phasized, however, that the absolute sign of the hyperfine interaction was not measured for either atomic state in the present experiment.

DISCUSSION

The measured nuclear spin $I=\frac{1}{2}$ for Ge^{71}, while entirely consistent with the nuclear shell model, could not be theoretically predicted with confidence because of closely competing orbits. The simplest interpretation is that the angular momentum is due entirely to the odd neutron in the $^3p_{1/2}$ orbit. The shell-model magnetic dipole moment expected from this configuration is $+0.64$ nm, in close agreement with both the measured value of $+0.65\pm0.20$ nm and the value $\pm(0.62\pm0.06)$ nm deduced theoretically from the measured value of $a(^3P_2)$.

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Electronic Polarizabilities and Sternheimer Shielding Factors

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A new method is developed for determining the distortions (polarizabilities) induced in electronic distributions by valence electrons and/or crystalline fields and their effect (expressed as Sternheimer shielding factors) on magnetic and electric hyperfine interactions. For illustrative purposes emphasis is placed in this paper on the calculation of Sternheimer antishielding factors (γ_∞). Working within the framework of the Hartree-Fock self-consistent field formalism, it is shown that the 'angular' excitations are gotten by relaxing the usual restriction that the spatial part of the one-electron functions be separable into a radial function times an angular function; relaxing the restriction that electrons of the same shell but differing in magnetic quantum number (m_l) have the same radial function yields the 'radial' excitations. To illustrate the method, calculations are reported for several spherical ions (Cl^- and Cu^+) in an external field, but the scheme is also applicable to the problem of induced electric quadrupole (and magnetic dipole and higher multipole) distortions of an ion by its own aspherical charge distribution. The problems of orthogonality, exchange, and self-consistency, which have complicated applications of the perturbation method are easily resolved by this approach. Further, since a self-consistent field procedure is followed, the distortions induced in the inner closed shells by the distorted outer shells are included in a natural way and by comparison with the results of the perturbation-variation method (which does not take these into consideration) these additional effects are shown to be significant.

I. INTRODUCTION

ELECTRIC quadrupole and magnetic dipole interactions between atomic nuclei and outer electron distributions have been measured in atoms and molecules, and in metals and salts by a variety of methods and most recently by recoilless emission and absorption of γ rays (the Mössbauer effect). As emphasized by Sternheimer,[1] the interpretation of these experiments (such as the measurement of the nuclear quadrupole moment Q) is complicated by the contributions to the hyperfine interactions arising from the distortion of the otherwise spherical closed electronic shells of the system. One of Sternheimer's important contributions was the striking demonstration that, for an ion having a nuclear quadrupole moment, the quadrupole interaction arising from the field induced (1) by external charges (as in a salt) or (2) from the ion's own aspherical charge distribution (if the ion is not spherically symmetrical) was changed appreciably by the distortion

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[1] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950); **84**, 244 (1951); **96**, 951 (1954); **107**, 1565 (1957); **115**, 1198 (1959); **123**, 870 (1961); **127**, 812 (1962); R. M. Sternheimer and H. M. Foley, *ibid.* **92**, 1460 (1953). H. M. Foley, R. M. Sternheimer, and D. Tycko, *ibid.* **93**, 734 (1954).

of the ion's closed shells. Following Sternheimer's pioneering investigation,[1] much work has been done using the perturbation techniques which he developed; more recently Das and Bersohn have used[2] a (less precise) analytic function, instead of the more laborious numerical integration procedure in solving the perturbation theory equations.

In this paper,[3] we develop a method for calculating, within the Hartree-Fock formalism, the distortions induced in electronic distributions by valence electrons and/or crystalline fields and their effects on magnetic and electric hyperfine interactions. The method was anticipated by Nesbet[3a] in his work on the symmetry characteristics of Hartree-Fock orbitals. For illustrative purposes emphasis is placed on the calculation of Sternheimer quadrupole polarizabilities and antishielding factors (γ_∞) of Cu^+ and Cl^-. Since a self-consistent field procedure is followed the distortions induced in the inner closed shells by the distorted outer closed shells are included in a natural way and by comparison with the results of the perturbation method (which does not take these into consideration) these additional effects are shown to be significant. The problems of orthogonality, exchange, and self-consistency which have complicated applications of the perturbation method are easily resolved by this approach. Although the present results are for spherical ions in an external field our method is also applicable to the problem of induced electric quadrupole (and magnetic dipole and higher multipole) distortions of an ion by its own aspherical electronic charge distributions (e.g., $3d$ or $4f$ electrons), a problem recently highlighted by Mössbauer measurements. In contrast to the present approach, perturbation theory calculations for these are difficult to carry out.

II. PERTURBATION-VARIATION METHOD

The perturbation theory approach to the problem of the polarization of electron shells of atoms and ions has been discussed previously at length.[1,4,5] Some brief details are given here in order to provide for making comparisons.

Writing the Hamiltonian in the usual form, $H=H_0+H_1$, with H_0 the unperturbed Hamiltonian and H_1 a perturbing potential, the first-order perturbation $\psi_1(r)$ to the perturbed solution, $\psi_0(r)$, is determined from the relation

$$(H_0-E_0)\psi_1(r)=-(H_1-E_1)\psi_0(r), \qquad (1)$$

which is the second-order perturbation theory relation. Here,

$$E_0=\langle\psi_0|H_0|\psi_0\rangle, \quad E_1=\langle\psi_0|H_1|\psi_0\rangle, \quad \text{and} \quad \langle\psi_0|\psi_1\rangle=0.$$

Equation (1) has been solved in two distinct ways: (a) directly by exact numerical solution, as was done by Sternheimer and collaborators[1] and (b) by the analytic approach of Das and Bersohn[2] in which the radial part of $\psi_1(r)$ is assumed to be related to the radial part of $\psi_0(r)$ by

$$u_1'(r)=u_0'(r)\sum_m a_m r^m \qquad (2)$$

and the parameters a_m are determined by minimizing the second-order perturbation energy with respect to variation of these parameters. This technique has the advantage of being easier to carry out than Sternheimer's but is inferior because full variational freedom is not accorded to u_1' (e.g., if u_0' is a noted function then u_1' is constrained to have the same nodes). In more recent applications the problems of properly maintaining orthogonality,[6] self-consistency,[7] and including exchange,[8] have been emphasized.

Since for quadrupole interactions the perturbing potential H_1 has $Y_2^0(\theta,\varphi)$ symmetry, perturbed orbital character will be mixed into the unperturbed orbitals, ψ^0, in the following ways:

$$\begin{aligned}
&\psi_s^0 \rightarrow N_s(\psi_s^0+\psi_d'),\\
&\psi_p^0 \rightarrow N_p(\psi_p^0+\psi_p'+\psi_f'),\\
&\psi_l^0 \rightarrow N_l(\psi_l^0+\psi_l'+\psi_{l-2}'+\psi_{l+2}'); \quad l>1,
\end{aligned} \qquad (3)$$

where the N_i are normalization constants. The mixing of a ψ' of l in common with ψ^0 is called a "radial" excitation whereas the ψ' components having $l\pm2$ are called "angular" excitations.

Sternheimer first discussed the two cases already referred to: (1) H_1 arising external to the ion and (2) H_1 due to an aspherical unclosed electron shell within the ion. Case (2) and, in particular, the associated magnetic hyperfine effects will be discussed in subsequent papers; in what follows we outline our method and present results only for case (1).

For a quadrupole potential due to charges external to the central ion, the interaction with the nuclear quadrupole moment, Q, is given as e^2qQ, where q is the external charge electric-field gradient at the nucleus. Sternheimer found that the external potential distorted the electron shells of the ion and that this distortion also interacted with Q giving a total interaction of the form

$$H_Q=e^2qQ(1-\gamma_\infty). \qquad (4)$$

Here γ_∞ is the Sternheimer antishielding factor. For ions

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[2] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).

[3] A preliminary report of this work was given earlier by A. J. Freeman and R. E. Watson, Bull. Am. Phys. Soc. **6**, 166 (1961).

[3a] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

[4] For a complete review see A. Dalgarno, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis Ltd., London, 1962), Vol. 11, p. 281.

[5] See also A. J. Freeman and R. W. Watson, in *Treatise on Magnetism*, edited by G. Rado and H. Suhl [Academic Press Inc., New York (to be published)].

[6] R. Ingalls, Phys. Rev. **128**, 1155 (1962).

[7] A. Dalgarno, Proc. Roy. Soc. (London) **A251**, 282 (1959) and references listed in reference 4.

[8] The methods discussed in references 1 and 2 are essentially a Hartree perturbation theory. More recently, exchange has been introduced into the formalism by A. Dalgarno (reference 7); S. Kaneko, J. Phys. Soc. (Japan) **11**, 1600 (1959); and L. C. Allen, Phys. Rev. **118**, 167 (1960).

consisting of more than closed s shells, γ_∞ is negative and large (typically -10 to -100). The "radial" contributions to γ_∞ are generally much larger than (and of opposite sign to) the "angular" contributions.

III. HARTREE-FOCK SELF-CONSISTENT FIELD METHOD AND QUADRUPOLE POLARIZABILITIES

Spin (or exchange) polarized Hartree-Fock calculations have recently played a prominent role in understanding magnetic hyperfine interactions.[9] As has been previously discussed, such calculations involve relaxing the restriction imposed on conventional atomic Hartree-Fock solutions that electrons in the same shell but differing in spin (i.e., m_s quantum number) have the same radial wave function.

The m_s restriction is not the only one imposed on H-F solutions.[9] Two other constraints, which concern us here, are: (a) that the spatial part of the one-electron functions be separable into a radial function times and angular function (for free ions this is a single spherical harmonic) and (b) that electrons of the same shell but of differing magnetic quantum number (m_l) have the same radial wave function. Restrictions (a) and (b) are called the "symmetry" and "equivalence" restrictions, respectively, by Nesbet.[3a] These restrictions lead to the shell structure description of atoms, molecules, and solids but are only rigorously valid for closed shell atoms; their imposition gives not only a physically simple picture of electronic systems but also allows the computations to be of reasonable magnitude. By analogy with the well-known spin polarized H-F calculations one may conveniently define calculations in which restriction (b) is relaxed as "orbitally" polarized H-F calculations.

We have investigated the physical consequences of relaxing conditions (a) and (b) and have found that quadrupole polarizabilities and Sternheimer antishielding factors can be obtained by these means. Relaxing (a) results in "angular" distortions of the electron shells whereas relaxing (b) yields "radial" distortions. [Equation (3) was written so as to make this appear more self-evident.] The method is applicable to the distortions due to either the case of an external perturbing field[10] or that arising from an ions's aspherical charge distribution. For a purely ionic crystal "potential," such as the one we discuss in this paper, only electric hyperfine effects are induced[11]; the case of induced magnetic and electric hyperfine interactions due to an unclosed shell with the ion, will be discussed in a future paper.

A. Method of Computation

For simplicity, consider a closed shell ion (e.g., Cl^- and Cu^+) in the field of a single *external* point charge a distance R away. In atomic units, the quadrupole term of the potential expanded in spherical harmonics and powers of r (the distance from the nucleus having quadrupole moment, Q, to some point P), is simply

$$V_q = -Z(8/5)^{1/2}\Theta(2,0)(r^2/R^3), \qquad (5)$$

where Z is the magnitude of the point charge and $\Theta(2,0)$ is the normalized spherical harmonic defined by Condon and Shortley. In order to carry out the computations, we include V_q in our free ion Hamiltonian and rederive the Hartree-Fock equations. These equations are then solved (in principle) in a straightforward way; in practice, only the radial antishielding terms have been obtained as this can be done with existing H-F computational machinery. The less important angular distortions require a H-F treatment involving functions of mixed angular character and can be obtained if one utilizes and extends existing analytic H-F techniques.[12] Since any errors associated with crude estimates of angular antishielding tend to be dwarfed by inadequacies associated with the crystal field model used in γ_∞ investigations (to be discussed later), the effort necessary to extend the H-F computational machinery to include angular antishielding did not seem warranted here.

The computations were done with analytic H-F methods used and described previously.[13,14] A quadrupole field due to an external charge distribution was included in the Hamiltonian from which the H-F equations were derived, subject to restriction (b) being relaxed. In the solution of these equations, the ion's shells were self-consistently distorted and the quadrupole interaction of these distortions with the ion's nucleus then yielded[15] γ_∞.

Using this scheme, calculations have been done for

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[9] See, for example, reference 5 and R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1125 (1960); **123**, 2027 (1961), and references therein.

[10] For example, external electric hexadecapole antishielding [R. M. Sternheimer, Phys. Rev. **123**, 870 (1961)] has been investigated with perturbation methods. Also, for the case of external magnetic fields, the shielding arising from the second-order paramagnetic susceptibility (Van Vleck paramagnetism) may be calculated by the present scheme.

[11] A crystalline exchange potential can induce magnetic hyperfine terms by polarization. See, for example, A. J. Freeman and R. E. Watson, Suppl. J. Appl. Phys. **34**, 1032 (1963) and reference 5.

[12] For details on the analytic approach see C. A. Coulson, Proc. Cambridge Phil. Soc. **34**, 204 (1938); C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951); R. K. Nesbet, Rev. Mod. Phys. (to be published) and reference 3a.

[13] See, for example, R. E. Watson, Technical Report No. 12, Solid State and Molecular Theory Group, MIT, 1959 (unpublished).

[14] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961).

[15] Calculations where the field due to a nuclear Q was included in the Hamiltonian could not be done because this term is insignificant compared with kinetic and nuclear Z/r terms. The H-F equations were solved with normal accuracy and this was insufficient for the meaningful inclusion of such a term in the SCF calculation. This has several unfortunate implications among which is the fact that we could not test the validity of the perturbation approach of turning on q (or Q), allowing the ion to distort and investigate the interaction of the distortion with Q (or q). What information was available appeared to completely justify this approach.

Cl^- and Cu^+. The antishielding for these ions is of considerable interest; numerical and analytic perturbation results already exist so that comparisons may be readily made. In the course of the investigation, a conventional H-F calculation was also done for Cu^+ which is of greater accuracy than those appearing in the literature. The resulting one-electron functions are tabulated in Appendix I. The basis set appearing in this calculation was used in the γ_∞ calculation. A previously published conventional H-F[14] basis set was then used for Cl^-.

B. Results

The radial contributions to γ_∞ as given by orbitally polarized H-F self-consistent field (SCF) and perturbation theory calculations for Cu^+ and Cl^- are listed in Table I. The three sets of results are seen to be in very good agreement for Cu^+ but differ markedly for Cl^-. Perhaps the most significant feature of the results is the increase in $\gamma_{2p\to p}$ by a factor of 2 for Cu^+ and 8 for Cl^-. These increases arise from the distortions produced in the inner $2p$ shells by the distorted outer $3p$ (and $3d$) shells—distortions which are included in our SCF treatment but not in the perturbation theory approach. Upon reflection it may appear somewhat surprising that the inner shell enhancement is not even greater for this shell in view of the large distortions of the outer shells produced by the applied field. However, the $\gamma_{2p\to p}$'s are not enhanced by factors proportional to the $\gamma_{3p\to p}$'s because unlike the nucleus, the $2p$ shell is overlapped by the $3p$ (and $3d$) shell. As soon as the perturbing charge overlaps the perturbed shell one must replace the point charge potential V_q given by Eq. (5) by

$$V_q(r) \sim \int_0^r \rho(x)\frac{x^2}{r^3}dx + \int_r^\infty \rho(x)\frac{r^2}{x^3}dx, \tag{6}$$

where $\rho(x)$ is the radial distribution of the perturbing charge density. Such a distributed charge yields a smaller $\gamma_{2p\to p}$ than would either a V_q given by Eq. (5) or one arising from a distributed charge completely external to the $2p$ shell. In fact, a perturbation theory estimate of the Cl^- $\gamma_{2p\to p}$, utilizing Eq. (6) and a $\rho(x)$ consisting of the external charge plus the distorted $3p$ shell, crudely reproduces (to better than a factor of 2) the value appearing in Table I. In other words, a shell such as the $2p$ is far from being completely "inside" a $3p$ (or $3d$) shell, where antishielding is concerned (If it were otherwise we would have a Cl^- $\gamma_{2p\to p}$ of ~ -100.)

Table I. Comparison of "radial" contributions to γ_∞.

		Second-order perturbation theory	
Cl^-	Present results	Numerical[a]	Analytical-variational[b]
$2p$	-12.1	-1.5	~ -1
$3p$	-78.3	-56.5	-50 to -60
Cu^+			
$2p$	-1.2	-0.62	-0.6
$3p$	-7.8	-7.9	-5.8
$3d$	-8.6	-8.5	-8.6

[a] R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956).
[b] E. G. Wikner and T. P. Das, Phys. Rev. **109**, 360 (1958).

Table II. Radial and angular contributions to γ_∞ for Cl^- and Cu^+.

	Cl^-		Cu^+	
	Present results	Second-order perturbation theory	Present results	Second-order perturbation theory
γ_∞ (radial)	-90.4	-58.0	-17.6	-17.0
γ_∞ (angular)	3.4 to 5.5	1.5^a	~ 0.6	~ 0.1
Total γ_∞	-87.0 to -84.9	-56.5	-17.0	-16.9

[a] R. M. Sternheimer (unpublished).

If one assumes that the enhanced SCF $\gamma_{l\to l}$ values are entirely associated with self-consistency (i.e., an aspherical potential which includes the effects of the closed shell distortions) one can use the results of Table I to estimate the same effect on the angular γ terms. Results are given[16] in Table II where estimates of the total γ_∞'s are also listed. One could instead directly estimate the angular Sternheimer antishielding utilizing Eq. (6); for Cl^- this method gave the γ_∞ (angular) value of 3.4 appearing in Table II.

It is, of course, naive to expect that the differences between the perturbation theory and SCF results of Table I are due entirely to self-consistency. Khubchandani, Sharma, and Das,[17] using a modification of Dalgarno's method[7] for including exchange, showed that the omission of exchange in the standard perturbation calculations can be numerically significant and Ingall's has shown[4] that the maintenance of orthogonality can have severe effects on a computed γ_∞. Let us now examine the most noticeable feature of the results listed in Table I, i.e., the substantially larger value for the Cl^--$3p$ term ($\gamma_{3p\to p}$) which we have obtained. In order to determine the cause of this difference we have carried out a series of analytic perturbation calculations for $\gamma_{2p\to p}$ and $\gamma_{3p\to p}$ of Cl^- maintaining orthogonality in a variety of ways. From the results we conclude that the increased SCF value for $\gamma_{3p\to p}$ is largely due to the proper maintenance of orthogonality with the $2p$ shell. (These computations also agree with Ingall's observation that the results are extremely sensitive to the way that orthogonalization is carried out; details will be given in a future publication.)

A detailed breakdown of the respective roles of self-consistency, exchange and orthogonality has not been attempted but it appears that the former is important

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[16] The γ_∞ (angular) values of Table II are in part based on analytic perturbation theory estimates of the authors and to a larger extent on unpublished results of R. M. Sternheimer for which we are grateful.

[17] P. G. Khubachandani, R. R. Sharma, and T. P. Das, Phys. Rev. **126**, 594 (1962).

for inner shells and that the latter contributes heavily to the final character of outer shell $\gamma_{l\rightarrow l}$ terms.

IV. DISCUSSION

Orthogonality, self-consistency, and exchange are naturally and properly handled by the method we are proposing; in addition, the method is computationally practicable. For these reasons, we believe it's use offers important advantages over the traditional methods for obtaining γ_∞'s.

A major defect of any of the methods for obtaining γ_∞ lies in the deficiencies introduced by the approximate form of the assumed perturbing potential. For a given external potential for which a γ_∞ has been computed, there still remains the question of agreement with a γ derived somehow from $qQ(1-\gamma)$ gotten from experiment. The absence of exact values of q and Q make it impossible to make definite statements concerning this question but it has been suggested[18] that γ's of the order of -10 to -15 are appropriate for Cl^- and Cu^+ implying that the calculated value of γ_∞ for Cl^- is a severe overestimate whereas the Cu^+ value is only slightly so. This comparison raises doubts concerning the accuracy of a computed q and the related V_q, which go beyond the question of defining a potential in that it involves the concept of an "ion" in a solid and of the "potential" associated with it. It may be argued that such a model is inadequate for the problems of interest to us here; let us consider this matter.

The lattice sum over ion point charges, which is normally done when estimating an electric-field gradient, yields a potential of the form of Eq. (5). Although the results may be adequate[19] for obtaining the direct quadrupole interaction with the nucleus, such a sum leaves much to be desired when used as the perturbing potential seen by the ion's electrons because the ion's charge density overlaps that of the neighboring ion electrons and nuclei. Hence, a potential of the form $r^2Y_0^2(\theta,\varphi)$ is clearly not appropriate over that region. In addition to more accurately defining an electrostatic field, problems associated with wave function orthogonality (between neighboring ions) and covalency (if some of the ions have unclosed shells) occur. Also the crystal potential will have components of other than quadrupole symmetry which may distort the ion and in turn affect the electronic quadrupole distortion. For example, it has been argued that the tendency of negative ions to contract when inserted into ionic crystals may possibly result in severe repercussions[18] for γ_∞.

The importance of some of these problems can be illustrated if we consider γ computed as a function of the distance (R) of the source of q from the nucleus in question; utilizing Eq. (6), with $\rho(x)=\delta(x-R)$, one obtains Sternheimer's $\gamma(R)$ factor.[1] The $\gamma_{3p\rightarrow p}$ result for Cl^- is plotted as the ratio $\gamma(R)/\gamma_\infty$ in Fig. 1. Since internuclear spacings are typically of the order of 5 a.u., the arguments of the previous paragraph are made more apparent by the variation of $\gamma(R)$ with R which is seen in the figure. At best, this means that non-quadrupole crystal field effects and orthogonalization repercussions must be dealt with before a realistic value is obtained for γ. At worst, it may mean that the tight binding approach of perturbing an essentially free ion by a crystalline environment must be abandoned before a substantial improvement over current γ_∞ estimates is made.

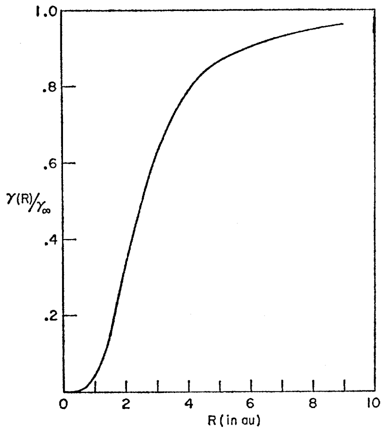

FIG. 1. The $3p\rightarrow p$ antishielding contribution, $\gamma(R)/\gamma_\infty$, for Cl^-. (See text for definition and discussion.)

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APPENDIX I

A conventional H-F Cu^+ wave function, superior to those in the literature, is tabulated here whose accuracy is similar to a previously reported[20] Mn^{2+} wave function. Orthonormal analytic Hartree-Fock orbitals, $U_i(r)$, of the form

$$U_i(r)=\sum_j C_{ij}R_j(r), \tag{A1}$$

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[18] G. Burns and E. G. Wikner, Phys. Rev. **121**, 155 (1961), and references contained therein.

[19] E. Brun, S. Hafner, and F. Waldner [Compt. Rend. Soc. Suisse Phys. **34**, 391 (1961)] have indicated that the standard point-charge lattice sum estimates of q for ionic crystals are inadequate and that in addition one should include lattice sums over the dipole and quadrupole moments induced in the ions.

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

TABLE III. Parameters (A_s and Z_s) and combining coefficients (C_{ij}) defining the Hartree-Fock orbitals for Cu^+.

j	A_j	Z_j	$C_{1s,j}$	$C_{2s,j}$	$C_{3s,j}$
1	0	84.8828	0.00037044	−0.00036468	−0.00038449
2	0	30.4491	0.91205876	−0.27950925	0.10652016
3	1	26.9961	0.10841891	−0.16245115	0.04976048
4	1	14.1023	−0.00647884	0.64460027	−0.21227812
5	2	13.3297	0.00561417	0.46415723	−0.38260515
6	2	8.5681	−0.00204424	0.06610429	0.17263958
7	2	5.0982	0.00065755	−0.00454834	0.94245212
8	2	2.8171	−0.00016921	0.00134453	0.07547339
			$C_{2p,j}$	$C_{3p,j}$	
9	0	34.5244	0.00103326	0.00096650	
10	0	18.9852	0.13481246	−0.05841121	
11	0	11.6372	0.84951100	−0.29915630	
12	1	10.8502	0.02041835	−0.11625686	
13	1	6.8083	0.02746109	0.54128259	
14	1	3.9668	−0.00525461	0.63298421	
15	1	2.2563	0.00172020	0.02228438	
			$C_{3d,j}$		
16	0	1.6956	0.19657400		
17	0	2.4954	0.25771318		
18	0	4.2881	0.46579549		
19	0	7.5015	0.24455545		
20	0	13.0768	0.02287090		

were obtained, normalized such that

$$\int_0^\infty |U_i(r)|^2 dr = 1. \tag{A2}$$

TABLE IV. One-electron energies for Cu^+ in atomic units (1 a.u.=2 Ry).

$\epsilon_{1s} = -329.11$	$\epsilon_{2p} = -35.928$
$\epsilon_{2s} = -\ 41.127$	$\epsilon_{3p} = -\ 3.641$
$\epsilon_{3s} = -\ 5.324$	$\epsilon_{3d} = -\ 0.8099$

The basis functions, R_j, are of the form

$$R_j(r) = N_j r^{(l+A_j+1)} e^{-Z_j r}, \tag{A3}$$

where N_j is a normalization constant and is expressible in terms of the other parameters, i.e.,

$$N_j = [(2Z_j)^{2l+2A_j+3}/(2l+2A_j+2)!]^{1/2}. \tag{A4}$$

$U_i(r)$ of common l value are constructed from a common set of $R_j(r)$'s. Z_j's, A_j's and combining coefficients (C_{ij}'s) are listed in Table III; the one-electron energies are given in Table IV. The C_{ij}'s define orthonormal functions to the number of digits reported but have by no means been uniquely determined to that number of digits. The total energy for the ion is -1638.724_5 a.u. as compared with -1638.705 a.u. obtained in a previous calculation.[13] The improvement is primarily associated with the greater variational freedom allowed to the outer parts of the 3*s* and 3*p* shells; repercussions on the 3*d* shells were small.

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Positron Mean Lives in Scandium, Yttrium, and the Rare-Earth Metals*

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Positron mean lives relative to that in aluminum are reported for scandium, yttrium, and all of the stable rare-earth metals. An automatic cycling procedure allows these relative measurements to be made with an accuracy of $\pm 3\times10^{-12}$ sec. The average positron lifetime in the trivalent rare earths and in yttrium is 0.675×10^{-10} sec longer than the positron lifetime in aluminum, with an average deviation of $\pm 0.035\times10^{-10}$ sec. The positron lifetimes in the divalent rare earths (europium and ytterbium) are appreciably longer, while the lifetime in scandium is somewhat shorter. The experimental results indicate a correlation between the positron lifetime and the conduction electron density, and they show that the 4*f* electrons do not participate in the annihilation process.

I. INTRODUCTION

If a positron is injected into a metallic sample with an energy of a few hundred kilovolts, it will be able to penetrate to the interior of the sample. There it will be thermalized in about[1] 3×10^{-12} sec via collisions with conduction electrons, and it will become part of the electronic system. Some time later the positron will annihilate with an electron, producing (usually) two 0.511-MeV annihilation gamma rays. These relatively high-energy gamma rays can then bring information about the annihilation process out of the sample with negligible attenuation or scattering. Thus, the investigation of the positron annihilation in a metal should provide some information on the electronic structure of the metal.

The first extensive measurements of positron mean lives in metals were made by Bell and Graham,[2] and

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[1] G. E. Lee-Whiting, Phys. Rev. **97**, 1557 (1955).

[2] R. E. Bell and R. L. Graham, Phys. Rev. **87**, 236 (1952); **90**, 644 (1953).