Corresponding to our $p\mu p$ binding energy in Table II is a dissociation energy of 253 eV. The difference of 1.3 eV is too large to be explained by the difference[10] in values assumed for the muon mass. A satisfactory explanation will have to await further calculations.

For the case of $p\mu d$, the difference between our results and those of Frost, Inokuti, and Lowe[4] may be due to their use of a nonorthogonal set of basis functions. It has been pointed out[11] that the series-recursion method is not always equivalent to a variational calculation, for such a basis.

ACKNOWLEDGMENT

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[11] C. Schwartz, J. Comp. Phys. (to be published), Appendix IV.

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Polarization Corrections for Shielding and Antishielding Configurations of the Copper Atom

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The level-crossing technique has been used to measure the hyperfine structure constants of the Cu^{63} nucleus in the $(3d)^{10}4p\ ^2P_{3/2}$ state. To extract a value for the nuclear quadrupole moment, configuration interaction effects are allowed for by performing a least-squares fit to the energy levels. The value obtained is in serious disagreement with a value for Q inferred from the $(3d)^9(4s)^2$ configuration. The copper moment may therefore serve as a test for Sternheimer or other polarization corrections that must be invoked to explain the discrepancy.

INTRODUCTION

THE phenomenon of configuration interaction has continually plagued efforts to extract values for nuclear moments from hyperfine structure (hfs) data. The problem is especially severe for excited atomic states. Thus, much of the precision of data obtained by modern techniques of optical spectroscopy, including optical and electron pumping, is lost as far as the nuclear moments are concerned. However, the problem is by no means restricted to excited states. Nuclear quadrupole moments deduced from ground-state hfs measurements must be subjected to the so-called Sternheimer correction.[1] This correction and other limited configuration interaction approaches, which we may call polarization corrections, remain in vogue because of the absence of accurate unrestricted Hartree-Fock functions for the great majority of atoms and ions. Polarization corrections are often cast in the form of a perturbation expansion. As such, they may be gradually refined. One such refinement is inclusion of excitations to states of the continuum.[2] Needless to say, unambiguous tests of the various polarization correction schemes would be highly desireable. A determination of a nuclear quadrupole moment from its interaction in two dissimilar electronic configurations, for instance, could constitute a stringent test. Moreover, certain forms of configuration interaction are not tractable in a perturbation approach, or can be treated in a more consistent way by other techniques.

To illustrate these ideas, we discuss below the extraction of the quadrupole moment, Q, of the Cu^{63} nucleus from the measured value of the hyperfine interaction constant in the $(3d)^{10}4p$ configuration. We first show that standard Racah techniques can be used to take the configuration interaction of $(3d)^{10}4p$ with $(3d)^9 4s 4p$ into account. The procedure is to deduce the configuration interaction from a least-squares fit to the energies of the observed levels. With the improved electronic wave function so obtained, a value for the nuclear quadrupole moment is inferred. Using this procedure, we find that our measured value $B=-28.75(70)$ Mc/sec implies $Q=-0.315(12)$ b. In a recent optical measurement, the quadrupole constant for Cu^{65} was determined in the $(3d)^9(4s)^2$ configuration.[3] The relevant energy levels are shown in Fig. 1. When this is scaled up by the known ratio of the moments,[4] a value $Q=-0.176(5)$ b is obtained. The size of the discrepancy suggests that copper may provide a sensitive testing ground for polarization corrections to quadrupole moments. It also emphasizes the importance of $d^n \rightarrow d^{n-1}s$ configuration interaction for hfs. This is neither of the angular nor of the radial type considered by Stern-

[1] R. M. Stermenheir, Phys. Rev. **105**, 158 (1957), and earlier papers.
[2] H. Wolter, in *La Structure Hyperfine des Atomes et des Molecules* (Comite National pour les Recherches Scientifique, Paris, 1966).
[3] W. Fischer, H. Hühnermann, and K.-J. Kollath, Z. Physik **200**, 158 (1967).
[4] H. L. Cox and D. Williams, J. Chem. Phys. **32**, 633 (1960).

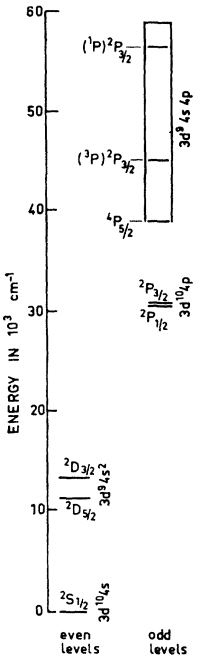


FIG. 1. Relevant energy levels of the copper atom for which accurate hfs constants have either been measured or estimated.

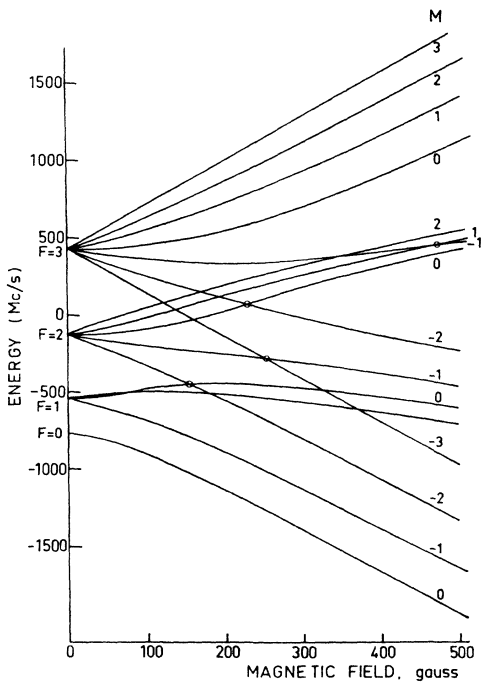


FIG. 2. Zeeman effect of the hyperfine levels of the $^2P_{3/2}$ state ($I=\frac{3}{2}$). Observable level crossings are circled.

heimer, but resembles the exchange type which Sternheimer discusses but does not tabulate.[1]

EXPERIMENTAL

The technique used to measure the hfs interaction constants of the Cu^{63} nucleus in the $(3d)^{10}4p\ ^2P_{3/2}$ level was that of level crossing spectroscopy.[5] The method may be understood with reference to Fig. 2. Circles indicate points at which two energy levels differing in magnetic quantum number m become degenerate. These levels may be excited by a single photon from a single level in the ground state and may also decay to the same level. Observable signals resulted from an interference produced in the scattered light as the magnetic field was swept through the crossing point. A least-squares fit to the crossing fields then yielded the hfs constants.

The experimental apparatus and procedure were very similar to those used in experiments on the isotopes of silver and have been described elsewhere.[6] The wavelength of the resonance radiation, 3248 Å, is sufficiently close to that of silver, that the same optics and light filters could be used. One striking difference was the absence of any pronounced coherence narrowing of the zero-field level-crossing signal. A very slight decrease in the Hanle-effect linewidth was observed at the highest temperatures permissible before lens coating became severe. Presence of cross-fluorescence lines to $(3d)^9(4s)^2$-^2D may partially explain the greatly reduced narrowing.

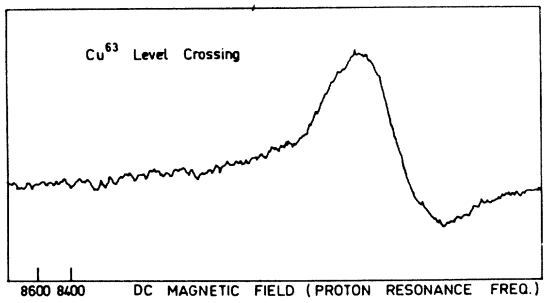
In our first experiments, naturally occurring copper was used.[7] Because of the similarity of the nuclear moments of Cu^{63} and Cu^{65}, the signals were complicated superpositions of level crossings from the two isotopes. The signals shown in Fig. 3 were obtained, using a sample enriched to 99.9% in Cu^{63}. Phase-sensitive detection at 28 cps was used to improve the signal-to-noise ratio. Proton NMR served to measure the magnetic field. Our signals are derivatives of sums of absorption- and dispersion-type curves due to a slight misalignment of our optics. This has since been verified in more recent experiments in which symmetric signals were observed. The mixture of absorption and dispersion could be determined and the curves interpreted using an analysis due to Shaltiel,[8] based on the amplitudes of the major and minor peaks. The results were in excellent agreement with a treatment of the same problem based on the positions of the observed peaks.[9]

Table I lists the positions and full widths at half-maximum of all observed signals. The third and fourth columns list the calculated slopes of the crossings and the resulting lifetimes. Lifetime and linewidth are related by

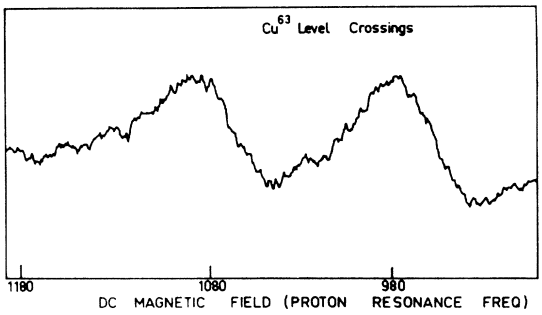
$$\tau=\frac{1}{\pi(\partial\nu/\partial H)\Delta H}. \tag{1}$$

A lifetime value of $\tau=6.8(4)\times10^{-9}$ sec embraces all the observations. The values we obtain for the hfs constants

[5] P. A. Franken, Phys. Rev. **121**, 508 (1961).
[6] B. Budick and L. A. Levin, in *La Structure Hyperfine des Atomes et des Molecules* (Comite National pour les Recherches Scientifique, Paris, 1966).
[7] B. Budick and L. A. Levin, Bull. Am. Phys. Soc. **11**, 168 (1966).
[8] M. Peter *et al.*, Phys. Rev. **126**, 1395 (1962).
[9] A. Lurio and R. Novick, Phys. Rev. **134**, A608 (1964).



(a)



(b)

FIG. 3. Level-crossing signals observed using enriched sample. (a) Shows a trace of the crossing at 155 G. (b) Shows overlapping signals near 240 G.

are $A=195.23(25)$ Mc/sec and $B=-28.75(70)$ Mc/sec.[10] Only the relative sign of B and A was determined in our experiment. The sign of A is assumed to be the same as that of the magnetic dipole moment. Furthermore, these values were arrived at by taking $g_j=1.338$, the optically determined g value. The values of A and B determined in a level-crossing experiment are linearly dependent on g_j.

TABLE I. Positions, widths and identifications of observed signals.

$H(G)$	$\Delta H(G)$	$\partial\nu/\partial H$ [(Mc/sec)/G]	τ (10^{-9} sec)	Identification
0	23.5	1.87	7.2	
155.0	19.2	2.55	6.5	$2,-2\rightleftarrows 1,0$
230.5	17.6	2.72	6.7	$3,-2\rightleftarrows 2,0$
254.3	21.9	2.19	6.6	$3,-3\rightleftarrows 2,-1$

THEORY

The second phase of our work has involved a fit to the energy levels as mentioned above. We are able to predict all of the odd energy levels to ± 100 cm^{-1}. Table II lists the calculated radial parameters, which are in fact Slater integrals, in the column headed Cu I. For comparison we give preliminary values for the same parameters for some neighboring metals.[11] The general consistency of the results illustrates the reliability of Racah techniques in elucidating problems of configuration interaction.

In addition, the magnetic hyperfine interaction constants can now be evaluated and compared with experiment. Such a comparison is presented in Table III. The set of single-electron interaction constants $a_s=7427$ Mc/sec, $a_p=150$ Mc/sec, and $a_d=1132$ Mc/sec was sufficient to compile Table III. The agreement between calculated and experimental values is excellent for all of the recent high-precision experiments. Discrepancies exist for older measurements in which natural copper was used and/or the quadrupole interaction was not treated correctly.

The procedure we have followed in calculating the Sternheimer uncorrected quadrupole moment is as follows: The formal notation is similar to that of Elbel.[12] We express the wave function of the $d^{10}p^2P_{3/2}$ level as

$$\alpha\psi(d^{10}p)\,{}^2P_{3/2}+\beta\psi(d^9sp\,{}^1P)\,{}^2P_{3/2}+\gamma\psi(d^9sp\,{}^3P)\,{}^2P_{3/2}. \quad (2)$$

TABLE II. Slater integrals and radial parameters for copper and neighboring metals. The data for Ni is less precise and is omitted. Cu I contains results of the authors. Cu II are results of Elbel. J and K are defined by $J=R^2(dp,sp)/5$, $K=R^1(dp,ps)/3$. Constants are in cm^{-1}.

Parameter	Fe	Co	Cu I	Cu II
$G_1(s,p)$	7116	7038	8085	
$F_2(d,p)$	305	303	318	
$G_1(d,p)$	245	200	241	
$G_3(d,p)$	20	14	47	
$G_2(d,s)$	1536	1607	1104	
J	1133	1245	1439	1882
K	2450	2331	3611	1077

TABLE III. Comparison of observed and calculated A values. The level $^4F_{9/2}$ has been used to estimate a_s and therefore serves a normalization function. We have tabulated all available data. Constants are in Mc/sec.

Level	Calculated A	Experimental A	Reference
$^4F_{9/2}$	1269	1269	a
$^4D_{7/2}$	1554	1545	b
$^4F_{7/2}$	1261	1140	b
$^2F_{7/2}(^3P)$	1393	1920	b
$^4P_{5/2}$	2027	2031.3	c
$^4D_{5/2}$	1089	1200	b
$^4F_{5/2}$	1088	450	b
$^2D_{5/2}(^3P)$	1625	2535	b
$^2D_{5/2}(^1P)$	738	600	d
$^2F_{5/2}(^3P)$	795	750	e
$^4P_{3/2}$	2413	2130	b
$^4P_{1/2}$	2802	2280	d
$^4D_{1/2}$	−48	−510	d
$^2P_{1/2}(d^{10}p)$	544	507.5	f
$^2P_{3/2}(d^{10}p)$	198	195.23	This paper

[a] M. Elbel and W. Fischer, Z. Physik **165**, 151 (1962).
[b] S. Wagner, Z. Physik **141**, 122 (1955).
[c] See Ref. 15.
[d] M. Elbel, Ann. Physik **13**, 217 (1964).
[e] R. Ritschl, Z. Physik **79**, 1 (1932).
[f] W. Fischer, H. Hühnermann, and K. J. Kollath, Z. Physik **194**, 417 (1966).

[10] Similar results have been obtained independently by J. Ney, Z. Physik **196**, 53 (1966).
[11] C. Roth, thesis, Hebrew University (unpublished).
[12] M. Elbel and H. Wilhelm, Ann. Physik **18**, 42 (1966).

Other $J=\frac{3}{2}$ levels are admixed in negligible amounts. We evaluate the quadrupole interactions using this wave function. Each LS-coupled state is expressed as a linear combination of products of one-electron wave functions of the form $j_1m_1\rangle j_2m_2\rangle j_3m_3\rangle$ where the subscripts refer to d, p, and s electrons, respectively.

The relevant matrix elements can be found in a paper by Lurio, Mandel, and Novick.[13] The diagonal contributions are

$$B(^2P_{3/2})=\alpha^2b(p_{3/2})+\beta^2[(63/125)b(d_{5/2})+(1/30)b'(p_{3/2})+(1/50)b(d_{3/2})+(1/15)\eta b'(p_{3/2})-(21/125)\times\eta b(d_{5/2})]+\gamma^2[(7/125)b(d_{5/2})+(9/50)b(d_{3/2})-(17/90)b'(p_{3/2})+(13/45)\eta b'(p_{3/2})+(21/125)\eta b(d_{5/2})], \quad (3)$$

where η is a relativistic factor computed by Schwartz[14] and the single-electron $b(p_{3/2})$ and single-hole $b(d_{5/2})$, $b(d_{3/2})$ constants have been assumed to be configuration-dependent.

Off-diagonal elements of the type $\beta\gamma$ vanish identically and those of the type $\alpha\beta$ and $\alpha\gamma$ have been calculated by Elbel[13] and are very small. In the approximation $\eta=1$ and $b(d_{3/2})=(7/10)b(d_{5/2})$ the coefficients of β^2 and γ^2 are identical and we may write

$$B(^2P_{3/2})=\alpha^2b(p_{3/2})+(1-\alpha^2)\times[(7/20)b(d_{5/2})+\tfrac{1}{10}b'(p_{3/2})], \quad (4)$$

where $b(d_{5/2})$ and $b'(p_{3/2})$ are not known. However, precisely this combination occurs in the expression for $B(^4P_{5/2})$ of the same configuration which has been measured by Lurio in a metastable atomic beam.[15] (See Fig. 1). We have finally

$$b(p_{3/2})=[B(^2P_{3/2})-(1-\alpha^2)B(^4P_{5/2})]/\alpha^2. \quad (5)$$

The value for α^2 given by our least-squares fit is 0.91. For the two measured quantities we have $B(^2P_{3/2})=-28.75$ Mc/sec. and $B(^4P_{5/2})=+79.2$ Mc/sec. This gives $b(p_{3/2})=-39.4$ Mc/sec. Using the value $\langle 1/r^3\rangle=1.29/a_0^3$ obtained from our calculated fine-structure splitting we find $Q=-0.315(12)$ b. This is to be compared with the value $Q=0.176(5)$ b deduced from the $(3d)^9(4s)^2\,{}^2D$ levels.

[13] A. Lurio, M. Mandel, and R. Novick, Phys. Rev. **126**, 1758 (1962).
[14] C. Schwartz, Phys. Rev. **97**, 380 (1955).
[15] A. Lurio, in *Nuclear Data Sheets*, compiled by G. H. Fuller and V. W. Cohen (National Academy of Sciences—National Research Council, Washington, D. C., 1965), Appendix I.

DISCUSSION

In a note added in proof, Elbel[12] has pointed out that the Sternheimer correction is in the opposite direction for the two configurations. He has also attempted to take the configuration interaction of $d^{10}p$ and d^9sp into account. His method is to infer the amount of configuration interaction from the magnetic hfs constants themselves. He thus obtains a set of α^2, β^2, and γ^2 with which he proceeds to calculate the quadrupole moment. However, our fit to the magnetic hfs constants is of roughly the same quality, indicating that Elbel's procedure is not unique. Moreover, his values for the Slater integrals that are mainly responsible for the configuration interaction are given in the last column of Table II.[16] They are substantially different in both absolute and relative magnitude from the values calculated using Racah techniques. We should emphasize the sensitivity of the quadrupole moment as calculated from Eq. (5) to the value of α^2. The value $\alpha^2=0.975$ deduced by Elbel gives a quadrupole moment smaller by some 20%. It is precisely this sensitivity that demands a consistent approach to the problem of configuration interaction.

CONCLUSION

We condlude that: (1) Configuration interaction of the exchange type will be very important in deducing quadrupole moments of transition-metal atoms from measured B values. These interactions can be successfully calculated using standard Racah techniques. (2) Measurements of the copper-63 quadrupole moment in shielding and antishielding one-electron configuration can serve as a sensitive test for any proposed polarization corrections, and (3) in particular, if we accept the Sternheimer correction factor of 1.34 for the d^9s^2 configuration, a net correction factor of 0.75(6) is required from the usual angular and radial excitation of the $d^{10}p$ configuration to bring the inferred Q values into coincidence. The value of $Q(\mathrm{Cu}^{63})$ so obtained is $-0.235(10)$ b.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the help of Dr. Z. B. Goldschmidt in obtaining the least-squares fit to the energy levels.

[16] M. Elbel, 1966 (private communication).