0.435	1.400	−0.502	−0.518	−0.563
0.090	0.507	0.499	0.484				
0.100	0.548	0.539	0.526	1.600	−0.345	−0.361	−0.398
				1.800	−0.232	−0.246	−0.280
0.120	0.602	0.593	0.584	2.000	−0.152	−0.164	−0.194
0.140	0.620	0.610	0.608	2.200	−0.096	−0.105	−0.133
0.160	0.604	0.594	0.601	2.400	−0.056	−0.062	−0.091
0.180	0.560	0.551	0.568	2.600	−0.026	−0.028	−0.061
0.200	0.493	0.485	0.512	2.800	−0.015	−0.016	−0.041
0.220	0.408	0.401	0.439	3.000	−0.008	−0.007	−0.028
0.240	0.310	0.304	0.352	3.200	−0.002	−0.000	−0.019
0.260	0.202	0.198	0.256	3.400	−0.000		−0.012
0.280	0.089	0.088	0.154	3.600			−0.008
0.300	−0.025	−0.025	0.048	3.800			−0.005
0.350	−0.305	−0.301	−0.217	4.000			−0.004
				4.500			−0.001

NUMERICAL RESULTS

The direct results of the calculation are given in Tables I through IX. In Tables I through VII the normalized radial wave functions for each spin association are given, as well as the results of Manning and Goldberg.[6] Table VIII lists the one-electron energies for both spins as well as those found by the Hartree method. In Table IX the values of $W_4(\sigma,r)$ and $W_5(\sigma,r)$ for each spin are given. The degree of self-consistency can be seen by comparing these initial and final potentials.

The applicability of the free-electron model for the exchange charge density requires that the potential vary but little over the radius of the exchange hole. As shown by Slater,[4] this radius $r_0(\sigma,r)$ is the radius of a sphere about an electron which is at r which contains one electronic charge. Thus

$$\tfrac{4}{3}\pi[r_0(\sigma,r)]^3\rho(\sigma,r)=e,$$

where $\rho(\sigma,r)$ is the charge density of electrons of spin σ at r. The radius of the exchange hole is given in Fig. 1 as a function of r and for each spin. In Fig. 2 the net spin density $\rho(\alpha,r)-\rho(\beta,r)$ is plotted as a function of r.

The degree of self-consistency is shown in Table I. It is seen to be quite high, although better for the α-spin case than for the β-spin case. Just as was found in the Cu^+ calculation, the one-electron energies, given in Table VIII, lie rather close to those given by the Hartree calculation except for the innermost and outermost electrons. In every case the E_{nl} value associated with α spin is lower than that associated with β spin. This is of course due to the difference in exchange interactions. The wave functions as found by the present method are all pulled in toward the nucleus relative to the Manning and Goldberg Hartree solution. The effect of exchange polarization is appreciable only in the *3d* and *4s* functions.

MAGNETIC FORM FACTOR

Steinberger and Wick[7] have shown that the magnetic form factor of Fe is rather sensitive to the shape of the

TABLE VI. The *3d* radial wave functions as determined by the Slater approximation and by the Hartree method (labeled MG).

r	$P_{3d}\alpha$	$P_{3d}\beta$	P_{3d}MG	r	$P_{3d}\alpha$	$P_{3d}\beta$	P_{3d}MG
0.000	0.000	0.000	0.000	0.700	0.982	0.933	0.871
0.005	0.000	0.000	0.000	0.800	0.961	0.919	0.918
0.010	0.000	0.000	0.000	0.900	0.918	0.886	0.851
0.015	0.000	0.000	0.000	1.000	0.862	0.841	0.821
0.020	0.001	0.001	0.001	1.100	0.801	0.791	0.784
0.025	0.002	0.002	0.002	1.200	0.738	0.738	0.745
0.030	0.004	0.003	0.003	1.300	0.676	0.685	0.688
0.035	0.006	0.005	0.004	1.400	0.617	0.635	0.663
0.040	0.008	0.007	0.005				
				1.600	0.509	0.541	0.584
0.050	0.014	0.013	0.010	1.800	0.417	0.460	0.512
0.060	0.023	0.021	0.018	2.000	0.340	0.390	0.445
0.070	0.033	0.031	0.025	2.200	0.277	0.331	0.387
0.080	0.046	0.043	0.035	2.400	0.225	0.281	0.335
0.090	0.061	0.057	0.047	2.600	0.183	0.239	0.289
0.100	0.078	0.073	0.059	2.800	0.148	0.203	0.249
				3.000	0.120	0.173	0.215
0.120	0.116	0.109	0.089	3.200	0.097	0.147	0.185
0.140	0.160	0.150	0.124	3.400	0.079	0.124	0.159
0.160	0.209	0.196	0.162	3.600	0.064	0.105	0.136
0.180	0.260	0.244	0.203	3.800	0.051	0.089	0.117
0.200	0.313	0.293	0.246	4.000	0.041	0.076	0.101
0.220	0.367	0.344	0.290				
0.240	0.420	0.394	0.334	4.500	0.024	0.049	0.069
0.260	0.473	0.443	0.378	5.000	0.014	0.031	0.047
0.280	0.523	0.490	0.421	5.500	0.008	0.019	0.032
0.300	0.572	0.536	0.464	6.000	0.004	0.010	0.022
0.350	0.683	0.640	0.562				
0.400	0.775	0.727	0.647	7.000			0.010
0.450	0.849	0.797	0.717	8.000			0.009
0.500	0.905	0.851	0.773	9.000			0.004
0.550	0.944	0.889	0.814	10.000			0.002
0.600	0.969	0.914	0.843	11.000			0.001

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[7] J. Steinberger and G. C. Wick, Phys. Rev. **76**, 994 (1949).

TABLE VII. The 4*s* radial wave functions as determined by the Slater approximation and by the Hartree method (labeled MG).

r	$P_{4s}\alpha$	$P_{4s}\beta$	P_{4s}MG
0.000	0.000	0.000	0.000
0.005	0.038	0.034	0.028
0.010	0.067	0.060	0.049
0.015	0.087	0.078	0.064
0.020	0.100	0.089	0.074
0.025	0.106	0.095	0.079
0.030	0.108	0.096	0.081
0.035	0.105	0.094	0.079
0.040	0.099	0.089	0.075
0.050	0.080	0.071	0.061
0.060	0.053	0.047	0.042
0.070	0.022	0.020	0.020
0.080	−0.010	−0.009	−0.004
0.090	−0.042	−0.037	−0.027
0.100	−0.071	−0.064	−0.049
0.120	−0.122	−0.109	−0.087
0.140	−0.159	−0.142	−0.116
0.160	−0.181	−0.162	−0.134
0.180	−0.188	−0.168	−0.142
0.200	−0.182	−0.163	−0.141
0.220	−0.166	−0.149	−0.132
0.240	−0.142	−0.127	−0.116
0.260	−0.111	−0.100	−0.096
0.280	−0.076	−0.068	−0.073
0.300	−0.038	−0.034	−0.046
0.350	0.060	0.053	−0.023
0.400	0.149	0.132	0.090
0.450	0.220	0.197	0.147
0.500	0.271	0.242	0.190
0.550	0.300	0.270	0.219
0.600	0.309	0.279	0.235
0.700	0.278	0.255	0.232
0.800	0.202	0.190	0.237
0.900	0.100	0.103	0.136
1.000	−0.011	0.006	0.067
1.100	−0.122	−0.092	−0.006
1.200	−0.226	−0.184	−0.080
1.300	−0.319	−0.269	−0.147
1.400	−0.401	−0.345	−0.216
1.600	−0.528	−0.466	−0.330
1.800	−0.610	−0.551	−0.420
2.000	−0.655	−0.603	−0.487
2.200	−0.672	−0.630	−0.534
2.400	−0.666	−0.637	−0.563
2.600	−0.645	−0.628	−0.577
2.800	−0.614	−0.612	−0.580
3.000	−0.576	−0.587	−0.575
3.200	−0.535	−0.556	−0.562
3.400	−0.491	−0.522	−0.543
3.600	−0.448	−0.486	−0.521
3.800	−0.406	−0.449	−0.497
4.000	−0.365	−0.412	−0.470
4.500	−0.275	−0.325	−0.401
5.000	−0.202	−0.249	−0.335
5.500	−0.146	−0.187	−0.274
6.000	−0.103	−0.137	−0.221
7.000	−0.046	−0.065	−0.140
8.000	−0.012	−0.017	−0.131
9.000			−0.083
10.000			−0.052
11.000			−0.032
12.000			−0.019
13.000			−0.012
14.000			−0.007
15.000			−0.004
16.000			−0.003
17.000			−0.002

TABLE VIII. The one-electron energy parameters as determined by the Slater approximation and by the Hartree method. Values are in rydbergs.

Function	Hartree (MG)	Present calculation	Slater[a]
1*s*	−523.0	−584.5 α −584.2 β	−524.3
2*s*	− 60.79	− 61.08 α − 60.40 β	− 63.0
2*p*	− 53.02	− 53.16 α − 52.65 β	− 52.8
3*s*	− 6.973	− 7.463 α − 6.930 β	− 7.3
3*p*	− 4.600	− 5.061 α − 4.540 β	− 4.4
3*d*	− 0.7578	− 1.1223α − 0.6636β	− 0.64
4*s*	− 0.4836	− 0.5315α − 0.4275β	− 0.53

[a] J. C. Slater, Phys. Rev. 98, 1039 (1955).

d-functions. Since exchange interactions strongly affect the *d*-electron charge density, it is of interest to compare the magnetic form factor as calculated from the 3*d* atomic orbitals found in the present work with experiment. This has been done by Weiss[8] using the α-spin 3*d* orbital and his results are shown in Fig. 3. The very good agreement with experiment reveals a fault in the free-atom functions reported here. The *d*-electron charge density of interest for calculating the magnetic form factor should be more compact in the solid than in the isolated atom. The unpaired *d*-electrons are near the top of the band and the corresponding cellular wave function vanishes at the cell boundary. Forcing the wave function to zero there and maintaining normalization to unity within the cell leads to a more contracted charge density than for the atomic function

TABLE IX. The initial and final potential functions for the last cycle of the self-consistent-field procedure. These include the averaged exchange potential functions.

r	$W_4(\alpha,r)$	$W_5(\alpha,r)$	$W_4(\beta,r)$	$W_5(\beta,r)$
0.000	52.000	52.000	52.000	52.000
0.010	50.189	50.121	50.190	50.121
0.020	48.444	48.439	48.443	48.439
0.030	46.782	46.826	46.775	46.826
0.040	45.217	45.268	45.202	45.268
0.050	43.747	43.749	43.725	43.749
0.060	42.362	42.284	42.334	42.284
0.070	41.057	40.960	41.024	40.959
0.080	39.827	39.749	39.792	39.749
0.090	38.678	38.603	38.634	38.602
0.100	37.595	37.520	37.546	37.518
0.120	35.605	35.539	35.546	35.536
0.140	33.804	33.743	33.732	33.737
0.160	32.151	32.093	32.074	32.085
0.180	30.630	30.574	30.545	30.561
0.200	29.225	29.163	29.133	29.143
0.220	27.922	27.865	27.822	27.838
0.240	26.708	26.652	26.600	26.613
0.260	25.577	25.521	25.458	25.468
0.280	24.516	24.460	24.382	24.394
0.300	23.518	23.466	23.368	23.379
0.350	21.272	21.225	21.064	21.049
0.400	19.345	19.308	19.068	19.037
0.450	17.688	17.659	17.353	17.309
0.500	16.243	16.213	15.870	15.815
0.550	14.958	14.922	14.563	14.496
0.600	13.800	13.753	13.391	13.313
0.700	11.804	11.741	11.378	11.282
0.800	10.176	10.103	9.742	9.629
0.900	8.856	8.785	8.418	8.299
1.000	7.783	7.709	7.346	7.212
1.100	6.907	6.832	6.469	6.323
1.200	6.183	6.111	5.746	5.592
1.300	5.581	5.513	5.148	4.988
1.400	5.071	5.004	4.648	4.480
1.600	4.270	4.211	3.882	3.719
1.800	3.689	3.636	3.352	3.197
2.000	3.256	3.199	2.979	2.838
2.200	2.92	2.86	2.70	2.58
2.400	2.66	2.59	2.49	2.39
2.600	2.44	2.37	2.30	2.23
2.800	2.25	2.18	2.16	2.10
3.000	2.09	2.02	2.02	1.98
3.200	1.94	1.87	1.90	1.87
3.400	1.81	1.74	1.78	1.77
3.600	1.69	1.61	1.67	1.68
3.800	1.58	1.50	1.57	1.59
4.000	1.47	1.39	1.48	1.50
4.500	1.24	1.17	1.26	1.29
5.000	1.04	0.961	1.07	1.12
5.500	0.864	0.785	0.908	0.934
6.000	0.713	0.649	0.758	0.776

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[8] R. J. Weiss (private communication).

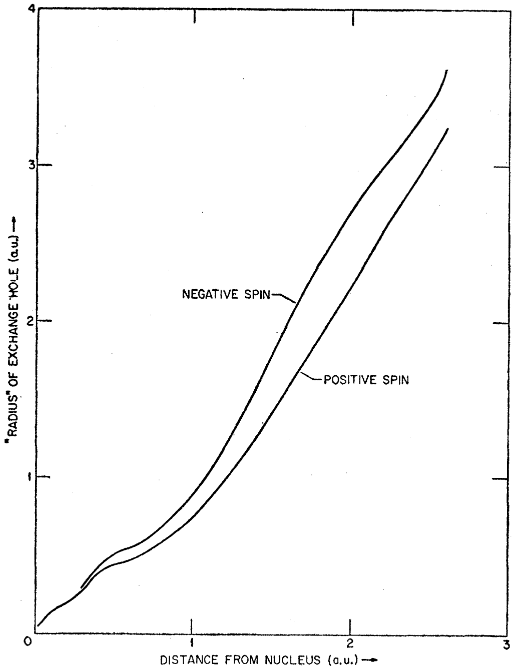

FIG. 1. Radii of the exchange holes (in atomic units) as computed from the respective charge densities.

which has a tail extending beyond the cell. This is shown in Fig. 1 of Steinberger and Wick's paper. The good agreement in form factors obtained here implies that the free-atom d-functions are more compact than is the actual case. This conclusion is in accord with the observation by Callaway[9] that the free-electron treatment overestimates the exchange interaction by perhaps 20% which would tend to contract unduly the atomic d orbitals.[10]

FINE STRUCTURE SPLITTING

The fine-structure splitting is another property of the atom which is very sensitive to the nature of the one-electron functions and can serve, therefore, as a good test of the orbitals reported here. In Russell-Saunders coupling the energy interval between different J levels of a given LS term, for example, between the $^5D_4$ and $^5D_3$ states of Fe, is proportional to the higher J value. Condon and Shortley[11] express this energy difference as

$$\Delta E = J\zeta(\gamma SL), \tag{7}$$

where $\zeta(\gamma SL)$ is the diagonal matrix component of the spin-orbit interaction operator. Expressed in Gaussian units, that operator has the form

$$\sum_i \xi(r_i)\mathbf{L}_i\cdot\mathbf{S}_i, \quad \xi(r_i)=\frac{e^4}{2\hbar^2 e^2}\left(\frac{1}{r}\frac{\partial U}{\partial r}\right), \tag{8}$$

where U is the appropriate central-field potential. The experimental value of $\zeta(\gamma SL)$ for Fe is given by Moore[12] as -104 cm^{-1} for the $^5D_4$, $^5D_3$ separation and it is found to decrease slowly as the J value decreases.

Evaluation of (7) using the results of Manning and Goldberg's Hartree calculation leads to a value of -96.6 cm^{-1}. In the single-determinant approximation used in this work, $\zeta(\gamma SL)$ is given by

$$\zeta(\gamma SL) = -\frac{\hbar^2}{4}\int_0^\infty P_{3d\beta}{}^2(r)\xi(r)dr, \tag{9}$$

where the central-field potential employed for $\xi(r)$ was $W_5(\beta,r)$. The result is $\zeta(\gamma SL)$ equals -132 cm^{-1} which does not compare favorably with the Hartree value. This indicates that the self-consistent treatment reported here tends to contract excessively the electronic charge density about the nucleus as it was concluded from the magnetic form-factor results.

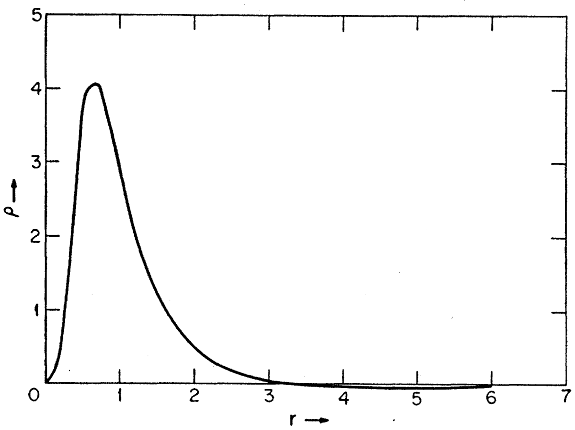

FIG. 2. Net radial "spin density" as computed from $\rho(\alpha,r)-\rho(\beta,r)$, plotted as a function of r (atomic units).

HYPERFINE STRUCTURE

Abragam and Pryce[13] have suggested that the hyperfine structure in transition elements is essentially a property of the free ion and is not due primarily to perturbation by the crystalline field, which leads to a much too small effect. In their treatment, the hyperfine splitting arises from a term W_N of the Hamiltonian representing the interaction of the electrons with the nuclear spin. W_N consists of a magnetic interaction of the electrons with the magnetic moment of the nucleus and an electrostatic interaction with the electric quadrupole moment of the nucleus.

The so-called "contact term" W_C of the Hamiltonian is that portion of W_N describing the delta-function interaction at the nucleus:

$$W_C = (16/3)\pi\gamma\beta\beta_N \sum_k \delta(\mathbf{r}_k)\mathbf{S}_k\cdot\mathbf{I}.$$

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[9] J. Callaway, Phys. Rev. **99**, 500 (1955).

[10] See also Herman, Callaway, and Acton, Phys. Rev. **95**, 371 (1954).

[11] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1953), p. 194.

[12] Charlotte E. Moore, *Atomic Energy Levels*, National Bureau of Standards, Washington, D. C., 1952 (unpublished).

[13] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

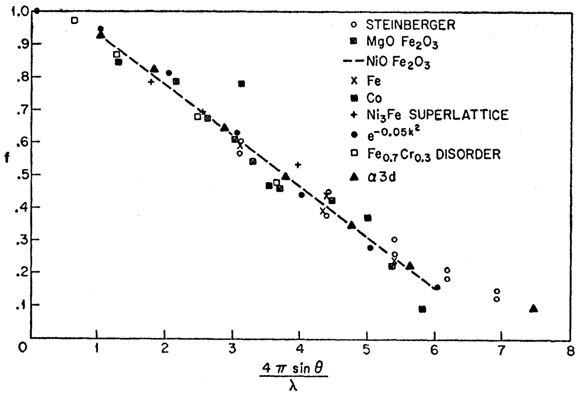

FIG. 3. Magnetic form factors furnished by R. J. Weiss. "Steinberger" refers to the calculations of reference 7. The form factor calculated by Weiss from the function of this calculation is that labeled "$\alpha 3d$." The Gaussian fit to the experimental data is $\exp(-0.05k^2)$.

The effect of this term on the hyperfine structure can be determined from the experimental data. In particular, Abragam, Horowitz, and Pryce[3] define for an ion of spin S a quantity χ, where

$$\chi=\frac{4\pi}{S}\langle\textstyle\sum_k\delta(\mathbf{r}_k)\mathbf{S}_{kZ}\rangle_{S_z=S},$$

characteristic of the unbalanced "spin density" at the nucleus. The quantity χ is nearly the same for the ions V^{++}, Mn^{++}, Co^{++}, and Cu^{++} with a value of -3 atomic units.

Iron itself shows no hyperfine structure since the predominant isotope has no nuclear spin. However, we might expect that the wave functions for Mn^{++}, which does exhibit a hyperfine structure, would not be too unlike those for iron.

Mn^{++} has the ground state configuration $3s^2\,3p^6\,3d^5$ $({}^6S)$. We now construct a determinantal wave function for this state from the one-electron functions of this calculation and evaluate χ over this determinant. Again, because of the parametric spin dependence of these one-electron functions, this determinant is not a precise eigenfunction of S^2. However, it is just this parametric dependence which gives a nonzero χ for this simple model. In evaluating the operator χ over this function, we obtain the sum of the differences of the squares of the respective s functions at the origin (nucleus). We obtain nonzero contributions from $1s$, $2s$, and $3s$; the contributions from $1s$ and $2s$ are quite comparable in magnitude (and opposite in sign) to that arising from $3s$. The result is $\chi=-2.4$ atomic units.

Abragam, Horowitz, and Pryce[3] in their calculation of χ for such a system use the equivalence restriction in the single ground state determinant but construct a more elaborate total wave function consisting of the ground state determinant plus a function in which one of the $3s$ electrons is promoted to a higher lying, variationally determined, s-state. They obtain $\chi=-0.3$ atomic units.

CONCLUSIONS

The results of this calculation show that exchange polarization is a large effect for Fe. It is of particular importance in determining the wave functions and energies of the $3d$ and $4s$ electrons. The calculation of the hyperfine splitting for Mn^{++} indicates, however, that significant differences can arise between inner orbitals associated with different spins. Furthermore, the finding that the inner s-electrons are perturbed by their unequal exchange interaction with the outer electrons of the atom and hence make a net contribution to the magnetic field at the nucleus provides a better physical picture of the s-electron effect. The results of both the fine-structure and magnetic form-factor calculations indicate that Slater's averaged exchange potential somewhat overestimates the influence of exchange.

Exchange splitting of the $3d$ and $4s$ atomic levels will of course carry over to the solid, giving rise to a splitting of the d-band and of the conduction band. A consequence of having two conduction bands, one for each spin, with different energy dependences, is that there will in general be a different occupation of the two bands. This will result in a net magnetization of the conduction electrons which has been estimated by various methods to be from 0.07 μ_0 per atom to 0.20 μ_0 per atom.[9,14] In order to calculate the total magnetic moment per atom, the exchange splitting of the d-band as well as that of the conduction band must be taken into account.

ACKNOWLEDGMENT

The writers would like to express their appreciation for the interest and support of Professor J. C. Slater.

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[14] G. W. Pratt, Jr., Phys. Rev. (to be published).