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Analytic-Expansion Unrestricted Hartree-Fock Wave Function for the ^5D State of Fe*

P. S. Bagus and B. Liu
Argonne National Laboratory, Argonne, Illinois

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An accurate analytic-expansion unrestricted Hartree-Fock wave function is reported for the ^5D state of Fe. The computed values of the magnetic dipole hyperfine-interaction constants are compared with the experimental values obtained by Childs and Goodman and are in good agreement.

I. INTRODUCTION

In the restricted Hartree-Fock (RHF) method,[1] all the orbitals of a given shell are required to have the same radial dependence; thus closed shells cannot make a contribution to magnetic hyperfine interactions or neutron form factors. Several calculations have been made using an unrestricted Hartree-Fock (UHF) method for open-shell systems, which allows different radial functions for the orbitals of a given shell with different spins[2]; i.e., $R_{nl\alpha}\neq R_{nl\beta}$. In general, these UHF calculations have given results for hyperfine interactions which are in qualitative and often in fair quantitive agreement with experiment.

In order to compare the predictions of the UHF model of core polarization with the hyperfine interaction constants for the ^5D state of Fe experimentally determined by Childs and Goodman,[3] we have computed an accurate UHF wave function for this state of Fe. The UHF Fermi contact interactionc onstant is also compared to the value obtained from an earlier, less accurate, UHF calculation of Watson and Freeman[4] and is found to be in better agreement with experiment. Wood and Pratt[5] have also performed an UHF calculation for Fe; however, they used Slater's $\rho^{1/3}$ approximation[6] for the exchange potential in the Fock operator.

In our calculation of the UHF orbitals, we have used the analytic expansion method. With this method, the UHF orbitals, $\varphi_{nlm_lm_s}$, are given as a linear combination of basis functions, χ_{p,lm_lm_s}, by

$$\varphi_{nlm_lm_s}(\mathbf{x})=\sum_p C_{nlm_s,p}\chi_{p,lm_lm_s}(\mathbf{x})\,, \tag{1}$$

where nlm_lm_s are the usual one-electron quantum numbers and $\mathbf{x}$ includes space and spin co-ordinates. The basis functions are given by

$$\chi_{p,lm_lm_s}=R_{lp}(r)Y_{lm}(\theta,\phi)\eta_{m_s}\,. \tag{2}$$

The $Y_{lm}(\theta,\phi)$ are the usual normalized spherical harmonics; the radial functions R_{lp} are normalized nodeless Slater-type orbitals (STO's), namely,

$$R_{lp}(r)=[(2n_{lp})!]^{-1/2}(2\zeta_{lp})^{n_{lp}+1/2}r^{n_{lp}-1}e^{-\zeta_{lp}r}; \tag{3}$$

and the spin function η_{m_s} is

$$\begin{aligned}\eta_{m_s=+1/2}&=\alpha\,,\\ \eta_{m_s=-1/2}&=\beta\,.\end{aligned} \tag{4}$$

The integer n_{lp} is called the principal quantum number of the basis function and ζ_{lp} the orbital exponent. (In the RHF method the additional requirement that $C_{nlm_s=+1/2,p}\equiv C_{nlm_s=-1/2,p}$ is imposed.)

Our UHF procedure is a direct extension of Roothaan's RHF analytic expansion method for open-shell systems.[7,8] The matrix equations for the orbitals, obtained from arbitrary variation of the C's in Eq. (1), are solved without further approximation. This procedure can be applied to any open-shell system, provided that there is no more than one open subshell for each group $l\alpha$ or $l\beta$. Details of the method and computer program will be given in another paper.

II. RESULTS

A. The UHF Wave Function

The UHF calculation of Fe was performed for the configuration

$$1s\alpha)^1 1s\beta)^1 2s\alpha)^1 2s\beta)^1 2p\alpha)^3 2p\beta)^3 3s\alpha)^1 3s\beta)^1 3p\alpha)^3 3p\beta)^3 \\ 3d\alpha)^5 3d\beta)^1 4s\alpha)^1 4s\beta)^1;$$

the wave function is a single Slater determinant. It is an eigenfunction of L^2, L_Z, and S_Z; $L=3$ and $M_S=2$. The value of M_L is determined by the choice of m_l for the $3d\beta$ orbital, $M_L=m_l$; the UHF equations for the radial parts of the orbtials are independent of the choice of m_l. The wave function is not an eigenfunction of S^2 but it is very nearly one with $S\cong 2$. The value of $\langle S^2\rangle$ will be given later in this paper.

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* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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

[2] See, for example, N. Bessis *et al.*, Phys. Rev. **135**, A588 (1964); R. E. Watson and A. J. Freeman, *ibid.* **123**, 2027 (1961); D. A. Goodings, *ibid.* **123**, 1706 (1961). For a review of the UHF method and extensive references, see A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press, Inc., New York, 1965), Vol. IIA.

[3] W. J. Childs and L. S. Goodman, preceding paper, Phys. Rev. **148**, 74 (1966).

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

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

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

[7] C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).

[8] C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics* (Academic Press Inc., New York, 1963), Vol. II.

TABLE I. Basis functions and expansion coefficients for the UHF orbitals of Fe.

	Exponent		$1s\alpha$	$1s\beta$	$2s\alpha$	$2s\beta$	$3s\alpha$	$3s\beta$	$4s\alpha$	$4s\beta$
$\chi_1(1s)$	38.73300	C_1	0.02056	0.02057	0.00644	0.00629	−0.00290	−0.00274	0.00035	0.00046
$\chi_2(1s)$	25.87820	C_2	0.95050	0.95050	−0.31094	−0.31144	0.11682	0.11535	−0.02619	−0.02287
$\chi_3(2s)$	21.33300	C_3	0.04069	0.04071	−0.18016	−0.18129	0.07296	0.07273	−0.01796	−0.01496
$\chi_4(2s)$	11.01230	C_4	−0.00497	−0.00501	1.03806	1.04258	−0.42236	−0.41937	0.10017	0.08516
$\chi_5(3s)$	9.50024	C_5	0.00654	0.00653	0.14489	0.14567	−0.30850	−0.30949	0.07131	0.06729
$\chi_6(3s)$	6.99020	C_6	−0.00554	−0.00554	0.00437	−0.00182	0.36701	0.38109	−0.07413	−0.07917
$\chi_7(3s)$	4.63797	C_7	0.00277	0.00277	0.00415	0.00475	0.77597	0.75070	−0.24983	−0.19232
$\chi_8(4s)$	3.92345	C_8	−0.00101	−0.00101	−0.00023	−0.00079	0.16592	0.18267	0.01636	−0.00899
$\chi_9(4s)$	1.95370	C_9	0.00022	0.00022	0.00006	0.00015	0.00769	0.00796	0.52266	0.42196
$\chi_{10}(4s)$	1.15237	C_{10}	−0.00015	−0.00015	−0.00002	−0.00009	−0.00393	−0.00415	0.53953	0.57858
$\chi_{11}(4s)$	0.80019	C_{11}	0.00007	0.00007	0.00001	0.00004	0.00166	0.00175	0.03758	0.11002

	Exponent		$2p\alpha$	$2p\beta$	$3p\alpha$	$3p\beta$		Exponent		$3d\alpha$	$3d\beta$
$\chi_1(2p)$	17.02370	C_1	0.14292	0.14313	−0.04165	−0.04019	$\chi_1(3d)$	11.50000	C_1	0.03066	0.02931
$\chi_2(2p)$	10.09200	C_2	0.85741	0.86163	−0.35146	−0.34681	$\chi_2(3d)$	4.09542	C_2	0.26060	0.23644
$\chi_3(3p)$	6.47648	C_3	0.03107	0.02122	−0.12939	−0.10041	$\chi_3(3d)$	6.00405	C_3	0.27315	0.26013
$\chi_4(3p)$	5.46805	C_4	0.00174	0.00589	0.69843	0.65699	$\chi_4(3d)$	2.61691	C_4	0.46291	0.42528
$\chi_5(3p)$	3.45397	C_5	−0.00439	−0.00639	0.48392	0.48070	$\chi_5(3d)$	1.44880	C_5	0.13241	0.23606
$\chi_6(3p)$	2.55178	C_6	0.00238	0.00270	0.06146	0.08245					

The UHF wave function was computed using the basis set obtained by Clementi[9] for his analytic expansion RHF calculation on the ^5D state of Fe. Clementi optimized the values of the exponents of the STO's used in order to minimize the total RHF energy. Automatic exponent optimization procedures which make it possible to obtain very good values of the exponents are provided by the RHF computer program that Clementi used.[8] The exponent variation was careful enough and the basis set sufficiently large, 11 s-type, 6 p-type, and 5 d-type STO's, to permit a fairly good representation of the exact RHF orbitals.[10] We believe that this basis set, which very nearly spans the manifold of RHF orbitals, should also nearly span the UHF manifold. Almost all of the differences between the RHF and UHF orbitals can be obtained by allowing the $C_{nlm_s,p}$ to be different.

In Table I we give the symmetry type, principal quantum number, and orbital exponent of the STO's used and the UHF coefficients, $C_{nlm_s,p}$, obtained. The principal quantum number and symmetry type of the STO are given in parentheses after the symbol χ.

The orbitals are orthonormal. Since the basis functions used are normalized but not orthogonal, the condition of orthonormality for the $C_{nlm_s,p}$ becomes

$$\mathbf{c}_{nlm_s}{}^{\dagger}\mathbf{S}_l\mathbf{c}_{n'lm_s}=\delta_{nn'}\,, \tag{5}$$

where $\mathbf{c}_{nlm_s}$ is a vector formed from the coefficients $C_{nlm_s,p}$ and $\mathbf{S}_l$ is the overlap matrix of the STO's for symmetry l,

$$S_{lpq}=\int R_{lp}(r)R_{lq}(r)r^2dr\,. \tag{6}$$

In Table II we give several properties of the UHF wave function and compare them with values obtained from Clementi's RHF wave function.[9,11] We include the total electronic energy E and the virial coefficient V/T, the ratio of the potential to the kinetic energy. The nearness of V/T to the value -2 is a measure of how well the exponents of the STO's have been optimized.[10] The deviation of V/T from -2 is small and about the same for the RHF and UHF functions. This supports our belief that the choice of a large, carefully optimized RHF basis set is satisfactory for a UHF calculation. The value of $\langle S^2\rangle$ is given to indicate the deviation of the UHF function from an eigenfunction of S^2; the RHF function is an eigenfunction of S^2, $(S)(S+1)=6$. For each orbital we give the orbital energy ϵ and the expectation values of r and r^2; for s orbitals we give the absolute value of the orbital at the origin $|\varphi(0)|$, and for d orbitals we give the expectation value of $1/r^3$.

All units used in Table II are atomic units. The unit of energy is the Hartree, 1 Hartree = 27.211 eV; the unit of length, the Bohr (a_0), 1 Bohr = 0.52917×10^{-8} cm; and the unit of angular momentum $\hbar$.

B. The Hyperfine Interaction Constants

The Fermi contact interaction is given by

$$H_c=(8\pi/3)g_e\mu_e g_I\mu_N \textstyle\sum_i \delta(\mathbf{r}_i)\mathbf{s}_i\cdot\mathbf{I}\,, \tag{7}$$

where $g_e=2$ and g_I are the electronic and nuclear g factors, respectively; μ_e and μ_N are the electronic and nuclear magnetons (note that $\mu_e=|e|\hbar/2mc$), $\mathbf{I}$ is the nuclear spin, and $\mathbf{s}_i$ the spin of the ith electron. If LS coupling is assumed and if matrix elements are taken

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[9] E. Clementi, IBM J. Res. Develop. Suppl. 9 (1965).

[10] A detailed discussion of the accuracy to which analytic expansion orbitals may represent the exact HF orbitals and techniques of determining this accuracy are given in P. S. Bagus, Argonne National Laboratory Technical Report No. ANL-6959 (unpublished).

[11] In order to obtain properties of the RHF wave function not given in Ref. 9, we have recomputed the function with our computer programs using Clementi's basis set. Properties given in Table II but not available from Ref. 9 were obtained from our recalculation.

only between the degenerate states of the electrostatic Hamiltonian (different values of M_L and M_S for a given term), then the contact contribution to the hyperfine splitting may be written as[12,13]

$$E_c = c'\mathbf{I}\cdot\mathbf{S} = c'(g_J - 1)\mathbf{I}\cdot\mathbf{J} = c\mathbf{I}\cdot\mathbf{J}, \tag{8}$$

where

$$g_J = 1 + \frac{(J)(J+1)+(S)(S+1)-(L)(L+1)}{2(J)(J+1)}, \tag{9}$$

$$c' = \frac{8\pi}{3}\frac{g_e\mu_e g_I\mu_N}{S}\langle LS;\, M_L, M_S = S| \times \textstyle\sum_i \delta(\mathbf{r}_i) s_{zi} | LS;\, M_L, M_S = S\rangle. \tag{10}$$

Table II. Properties of the UHF wave function for Fe and a comparison with RHF values. (All values in atomic units; 1 Hartree = 27.211 eV, 1 Bohr = 0.52917 Å.)

	UHF		RHF[a]
E	−1262.4484		−1262.4425
V/T	−2.000009		−2.000009
$\langle S^2\rangle$	6.01808		6
	$1s\alpha$	$1s\beta$	$1s$
ϵ	−261.37445	−261.37484	−261.37311
$\lvert\varphi(0)\rvert$	73.39271	73.39303	73.39286
$\langle r\rangle$	0.05911	0.05911	0.05911
$\langle r^2\rangle$	0.004686	0.004686	0.004686
	$2s\alpha$	$2s\beta$	$2s$
ϵ	−31.99928	−31.87643	−31.93623
$\lvert\varphi(0)\rvert$	22.21865	22.27583	22.24735
$\langle r\rangle$	0.2688	0.2681	0.2685
$\langle r^2\rangle$	0.08526	0.08471	0.08498
	$3s\alpha$	$3s\beta$	$3s$
ϵ	−4.34862	−3.99403	−4.16972
$\lvert\varphi(0)\rvert$	8.28171	8.19521	8.23853
$\langle r\rangle$	0.8176	0.8209	0.8192
$\langle r^2\rangle$	0.7700	0.7767	0.7733
	$4s\alpha$	$4s\beta$	$4s$
ϵ	−0.27719	−0.24221	−0.25832
$\lvert\varphi(0)\rvert$	1.89744	1.63679	1.76340
$\langle r\rangle$	3.1258	3.3927	3.2577
$\langle r^2\rangle$	11.3694	13.4276	12.3672
	$2p\alpha$	$2p\beta$	$2p$
ϵ	−27.47531	−27.35667	−27.41431
$\langle r\rangle$	0.2367	0.2356	0.2361
$\langle r^2\rangle$	0.06875	0.06802	0.06838
	$3p\alpha$	$3p\beta$	$3p$
ϵ	−2.95830	−2.52954	−2.74242
$\langle r\rangle$	0.8617	0.8704	0.8658
$\langle r^2\rangle$	0.8735	0.8929	0.8827
	$3d\alpha$	$3d\beta$	$3d$
ϵ	−0.68803	−0.46872	−0.64710
$\langle r^{-3}\rangle$	5.0662	4.5522	4.9780
$\langle r\rangle$	1.0580	1.1596	1.0734
$\langle r^2\rangle$	1.4449	1.7908	1.4948

[a] The RHF values are obtained from Clementi's calculation on Fe; see Refs. 9 and 11.

Table III. Values of the contact hyperfine-interaction constants χ and c for the ^5D state of Fe^{57} (χ in atomic units).

	χ	c (Mc/sec)	Difference of c with experiment
Childs and Goodman Experimental results[a]		−5.1	
Present UHF Calculation	−0.768	−4.4[b]	14%
Watson and Freeman UHF Calculation [c]	−0.59	−3.4[b]	33%

[a] See Ref. 3.
[b] Obtained from χ for $g_I = +0.1806$.
[c] See Ref. 4.

If a UHF wave function is used to evaluate the matrix element in Eq. (10), we obtain

$$c' = \tfrac{2}{3} g_e\mu_e g_I\mu_N\chi, \tag{11}$$

$$\chi = (2\pi/S) \sum_{\substack{i \\ s\text{ orbitals}}} (|\varphi_{i\alpha}(0)|^2 - |\varphi_{i\beta}(0)|^2). \tag{12}$$

It should be recalled that the UHF wave function used to evaluate the matrix element in Eq. (10) is not an eigenfunction of S^2. An eigenfunction of S^2 may be obtained by projection from the UHF wave function. However, the value of χ calculated with the projected wave function is likely to be significantly different from the χ calculated directly with the UHF function; and it is not certain that the use of the projected χ is to be preferred to the use of the UHF χ.[14] Heine[15] has suggested an alternative procedure for forming an eigenfunction of S^2 which should produce only a small change in the value of χ. In this procedure, the UHF function is augmented only with determinants which are small. Because of the computational difficulties in obtaining these eigenfunctions of S^2, we only give the value of χ for the UHF function.

In Table III we give the value of χ obtained from our values of $|\varphi(0)|$, listed in Table II, together with the χ obtained by Watson and Freeman[4] from their earlier UHF calculation. Using the value[16] of $g_I = +0.1806$ for Fe^{57}, we also give in Table III the values of c obtained from our calculation and Watson and Freeman's calculation together with the value obtained from experimental data by Childs and Goodman.[3] Our value of the contact hfs constant is in good agreement with experiment and in rather better agreement than that obtained from Watson and Freeman.

The remaining contribution to the magnetic dipole hyperfine interaction is

$$H_l = g_e g_I \mu_e \mu_I \left(\sum_i \frac{\mathbf{l}_i\cdot\mathbf{I}}{r_i^3} + \frac{3(\mathbf{s}_i\cdot\mathbf{r})(\mathbf{r}_i\cdot\mathbf{I}) - (\mathbf{r}_i\cdot\mathbf{r}_i)\mathbf{s}_i\cdot\mathbf{I}}{r_i^5} \right). \tag{13}$$

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[12] R. E. Trees, Phys. Rev. **92**, 308 (1953).

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

[14] For a review of these problems see Sec. III.5 of the article by A. J. Freeman and R. E. Watson in *Magnetism*, cited in Ref. 2.

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

[16] G. W. Ludwig and H. H. Woodbury, Phys. Rev. **117**, 1286 (1960).

With the same assumptions as before about LS coupling and the matrix elements taken and using the notation and expressions given by Trees,[12] we obtain for the ^5D state of Fe

$$E_l = r_J a_l \mathbf{I}\cdot\mathbf{J} \tag{14}$$

$$a_l = g_e g_I \mu_e \mu_I \langle 3d\beta|1/r^3|3d\beta\rangle, \tag{15}$$

where r_J depends only on J, L, and S. Using the value of $\langle 3d\beta|1/r^3|3d\beta\rangle$ given in Table II, we obtain $a_l = 78.4$ Mc/sec. The value obtained from experimental data by Childs and Goodman[3] is $a_l = 74.8$ Mc/sec; the error of the UHF value is 5%.

Because the UHF wave function is not an eigenfunction of S^2, equivalent expressions for E_l will give different results when evaluated with an UHF function.[17] The results will involve different combinations of $\langle 3d\alpha|1/r^3|3d\alpha\rangle$ and $\langle 3d\beta|1/r^3|3d\beta\rangle$ in the expression for E_l. However, since these integrals have nearly the same value (see Table II), the numerical results for E_l will be nearly the same, and we will not pursue the matter further.

III. CONCLUSION

Good agreement between the magnetic dipole hyperfine-interaction constants obtained from an UHF calculation and from experimental data[4] has been found. In particular, the agreement for the Fermi contact interaction constant (14%) supports the model of exchange core-polarization used in the UHF method.

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The authors would like to thank Dr. Leonard Goodman and Dr. Brian Wybourne for informative and helpful discussions. In particular, they would like to thank Dr. Goodman for having suggested this calculation.

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[17] D. A. Goodings, Phys. Rev. 123, 1706 (1961).

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Excited-State Mixing in the Optical Pumping of Alkali-Metal Vapors

FRANK A. FRANZ*
Physics Institute, Swiss Federal Institute of Technology, Zurich, Switzerland

AND

JUDY R. FRANZ
IBM Zurich Research Laboratory, 8803 Rüschlikon-ZH, Switzerland

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The effect of excited-state mixing on the optical pumping of alkali-metal vapors is considered for the case where the energy separation between the $^2P_{1/2}$ and $^2P_{3/2}$ first excited states is relatively large, allowing the isolation of mixing effects within a particular J level. Two models for the mixing process are proposed, one a random reorientation of the total electronic angular momentum $\mathbf{J}$, and the other a reorientation of $\mathbf{J}$ subject to the selection rule $\Delta m_J = 0, \pm 2$. The probabilities for mixing transitions among J-state sublevels have been calculated for an alkali atom of nuclear spin $\frac{3}{2}$, and can be used to calculate the optical-pumping transition probabilities for a vapor subject to any degree of excited-state mixing. Several possible experiments suggested by these calculations are discussed.

I. INTRODUCTION

THE primary purpose of this paper is to analyze the role that excited-state interactions play in the optical pumping of alkali-metal vapors. In an experiment typical of those to be considered,[1] a beam of circularly polarized $D_1(^2S_{1/2} \leftrightarrow {}^2P_{1/2})$ photons is passed through a cell containing the vapor to be studied. Since the prevailing selection rules are $\Delta m_F = +1$ for absorption, and $\Delta m_F = \pm 1, 0$ for re-emission, the vapor is gradually pumped from ground-state sublevels of low to high (F,m_F), with all atoms ultimately being forced into the highest sublevel if there is no ground-state relaxation. In practice, of course, relaxation exists, being caused by collisions of the alkali atoms with buffer gas molecules, impurity atoms, or the walls of the cell. Collisional interactions can also disrupt the optical pumping process by transferring or mixing atoms among excited-state sublevels prior to de-excitation. The equilibrium population distribution in the ground state is thus determined both by the strengths and characteristics of the relaxation mechanisms involved, and by the various perturbations that the alkali atoms may suffer while in the excited state.

In order to calculate the equilibrium electronic and nuclear spin polarizations, and to describe the transient

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* National Science Foundation Postdoctoral Fellow.

[1] Comprehensive surveys of optical pumping techniques can be found in: G. V. Skrotskii and T. G. Izyumova, Usp. Fiz. Nauk 73, 423 (1961) [English transl., Soviet Phys.—Uspekhi 4, 177 (1961)]; and R. Benumof, Am. J. Phys. 33, 151 (1965).