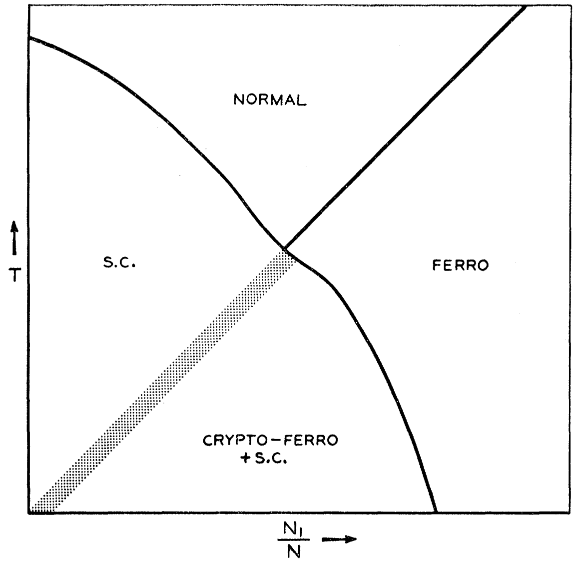

FIG. 2. Phase diagram for ferromagnetism, superconductivity, and cryptoferromagnetism.

so that

$$\sum_{\mathbf{q}\neq\mathbf{q}_d} |\mathbf{S}(\mathbf{q})|^2=(N_I/N)\left[S+S^2\left(1-\frac{N_I}{N}\right)\right]. \quad (13)$$

That is, the random magnetic scattering is reduced in proportion to N_I/N and replaced by a spin-dependent periodic potential of wavelength λ_d. This situation is shown in the second half of Fig. 1.

One can show that the energy of the superconducting cryptoferromagnetic state may possibly be lowered relative to that of the superconducting, normal state by an additional amount $(N_I/N)^{\frac{2}{3}}$ times the Herring-Suhl-Matthias[3] scattering effect, so that the superconducting transition in the aligned state may actually be slightly higher than in the paramagnetic state. Figure 2 shows schematically the type of phase diagram which might be expected to result from the above considerations.

A final remark is that these considerations do not depend seriously on the special features of the B.C.S. theory, but only upon a reduction, for superconductors, in the long-wavelength paramagnetic susceptibility (not necessarily to zero). In particular, we can conclude that a long-range purely ferromagnetic alignment in a superconductor cannot occur unless (a) the paramagnetic susceptibility of the superconductor is not reduced, contradicting the experimental and theoretical results; or (b) the exchange interaction of conduction electrons and ionic spins is inexplicably small; otherwise the ferromagnetic normal state is necessarily far lower in energy than the superconductor. Unfortunately, present experiments indicate such alignment in some cases.[8]

ACKNOWLEDGMENTS

We would like to thank T. H. Geballe, B. T. Matthias, and N. Phillips for calling our attention to their unpublished work.

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[8] B. T. Matthias (private communication) shows that homogeneous superconducting samples exhibit a ferromagnetic moment, but it is not clear to what extent the observed remanence is affected by trapped flux.

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Initial Estimates for Self-Consistent Field Calculations for Atoms with Large Atomic Number

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Absolute rather than interpolation methods are described for obtaining initial estimates for self-consistent field calculations with exchange. Tables have been computed so that the procedure is entirely numerical which makes it more convenient than Hartree's graphic interpolation scheme.

INTRODUCTION

SELF-CONSISTENT field calculations with exchange require initial estimates of the following three quantities: (i) the radial wave functions, $P(nl;r)$, (ii) $a_0=P(nl;r)/r^{l+1}$, for $r\rightarrow 0$, and (iii) the energy parameter $\epsilon_{nl,\,nl}$. In this paper methods will be described for estimating these quantities when the atomic number N is large; they all depend on knowing the limiting behavior of the estimate as $N\rightarrow\infty$.

Previous papers[1,2] showed that if we represent the wave functions by a series in $1/N$ so that

$$N^{-\frac{1}{2}}P(nl;r)=P_H(nl;\rho)+[Q(nl;\rho)/N] +[R(nl;\rho)/N^2]+\cdots,\quad \rho=Nr, \quad (1)$$

and if we assume that

$$\epsilon_{nl,\,nl}=(1/n^2)+(\epsilon_1/N)+(\epsilon_2/N^2)+\cdots, \quad (2)$$

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[1] C. Froese, Proc. Roy. Soc. (London) **A239**, 311 (1957).
[2] C. Froese, Proc. Roy. Soc. (London) **A244**, 390 (1958).

then the functions $Q(nl;\rho)$ and $R(nl;\rho)$ are the solutions of second order differential equations. These have been solved for a large number of configurations and the results together with the values of ϵ_1 and ϵ_2 should, therefore, assist us in obtaining initial estimates for self-consistent field calculations.

In (1) the term of order $1/N^2$ is significant. Hartree[3] found that the variation with respect to $\bar{r}$ of a reduced wave function,

$$P^*(nl;s)=\bar{r}^{\frac{1}{2}}P(nl;r),\quad s=r/\bar{r},$$

for fixed s, was more nearly constant than the variation of (1) with respect to $1/N$. Therefore, if we represent $P^*(nl;s)$ by a series in $\bar{r}$, only the first two terms will be required for fairly accurate estimates of the wave function. Similarly reduced quantities a_0^* and $\epsilon_{nl,nl}^*$ are defined and the variation with respect to $\bar{r}$ compared with the variation with respect to $1/N$ of $a_0/N^{l+\frac{1}{2}}$ and ϵ/N^2. Tables have been computed so that estimates of $P(nl;r)$, a_0, and $\epsilon_{nl,nl}$ can be determined from series expansions.[4]

ESTIMATES OF THE RADIAL WAVE FUNCTION

Suppose $\bar{r}$ has been determined for the (nl) wave function of an atom with atomic number N using the method described by Hartree.[3] From the limiting behavior of (1) it can be shown that $P^*(nl;s)\rightarrow P_H^*(nl;s)$ as $N\rightarrow\infty$, and if

$$P^*(nl;s)=P_H^*(nl;s)+\bar{r}Q^*(nl;s)+O(\bar{r}^2),\tag{3}$$

then[5]

$$Q^*(nl;s)=\bar{r}_H^{-\frac{1}{2}}\{\sigma_0[\tfrac{1}{2}P_H(nl;\rho)+\rho P'(nl;\rho)]+Q(nl;\rho)\},\quad \rho=s\bar{r}_H,$$

where

$$\sigma_0=\lim_{N\rightarrow\infty}[\sigma(nl)=N-\bar{r}_{\mathrm{H}}/\bar{r}].$$

Values of σ_0 have been computed for several configurations.[1,6]

The fact that, for available results, $P^*(nl;s)$ is very nearly linear with respect to $\bar{r}$ over a relatively large range of $\bar{r}$ for fixed s, suggests that the term $O(\bar{r}^2)$ is small and a fairly accurate estimate for $P^*(nl;s)$ can be obtained from the first two terms of the series; then

$$P(nl;r)=\bar{r}^{-\frac{1}{2}}P^*(nl;s),\quad r=\bar{r}s.$$

The functions $Q^*(nl;s)$ were computed for several configurations and tabulated together with $P_H^*(nl;s)$.[4]

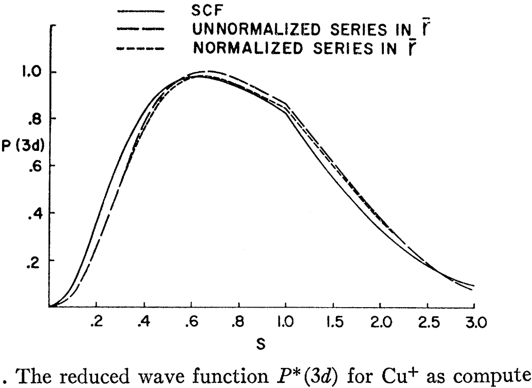

FIG. 1. The reduced wave function $P^*(3d)$ for Cu$^+$ as computed from self-consistent field results and from a series in $\bar{r}$.

The accuracy of the method was tested by comparing the reduced wave function as calculated from the first two terms of (3) with the known results for Cu$^+$.[7] Figure 1 shows the difference between the two functions for the $(3d)$ wave function. Part of the discrepancy is due to the fact that the reduced wave function is now no longer normalized since

$$\int_0^\infty P^*(s)^2ds=\int_0^\infty [P_{\mathrm{H}}^*(s)+\bar{r}Q^*(s)]^2ds$$

$$=1+\bar{r}^2\int_0^\infty [Q^*(s)]^2ds.$$

The normalized series approximates more closely to the known result in the region where $P^*(s)$ is large.

The method described here will not be as accurate as the interpolation procedure suggested by Hartree but it has several advantages. First of all, it is entirely numerical; no plots of $P^*(nl;s)$ as a function of $\bar{r}$ are required for each s, and no graphic interpolation is necessary. As a result, estimates can be obtained readily on an automatic computer. Secondly, the method is independent of available self-consistent field results, except for the determination of $\bar{r}$. This is an advantage because an interpolation procedure requires at least one set of results besides the limiting value as $N\rightarrow\infty$, whereas the series approximation merely requires the functions $P_H^*(s)$ and $Q^*(s)$ which are independent of N. When self-consistent field results with exchange are available[5] (usually for the larger values of $\bar{r}$), estimates of the next term in the series, $R^*(s)$, can be obtained by assuming that

$$P^*(s)=P_H^*(s)+\bar{r}Q^*(s)+\bar{r}^2R^*(s)\tag{4}$$

for these results and solving for $R^*(s)$ as a function of s.

The accuracy of both Hartree's interpolation procedure and the series method is limited by the accuracy to which $\bar{r}$ can be determined. Therefore, $\bar{r}$ should be computed as accurately as possible using graphs of the screening number σ, as described by Hartree.[3]

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[3] D. R. Hartree, Proc. Cambridge Phil. Soc. **51**, 684 (1955).

[4] Copies of these tables may be obtained by writing the author. The tables have also been deposited as Document No. 6092 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[5] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley and Sons, New York, 1957), pp. 123, 129, 167.

[6] C. Froese, Proc. Roy. Soc. (London) **A251**, 534 (1959).

[7] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A157**, 490 (1936).

Table I. Comparison of the values of a_0 computed from the series in $1/N$, and from the series in $\bar{r}$, with the self-consistent field results for Cu$^+$ (in atomic units).

(nl)	$1/N$	$\bar{r}$	SCF
$(1s)$	307.4	$\cdots$	307.0
$(2s)$	94.0	93.5	94.5
$(2p)$	710.6	710.0	708.0
$(3s)$	32.73	32.2	35.25
$(3p)$	247.9	287.0	260.5
$(3d)$	300.8	225.7	244.5

ESTIMATES OF $a_0=[P(nl;r)/r^{l+1}]_{r=0}$

For hydrogen-like ions, $a_0/N^{l+\frac{3}{2}}=a_{0,H}$, where $a_{0,H}$ is the value for the hydrogen wave function, so in general, for atoms with large atomic number we may assume that it can be expanded in series in $1/N$, namely

$$a_0/N^{l+\frac{3}{2}}=a_{0,H}[1+(a_1/N)+(a_2/N^2)+\cdots]. \quad (5)$$

The functions $Q(nl;\rho)$ and $R(nl;\rho)$ of Eq. (1) will determine a_1 and a_2.

By analogy to Hartree's method, we may also define a reduced a_0^* as

$$a_0^*=\bar{r}^{l+\frac{3}{2}}a_0.$$

From the limiting behavior of a_0 and $\bar{r}$ as $N\rightarrow\infty$, it can be shown that

$$\begin{aligned}a_0^*=\bar{r}_H{}^{l+\frac{3}{2}}a_{0,H}[1&+(\bar{r}/\bar{r}_H)\{(l+\tfrac{3}{2})\sigma_0+a_1\}\\&+(\bar{r}/\bar{r}_H)^2\{(l+\tfrac{3}{2})(l+\tfrac{1}{2})\sigma_0{}^2+(2l+1)\sigma_0a_1+2a_2\\&+(2l+3)\bar{r}_H(d\sigma/d\bar{r})_0\}+\cdots], \quad (6)\end{aligned}$$

where $(d\sigma/d\bar{r})_0$ is the slope of σ as a function of $\bar{r}$ at $\bar{r}=0$; values of the slope have been tabulated for several configurations.[2,6]

Values of a_0 were computed for Cu$^+$ using the series (5) and (6); the results are compared in Table I. It will be seen that the series in $1/N$ gives the better estimates in all cases except the $(3d)$. The explanation for this is as follows: a_0 is related to the way in which a wave function attains its first maximum. If it occurs at relatively small values of r, then the effective nuclear charge in this region is more nearly that of the atomic number N than the effective nuclear charge at $\bar{r}$, and so a series in $1/N$ will converge more rapidly than one in $\bar{r}$. If however, the screening effect is significant in the region of the first maximum, as it is in the case of the outer $(3d)$ wave function, then the series in $\bar{r}$ will provide the better estimate.

Values of a_1 and a_2 for several configurations have been tabulated.[4]

ESTIMATES FOR $\epsilon_{nl,nl}$

For large atomic numbers, $\epsilon_{nl,nl}/N^2$ is given by Eq. (2) as a series in $1/N$. We may also define a reduced energy $\epsilon_{nl,nl}{}^*$ as

$$\epsilon_{nl,nl}{}^*=\bar{r}^2\epsilon_{nl,nl}.$$

From the limiting behavior of $\bar{r}$ and $\epsilon_{nl,nl}$ as $N\rightarrow\infty$, it can be shown that

$$\begin{aligned}\epsilon_{nl,nl}{}^*=\bar{r}_H{}^2\{1/n^2&+(\bar{r}/\bar{r}_H)[(2\sigma_0/n^2)+\epsilon_1]\\&+(\bar{r}/\bar{r}_H)^2[2\bar{r}_H(d\sigma/d\bar{r})_0+(\sigma_0{}^2/n^2)\\&+\sigma_0\epsilon_1+\epsilon_2]+\cdots\}. \quad (7)\end{aligned}$$

In Table II values of $\epsilon_{nl,nl}$ for Cu$^+$ as computed from Eqs. (2) and (7) are compared with self-consistent field results. The series in $1/N$ provides the better estimates if the relative screening is small; for the outer wave functions where the screening effect is large, the series in $\bar{r}$ provides the better estimates. The error is approximately 10%; more accurate estimates can be obtained if self-consistent field results are available by using them to estimate the coefficient of the $\bar{r}^3$ term.

Table II. Comparison of the values of $\epsilon_{nl,nl}$ computed from the series in $1/N$, and from the series in $\bar{r}$ with the self-consistent field results for Cu$^+$ (in atomic units).

(nl)	$1/N$	$\bar{r}$	SCF
$(1s)$	654.3	$\cdots$	658.4
$(2s)$	74.99	72.00	82.30
$(2p)$	65.81	63.17	71.83
$(3s)$	6.92	9.99	10.65
$(3p)$	4.01	6.65	7.279
$(3d)$	−2.39	1.45	1.613

Values of ϵ_1 and ϵ_2 have been tabulated for several configurations.[4]

ESTIMATES FOR THE $(1s)$ WAVE FUNCTION

The $(1s)$ wave function approximates so closely to a scaled hydrogen wave function that Hartree introduced a special interpolation scheme for this case[5]: estimates of wave functions are obtained by assuming a small ($\sim$0.3) screening factor. Actually the series expansions in $1/N$ converge so rapidly that no modification is necessary. For the wave function, the first two terms of Eq. (1) are sufficient, but for a_0 and $\epsilon_{nl,nl}$, the first three terms of Eqs. (5) and (2), respectively, are required. The functions $P_H(1s;s)$, $Q(1s;s)$, $s=\rho/\bar{r}_H$, are included in the tables instead of the functions $P_H{}^*(1s;s)$ and $Q^*(1s;s)$.

The functions $P_H{}^*(nl;s)$ and $Q^*(nl;s)$ were computed on ALWAC, the automatic computer at the University of British Columbia.