Session **I**

ISOMER SHIFT AND QUADRUPOLE SPLITTING

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Application and Interpretation of Isomer Shifts

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I. INTRODUCTION

Since the first paper reporting the discovery of isomer shifts appeared in 1960,[1] their study has comprised a fast-growing area of modern physics. There are at present about 50 papers dealing with isomer shifts in the literature, and the number is rapidly increasing. The particular attraction of these shifts is that they provide a means for measuring the product of two quantities which are completely inaccessible to other experimental techniques. These quantities are, of course, the differential 2ρth moment of radial charge for two nuclear isomers and the differential electron density, evaluated at the nucleus, for an atom in two chemical environments. The first constitutes an interesting independent datum for comparison with nuclear models. The latter gives a unique measure of the role of s electrons in chemical bonds, and thus provides a physical foundation for the chemical concept of ionic character, both in ordinary compounds and in metals.

Any theoretical discussion of isomer shifts is heavily indebted to the theory of isotope shifts, which has been developed since 1931 in connection with atomic spectroscopy.[2–8] In the next section a derivation of equations useful in interpreting isomer shifts is outlined, following isotope shift theory quite closely. The present and potential applications of isomer shift measurements to chemistry and metal physics are discussed in Sec. III, and some conclusions that are emerging about chemical bonds are pointed out. In Sec. IV an equation relating isomer shifts to nuclear deformation is given and applications to the study of various types of collective nuclear excitation are

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[1] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters **4**, 412 (1960).

[2] J. H. Bartlett, Nature **128**, 408 (1931).

[3] G. Racah, Nature **129**, 723 (1932).

[4] J. E. Rosenthal and G. Breit, Phys. Rev. **41**, 459 (1932).

[5] G. Breit, Phys. Rev. **42**, 348 (1932).

[6] E. K. Broch, Arch. Math. Naturvidenskab. **48**, 25 (1945).

[7] A. R. Bodmer, Proc. Phys. Soc. (London) **A66**, 1041 (1953).

[8] G. Breit, Rev. Mod. Phys. **30**, 507 (1958).

discussed. Section V contains a short summary of present limitations of the method.

II. THE THEORY OF ISOMER SHIFTS

The simplest zero-order theories of atomic structure start with Z electrons in the Coulomb field of a point nucleus. After this problem has been treated by approximate methods, and electron–electron interactions have been satisfactorily dealt with, perturbation theory may then be used to derive the hyperfine structure, leading ultimately to a spin Hamiltonian.[9] One of the important perturbations is the effect of finite nuclear volume. This produces, in the magnetic dipole and electric monopole components of electron–nucleus interaction, shifts that are manifest as the hyperfine structure anomaly from the former,[10] and as isomer and isotope shifts from the latter. Thus, of the monopole interaction, only the small fraction arising from distortion of the Coulomb potential within the nucleus appears as a change in, for example, the binding energy of an s electron, and the observable isomer shift, which arises from the difference between the nuclear volumes of two isomeric states, is a very small fraction of this change. For two isomeric states of equal size the very large energy shifts due to finite nuclear volume would exactly cancel for any source and absorber, and the resonance would always appear at zero Doppler velocity.

A. Nonrelativistic Theory

For simplicity the nuclear charge distribution will be taken as uniform for $r < R$, the nuclear radius, and as zero for $r > R$. Thus equations will be given which, when compared with experimental data, yield the fractional change in charge radius, $\delta R/R$, of the uniform charge distributions that are "equivalent" to the true charge distributions of the real isomeric states. When comparing this quantity with a specific nuclear model, one must first find the uniform charge distribution which produces a shift equivalent (i.e., giving the same 2ρth moment of radial charge, as shown below) to that given by the model. The problem of charge distributions in relation to isotope shifts has been discussed by Rosenthal and Breit[4] and by Bodmer.[7]

Isotope-shift theory has been derived in two ways: by perturbation methods[3,4] and by direct calculation.[6,7] The perturbation theory derivation is outlined below. It should be noted that the perturbation result is too high, by as much as 30% for heavy elements. A correction factor is given in Sec. II C.

The perturbation Hamiltonian is just the difference between the potential arising from a uniform charge distribution within the nucleus, $V(r) = (Ze^2/R)\,[-\frac{3}{2} + \frac{1}{2}\,(r/R)^2]$, and the potential produced by a point nucleus at the origin, $-Ze^2/r$. Outside the nucleus both potentials are Coulombic and the perturbation disappears. In a nonrelativistic approximation the s electron density within the nucleus, $\psi^2(r)$, is essentially constant and may be approximated by $\psi^2(0)$. The shift is extremely small in this approximation for all but s electrons [$\psi_l^2(0) = 0$ for $l \neq 0$], but for relativistic $p_{1/2}$ electrons this is no longer true.[11] Integrating the perturbation over the nuclear volume, the energy shift, due to finite nuclear size, of an s electron is

$$\Delta E = \tfrac{2}{5}\,\pi Z e^2 R^2 \psi_s^2(0)\,,$$

and the resonant Doppler velocity in Mössbauer experiments is

$$v = \frac{4\pi Z e^2 R^2 c}{5E_\gamma}\left[\sum_A \psi^2(0) - \sum_S \psi^2(0)\right]\left[\frac{\delta R}{R}\right]. \qquad (1)$$

The sums are taken over electron density in source and absorber. The symbol δR denotes $R_{\text{excited}} - R_{\text{ground}}$, and the velocity is taken as positive for absorber moving toward source. This approximation is fairly accurate for very light elements. For heavy elements, relativistic corrections of up to a factor of 10 must be applied. Before evaluating these corrections we discuss the determination of $\psi^2(0)$.

B. Evaluation of $\psi^2(0)$

Only the *valence* s electrons are usually considered in isomer shifts because the inner s electrons are affected much less by chemical bonding (they are, however, shielded by the valence electrons). Outer electrons are strongly shielded from the nucleus and $\psi^2(0)$ can be obtained only by approximate methods. The simplest of these is the use of the Fermi–Segrè formula[12]

$$\psi_{ns}^2(0) = \frac{Z_i Z_0^2}{\pi a_0^3 n_e^3}\left(1 - \frac{d\sigma}{dn}\right). \qquad (2)$$

Here Z_i is the internal effective nuclear charge, usually taken as Z; Z_0 is the external charge felt by the valence electron, taken as $(1 + m)$, where m is the charge on the atom or ion; $n_e = n - \sigma$ is the effective

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

[10] J. Eisinger and V. Jaccarino, Rev. Mod. Phys. **30**, 528 (1958).

[11] H. Kopfermann, *Nuclear Moments*, English edition, translated by E. E. Schneider (Academic Press Inc., New York, 1958).

[12] E. Fermi and E. Segrè, Z. Physik **82**, 729 (1933).

quantum number; and σ is the quantum defect. A discussion of the validity and accuracy of this equation has been given by Breit.[8] The parameters in Eq. (2) may be obtained from optical spectroscopic data. An alternative method for determining $\psi_{ns}^2(0)$ is the comparison of the atomic hfs constant a_{ns} with the known nuclear moment, using the relation

$$a_{ns} = \tfrac{8}{3}\,\pi a_0^2 hcR_\infty \alpha^2 g_I' \psi_{ns}^2(0) K(Z)\ . \tag{3}$$

This equation may be obtained by combining Eq. (2) with Eq. (26.24) given by Kopfermann.[11] Here g_I' is the nuclear g factor in Bohr magnetons and $K(Z)$ is the product of three corrections given by Kopfermann: a relativity correction $F_r(j,Z_i)$, the Breit–Crawford–Schawlow correction for distributed electron magnetism, $(1-\delta)$, and the distributed-nuclear-magnetism correction, $(1-\epsilon)$. $K(Z)$ varies from 1 for the lightest elements to over 2 for the heaviest. Evaluating the natural constants we find

$$\psi_{ns}^2(0) = 2.54\times 10^{26}[a_{ns}/K(Z)g_I]\ \mathrm{cm}^{-3}\ , \tag{4}$$

with a_{ns} in cm^{-1} and with g_I now in nuclear magnetons. By the use of Eqs. (2) and (4), $\psi_{ns}^2(0)$ has been calculated from optical data[13] for several elements as free atoms (Fig. 1). We note: (1) There is reason to expect large isomer shifts from the $\psi^2(0)$ factor alone, and (2) care should be taken, when applying these data to compounds, to account for screening effects, illustrated for the case of 6s electrons by the points for unipositive ions, which are higher than those for the same neutral atoms.

The values of $\psi^2(0)$ in Fig. 1 are directly useful for optical isomer or isotope shift measurements on free atoms. For isomer shifts in solids, however, some modifications must be made. The next simplest case after atoms, namely, pure metals, is already quite complicated, and only in a few cases is $\psi^2(0)$ known accurately. In the Knight shift, the density, evaluated at the nucleus, of s (conduction) electrons on the Fermi surface, $|\psi_F(0)|^2$, is related to the frequency shift by

$$\Delta\nu/\nu_0 = \tfrac{8}{3}\,\pi\chi_P|\psi_F(0)|^2\ . \tag{5}$$

The experimental shifts may be compared with the Pauli spin susceptibility, χ_P, to yield $|\psi_F(0)|^2$. Physically the ratio $\xi = |\psi_F(0)|^2/\psi_A^2(0)$ might be expected to be less than 1 (here A denotes "free atom"). Kohn[14] and Kjeldaas and Kohn[15] have calculated ξ for the 2s electron in Li and the 3s electron in Na, finding $\xi_{\mathrm{Li}} = 0.49$ and $\xi_{\mathrm{Na}} = 0.80$, compared with the values $\xi_{\mathrm{Li}} = 0.44$ and $\xi_{\mathrm{Na}} = 0.70$ deduced from Knight shifts.

For metals, in general, and for chemical compounds, rather approximate methods must be used in estimating electron densities. These will, however, nearly always be based on or related to the atomic densities. Inasmuch as the Coulomb potential of its own ion core is always a large part of the total potential felt by an outer electron, the free atom electron density is probably always a fair first approximation. If the electron density in a metal must be estimated in the absence of any relevant data, a factor of ≈ 0.7 for $\xi' = |\psi(0)|^2/\psi_A^2(0)$ might provide a better approximation (here ξ' is defined for electrons not necessarily on the Fermi surface). Some empirical evidence for this choice is available from isomer-shift data on metals.

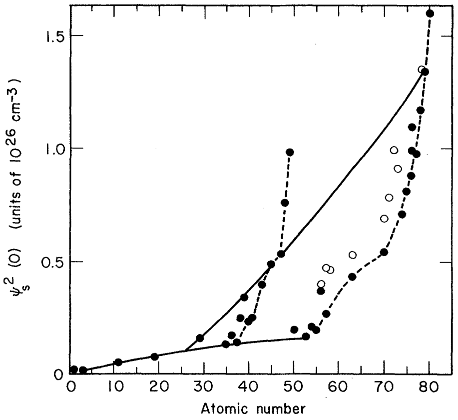

FIG. 1. Nonrelativistic density at the nucleus of valence s electrons in free atoms in the neutral (filled circles) and +1 (open circles) oxidation states. Data are representative rather than complete. In several elements more than one value was obtained for $\psi^2(0)$, using different configurations. In these cases the lowest values are most relevant to isomer shift discussions as they represent maximum shielding of the valence s electron [thus the configuration $(n-1)d^{x+1}ns$ is preferred over the configuration $(n-1)d^x\,ns\,np$ or $(n-1)d^x ns(n+1)s$ for obtaining the $\psi_{ns}^2(0)$ that is appropriate here]. The alkalis are interconnected by a solid curve, as are the *IB* metals (Cu, Ag, Au). Dotted curves intraconnect the 5s and 6s electron series. Decrease of slope through the rare earths may be explained as arising from the more complete shielding of 6s electrons by 4f electrons.

C. Relativity Corrections and Shielding

The electron density is very substantially modified by relativistic effects. Racah[3] and Rosenthal and

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[13] References to optical hyperfine structure data are conveniently found in nuclear moment tabulations. A particularly thorough tabulation, covering the literature up to about 1957, is given by G. Laukian in *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. 38, Part 1, p. 338. Other useful data were found in Refs. 11 and 17.

[14] W. Kohn, Phys. Rev. **96**, 590 (1954).

[15] T. Kjeldaas and W. Kohn, Phys. Rev. **101**, 66 (1956).

Breit[4] found solutions to the Dirac equation for an electron in the Coulomb field of a point nucleus, obtaining for the electron density near the nucleus

$$P(r) = \frac{2(1+\rho)\psi^2(0)}{\Gamma^2(2\rho+1)}\, y^{2\rho-2}, \qquad (6)$$

where $y = 2Zr/a_0$ and $\rho = (1 - \alpha^2 Z^2)^{1/2}$. Here $\psi^2(0)$ is the nonrelativistic electron density: As Z approaches zero, for light elements, ρ approaches 1 and $P(r)$ approaches $\psi^2(0)$.

Integrating the perturbation potential, weighted with $P(r)$, over space, the energy shift, for an s electron, due to finite nuclear volume becomes

$$\Delta E = \frac{6\pi R_\infty a_0^3 (1+\rho)\psi^2(0)}{Z\rho(2\rho+1)(2\rho+3)\Gamma^2(2\rho+1)}\, y_0^{2\rho}. \qquad (7)$$

Here y_0 is $y(r = R)$. After differentiation and substitution we obtain for the isomer shift

$$\delta\Delta E = \left(\frac{4\pi Z e^2 R^2}{5hc}\right) \left\{\frac{30(1+\rho)y_0^{2\rho-2}}{(2\rho+1)(2\rho+3)\Gamma^2(2\rho+1)}\right\} \times [\psi^2(0)] \left[\frac{\delta R}{R}\right]. \qquad (8)$$

The energy unit here is cm^{-1} and this equation may be compared directly with optical isomeric shifts. The right-hand side is written as the product of four factors so that it may easily be compared with the nonrelativistic expressions. These factors are, from left to right:

(1) A "constant factor," containing constants and the nuclear radius. Using the relation $R = 1.20\, A^{1/3}$ F, this factor becomes, in cm^2, $4.20 \times 10^{-29}\, ZA^{2/3}$.

(2) A dimensionless "relativity factor" which approaches 1 as $\rho \to 1$, for low Z. Apart from the $y_0^{2\rho-2}$ portion, this factor is a purely mathematical function. The entire relativity factor, which we shall denote as $S(Z)$, is tabulated in Table I. We have evaluated y_0 by using the relationship $R = 1.20\, A^{1/3}$ F and choosing $A(Z)$ along the line of β stability. This choice of A introduces an error of less than 1% into the factor.

(3) An "electronic factor," the electronic density difference for the optical electron, in units of cm^{-3}. This factor contains all the chemical information.

(4) A dimensionless "nuclear factor" which contains all the nuclear information about the isomeric pair.

Equation (9) may be rewritten in a form directly applicable to Mössbauer resonance experiments. The Doppler velocity at resonance is given by

$$v = \left(\frac{4\pi Z e^2 R^2 c}{5E_\gamma}\right) S(Z) \left[\sum_A \psi^2(0) - \sum_S \psi^2(0)\right] \times \left(\frac{\delta R}{R}\right). \qquad (9)$$

Here the sign conventions are the same as for Eq. (2), to which this reduces as $S(Z)$ approaches 1 in the nonrelativistic limit. With E_γ in keV, the constant factor in Eq. (9) is $15.6 \times 10^{-26}\, ZA^{2/3}\, E_\gamma^{-1}$ $\mathrm{cm}^4/\mathrm{sec}$. Refinements to Eqs. (8) and (9) are given below.

The above derivation makes use of first-order perturbation theory to introduce the effect of finite nuclear volume. As Breit has pointed out,[4,8] this approach is somewhat inaccurate because of wave-function distortion near the origin. Broch has done the problem directly[6] and Bodmer[7] has evaluated the shift, following Broch, using a series expansion in $a = \alpha Z$. He has given an expression for the ratio of $\delta\Delta E$ to $(\delta\Delta E)_{\mathrm{pert}}$, which we may regard as a correction factor for the relativity factor, to terms in a^5. We write this

$$\frac{S'(Z)}{S(Z)} = \frac{2\rho^2(2\rho+1)(2\rho+3)}{3(1+\rho)} \times \frac{1-(\rho+1)[(2/5)(1+0.106a^2+0.0105a^4)]}{1+(\rho-1)[(2/5)(1+0.106a^2+0.0105a^4)]}. \qquad (10)$$

This ratio is tabulated in Table I. The corrected relativity factor $S'(Z)$, rather than the perturbation value $S(Z)$, should be used in Eqs. (8) and (9).

Valence s electrons shield the inner s electrons from the nuclear charge to a slight extent.[16] The value of $\psi^2(0)$ for the inner s electrons is so large that even an extremely small fractional shielding produces a large decrease in $\psi^2(0)$. Crawford and Schawlow[16] calculated an approximate correction factor of 1.16 for this effect in the case of the $6s$ electron of Hg. About half of this effect arises from shielding of the $5s^2$ shell. Thus one might expect that this correction factor would not vary much among the heavy elements. This shielding effect is essentially independent of the chemical environment.

A shielding effect that varies with chemical environment is shielding of outer ns electrons by $(n-1)d$, ns, and np electrons. Brix and Kopfermann[17] estimate this effect as ~20% for $5d$ or $6s$

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[16] M. F. Crawford and A. W. Schawlow, Phys. Rev. **76**, 1310 (1949).

[17] P. Brix and H. Kopfermann, Rev. Mod. Phys. **30**, 517 (1958).

electrons shielding 6*s* electrons, and as ~10% for 6*p* electrons shielding 6*s* electrons.

In comparing Eqs. (8) and (9) with nuclear models it must be remembered that the shift really depends on the 2ρth moment of radial charge [Eq. (7)]. The quantity $\delta R/R$ refers to an equivalent uniform charge distribution and is used only for convenience.

III. CHEMICAL INFORMATION FROM ISOMER SHIFTS

The electronic factor in Eq. (9) is the only one which can be varied for a given isomeric pair. By varying this factor one may study the effects of environment on the electron density at the nucleus. Already a considerable amount of qualitatively new chemical information has emerged from such studies. We discuss below some applications of isomer shifts to (A) ordinary chemical compounds, (B) metals, and (C) intermetallic compounds. It should be noted that these distinctions, while customary, are somewhat artificial. Although the very simplest models that are used to describe these three types of solids make them appear to be quite different, there are also very basic similarities, such as a definite stoichiometry and well-defined chemical bond distances and angles. These similarities are manifest in the isomer shift, which does not behave very differently in metals and in compounds.

Table I. Relativity Factors.

Z	$S(Z)$[a]	$S'(Z)/S(Z)$[b]	$\psi^2_{ns}(0)$[c]	Z	$S(Z)$	$S'(Z)/S(Z)$	$\psi^2_{ns}(0)$
1	1.00	1.00	0.022	49	2.40	0.93	0.98
2	1.00	1.00		50	2.48	0.93	
3	1.00	1.00	0.016	51	2.56	0.93	
4	1.00	1.00		52	2.65	0.92	
5	1.01	1.00		53	2.75	0.92	0.17
6	1.01	1.00		54	2.85	0.92	0.21
7	1.02	1.00		55	2.95	0.91	0.19
8	1.03	1.00		56	3.05	0.91	
9	1.04	1.00		57	3.17	0.91	0.27
10	1.05	1.00		58	3.30	0.90	
11	1.06	1.00	0.051	59	3.44	0.90	
12	1.07	0.99		60	3.57	0.89	
13	1.08	0.99		61	3.71	0.89	
14	1.09	0.99		62	3.84	0.89	
15	1.10	0.99		63	3.99	0.88	0.43
16	1.12	0.99		64	4.18	0.88	
17	1.13	0.99		65	4.39	0.87	
18	1.15	0.99		66	4.59	0.87	
19	1.17	0.99	0.073	67	4.79	0.86	
20	1.18	0.99		68	5.00	0.86	
21	1.20	0.99		69	5.23	0.85	
22	1.22	0.99		70	5.49	0.85	0.54
23	1.24	0.99		71	5.71	0.84	
24	1.27	0.98		72	5.98	0.84	
25	1.29	0.98		73	6.26	0.83	
26	1.32	0.98		74	6.58	0.83	0.71
27	1.34	0.98		75	6.96	0.82	0.81
28	1.37	0.98		76	7.29	0.82	0.88
29	1.40	0.98	0.16	77	7.67	0.81	0.98
30	1.43	0.98		78	8.10	0.80	1.17
31	1.45	0.97		79	8.55	0.80	1.34
32	1.49	0.97		80	9.01	0.79	1.62
33	1.52	0.97		81	9.50	0.79	
34	1.56	0.97		82	10.1	0.78	
35	1.60	0.97	0.14	83	10.6	0.77	
36	1.64	0.96	0.17	84	11.2	0.77	
37	1.69	0.96	0.14	85	11.9	0.76	
38	1.73	0.96		86	12.6	0.76	
39	1.78	0.96		87	13.4	0.75	
40	1.83	0.95		88	14.1	0.74	
41	1.88	0.95		89	15.0	0.73	
42	1.93	0.95		90	16.0	0.73	
43	1.99	0.95	0.39	91	17.1	0.72	
44	2.05	0.94		92	18.2	0.71	
45	2.11	0.94	0.49	93	19.4	0.70	
46	2.18	0.94		94	20.7	0.69	
47	2.25	0.94	0.53	95	22.0	0.68	
48	2.32	0.94	0.76	96	23.6	0.67	

[a] 1% accuracy.
[b] 1% accuracy.
[c] Units of 10^{26} cm^{-3}. Values are for outer *s* electrons on free atoms, and are representative only. Accuracy is about 10%.

A. Isomer Shifts in Compounds

Since only the product of the electronic and nuclear factors is directly measurable, the first problem in interpreting the shifts for a given isomeric pair is the estimation of the relative importance of each factor. This must usually be done without the aid of any very rigorous theoretical guides because of the extreme complexity of the systems. In using some of the more empirical methods of chemistry it is well to remember that:

(1) Molecules and solids are not simply collections of atoms or ions. Although we often use atomic orbitals to discuss properties of electrons in molecules, this treatment is quite approximate, and its accuracy is difficult to assess.

(2) A study of the effect of variation of a chemical parameter is often subject, if made on only one or two compounds, to the criticism that the observed result was accidental. Thus it is always advisable to perform such studies systematically on several compounds.

Several isomer shifts in tin compounds are discussed below to illustrate the problems that arise in an analysis of this type. The original analysis of Sn^{119} shifts, from which this discussion does not differ importantly, was given by Boyle, Bunbury, and Edwards.[18] The shifts are plotted, in Fig. 2, against the electronegativity parameter for the ligand. This parameter was derived by Pauling from diatomic-molecule bond energies[19] and has been found to be strongly correlated with "ionic character," as deduced from electric dipole moments[20] and from quadrupole coupling constants,[21] of diatomic molecules. The data in Fig. 2, obtained by several groups,[18,22–26] are in good agreement for all the tetrahalides of Sn except SnI_4. A smooth curve can be drawn through the data for the tetrahalides and gray tin, suggesting that so long as the bond angles are the same (tetrahedral), the isomer shift is quite insensitive to whether the ligands are the same element or a different one. To calibrate the isomer shift scale in terms of electron density we reason as follows.

Fluorine is the most electronegative element and, more important, it is over two units more so than tin. Thus the Sn–F bonds in SnF_4 are probably quite ionic, with a net positive charge on the Sn. This does not indicate *a priori* that the electron density is lower on Sn in SnF_4 than, for example, in $SnBr_4$; the bonding must be understood in order to attach a sign to the change in $\psi^2(0)$. Atomic tin has the configuration $(4d^{10})$ $(5s^2)$ $(5p^2)$. In gray tin an s electron must be promoted to the p shell and the atom sp^3 hybridized. Thus the $5s$ electron density in Sn (gray) must be lower, by about half, than in free atomic tin, but higher than in SnF_4, in which Sn tends toward Sn^{4+} $(4d^{10})$. This might be regarded as a "normal" shift, in which $\psi^2(0)$ for tin is decreased as electrons leave the tin atom. "Reversed" shifts, in which $\psi^2(0)$ for tin decreases (increases) as electrons are added, (withdrawn) are well known in Fe^{57} and have re-

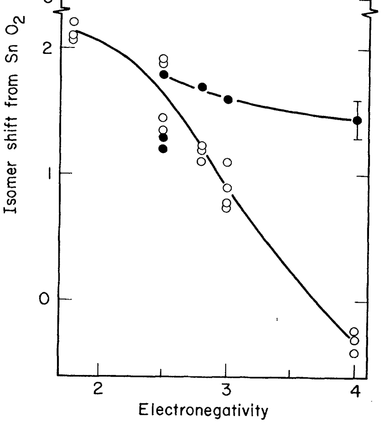

FIG. 2. Isomer shifts (relative to SnO_2) vs electronegativity for several tin compounds. The ligands (electronegativities) are: Sn(1.8), I(2.5), Br(2.8), Cl(3.0), F(4.0), and several organic complexes (filled circles). The electronegativity of carbon is 2.5. A curve connects four organic complexes of the type B_2SnX_2, where (B = butyl, X = a halogen), plotted against the electronegativity of X. The two filled circles at 2.5 are SnB_4(top) and tetraphenyl tin. The shifts above 3 mm/sec are those of stannous compounds; the rest are for stannic compounds. Note that only the stannic halides show a systematic large variation of shift with electronegativity. The shifts for compounds in which tin is bonded to carbon are all nearly the same. Several points are given for each of the tin halides (Refs. 18, 22–26).

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[18] A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, Proc. Phys. Soc. (London) **79**, 416 (1962).

[19] L. Pauling and D. M. Yost, Proc. Natl. Acad. Sci. U.S. **18**, 414 (1932); L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

[20] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1960), 3rd ed.

[21] For a recent discussion see C. H. Townes, in *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. 38, Part 1, p. 443.

[22] V. A. Bryukhanov, V. I. Goldanskii, N. N. Delyagin, L. A. Korytko, E. F. Makarov, I. P. Suzdalev, and V. S. Shpinel, Zh. Eksperim. i Teor. Fiz. **43**, 448 (1962) [English transl.: Soviet Phys.—JETP **16**, 321 (1963)].

[23] V. A. Bryukanov, N. N. Delyagin, A. A. Opaluko, and V. S. Shpinel, Zh. Eksperim. i Teor. Fiz. **43**, 432 (1962) [English transl.: Soviet Phys.—JETP **16**, 310 (1963)].

[24] A. Yu. Aleksandrov, N. N. Delyagin, K. P. Mitrofanov, L. S. Polak, and V. S. Shpinel, Zh. Eksperim. i Teor. Fiz. **43**, 1242 (1962) [English transl.: Soviet Phys.—JETP **16**, 879 (1963)].

[25] O. C. Kistner, V. Jaccarino, and L. R. Walker, in *Proceedings of the Second International Conference on the Mössbauer Effect* (John Wiley & Sons, Inc., New York, 1962), p. 264.

[26] M. Cordey-Hayes (private communication).

cently been invoked[27] to explain shifts in I^{129}. Here as $5p$ electrons are taken from $I^-(5s^25p^6)$, the $5s$ electrons are shielded less and $\psi^2(0)$ increases. Probably divalent Sn has reversed shifts in going from the covalent s^2p^2 to the ionic s^2 configuration.

From an electronegativity–ionic character correlation discussed below one may estimate that Sn in SnF_4 is ~85% ionic. An approximate value for $\psi_{5s}^2(0)$ for neutral Sn in the configuration $5s5p^2\ ns$ may be obtained by extrapolating the $5s$ curve in Fig. 1. This gives $\psi_{5s}^2(0) = 1.20 \times 10^{26}\text{cm}^{-3}$, with a probable error of a few percent.[28] The isomer shift of 2.48 mm/sec between SnF_4 and gray tin thus corresponds to an electronic factor of about $1.02 \times 10^{26}\text{cm}^{-3}$ (i.e., $0.85 \times 1.20 \times 10^{26}$. We have assumed that gray tin and SnF_4 have electron configurations equivalent, for these purposes, to sp^3 and $0.15(sp^3)$, respectively). A valence–electron shielding correction need not be made because it should not be very different from that in the atomic configuration. A correction factor of ~1.16 might be estimated for shielding of inner s electrons. This factor can be calculated, after Crawford and Schawlow,[16] although we have not done so here. We may now use Eq. (9), with $\nu = 0.25$, $E_\gamma = 23.8$, $S'(Z) = 2.30$, and a corrected electronic factor of $1.18 \times 10^{26}\text{cm}^{-3}$. From this we obtain $\delta R/R = 1.16 \times 10^{-4}$, in good agreement with the values obtained by Boyle *et al.*,[18] and by Cordey-Hayes[26] (1.1×10^{-4} and 1.2×10^{-4}, respectively). Although the final results agree, the three analyses differ somewhat in detail. For example, the assumption of purely ionic bonds in SnF_4 would have led to a $\delta R/R$ of 1.37×10^{-4} in this analysis. The final value of $\delta R/R$ is probably accurate to within about ±30%.

For the dihalides the data are more scattered, the crystal structures are unknown, and the bonding may be quite complicated. Still another estimate can be made of $\delta R/R$. Stannous chloride has the highest shift, falling at +4.7 mm/sec relative to SnO_2. The ionicity of the Sn–Cl bonds in $SnCl_2$ might naively be estimated as follows: Tin is usually considered about 0.1–0.2 units less electronegative as Sn^{2+} than Sn^{4+}. From Fig. 3 (discussed below) we can estimate the Sn–Cl bond in $SnCl_4$ as ~42% ionic. This agrees very well with Schawlow's estimate of 38% deduced from quadrupole coupling data on the chlorine nucleus.[29] Correcting for the smaller electronegativity of Sn^{2+} (using the slopes of the curves in Fig. 3), we might say that the stannous chloride Sn–Cl bonds were ~50% ionic. Then completely ionic $Sn^{2+}(5s^2)$ would fall, by extrapolation, at ~ +7.3 mm/sec, or 5.2 mm/sec from gray tin. This estimate for the shift accompanying the gain of a $5s$ electron ($sp^3 \rightarrow s^2$) in going from gray tin to Sn^{2+} disagrees badly with the above estimate of a shift of −2.9 mm/sec on losing a $5s$ electron ($d^{10}sp^3 \rightarrow d^{10}$) in going from gray tin to Sn^{4+}, and would yield a value of $\delta R/R$ 80% higher than the above estimate.

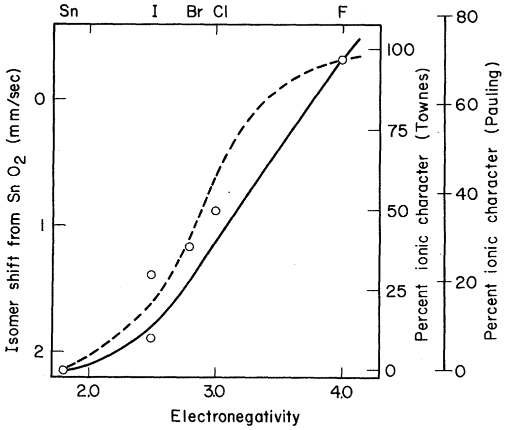

FIG. 3. Isomer shifts vs electronegativity for stannic halides. The solid (dashed) curves are after those of Pauling (Ref. 20) [Townes (Ref. 21)] for diatomic alkali halides. The curves were fitted at gray tin and SnF_4.

Fortunately this discrepancy is only apparent. The electronegativity is a parameter that can safely be used only in discussing an *isomorphous* series of compounds, in which the bonding may vary in ionicity, but not in bond type. Stannous chloride is probably almost completely ionic, according to other chemical evidence. For example, molten $SnCl_2$ exhibits electrolytic conductivity. Molten $SnCl_4$ does not.[30] Thus a better estimate of the isomer shift accompanying the change ($sp^3 \rightarrow s^2$) is +2.6 mm/sec, only 10% different from the shift estimated from the stannic compounds. One can, of course, turn the argument around and use the $SnCl_2$ shift as an argument for the ionicity of this compound.

In Fig. 3 are plotted the isomer shifts for gray tin and the stannic fluorides. Two curves are drawn through the data, representing percent ionic character vs electronegativity difference, after Pauling[20]

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[27] H. DeWaard, G. De Pasquali, and D. Hafemeister, Phys. Letters **5**, 217 (1963).

[28] Note that this *agrees* with the value of 1.5×10^{26} given for Sn IV by Boyle *et al.*, if the 20% shielding for two $5p$ electrons is taken into account. We use our shielded value throughout, obviating the necessity of shielding corrections.

[29] A. L. Schawlow, J. Chem. Phys. **22**, 1211 (1954).

[30] W. Hückel, *Structural Chemistry of Inorganic Compounds*, (Elsevier Publishing Company, Inc., Amsterdam, 1950), Vol. 1, p. 335.

and Townes.[21] The data favor neither curve (nor should they), but are in reasonable accord with both. To the extent that the curves and the data agree, this constitutes an independent indication that the concept of percent ionic character has some fairly general empirical significance. It should be emphasized that isomer shifts are independent in that they measure primarily the *s*-electron density, in contrast to electric dipole moments (measuring *s*- and *p*-electron distribution) and quadrupole coupling constants (measuring *p*-electron unbalance) from which the curves were derived. Of course we are also studying bonds in AB_4, rather than diatomic, molecules. It is gratifying that estimates of ionic character in the stannic halides agree well with Schawlow's estimates, which were deduced from quadrupole coupling constants of the halides.

Few isotopes are likely to yield as readily to analysis as did Sn^{119}. Often, however, we are able to draw chemical conclusions that would have been only conjectures without isomer shifts. An illustration is provided by the shifts in Eu^{151}. Atomic and ionic Eu have the configurations EuI $4f^7 6s^2$, EuIII $4f^7$, EuIV $4f^6$. One might expect these configurations to correspond, respectively, to metallic Eu, divalent, and trivalent Eu compounds, but the solid state isn't this simple.

We might more accurately represent the electron densities in these three oxidation states as $4f^7 5s^2 6s^x$, $4f^7 5s^2 6s^y$, and $4f^6 5s^2$. The $5s^2$ shell is written explicitly because this shell is shielded substantially from the nucleus by the $4f$ shell, and in going from $4f^7$ to $4f^6$ a substantial change in this shielding is produced, leading to an important contribution of the $5s$ electrons to the isomer shifts. In fact, the shift in the metal (−0.82 cm/sec) falls between EuO (−1.1 cm/sec) and Eu_2O_3 (zero),[31] indicating that x is greater than y. The fact that the EuO shift is not as large as that in some Eu^{2+} compounds indicates that $y > 0$. A detailed analysis of shifts together with internal fields gives $x \approx 1$. Coulson *et al.*[32] have studied bonding in some Group II–Group VI compounds and have found that charges of +0.5 may be associated with the cations. In the light of these calculations, it is perhaps not surprising if EuO is not completely ionic.

An isotope for which the sign of the calibration isn't established is Au^{197}. In Fig. 4 the isomer shifts, relative to platinum, for several gold halides[33,34] are displayed against electronegativity. The general trend is toward negative velocities with increasing ligand electronegativity. The aurous halides probably are *sp* hybridized, leading to "normal" shifts, and suggesting that electron density on Au increases with increasing isomer shift. The bonding in auric halides is not understood, but it seems probable that the Au atom has more $5p$ electrons in $AuCl_3$ than in AuCl. The small component of a relativistic $p_{1/2}$ electron is *s*-like, and the $6p$ shell contribution to $\Sigma\,\psi^2(0)$ is approximately $(\alpha Z)^2 = 0.3$ times that of the $6s$ shell. The shift from AuCl to $AuCl_3$ may arise largely from the *p* electrons, although this can only be decided when the hybridization of the auric halides is understood.

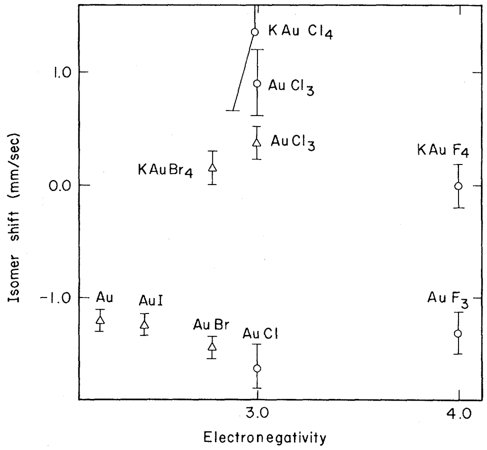

FIG. 4. Isomer shifts in several gold compounds, relative to a Au-in-Pt source, from Refs. 33 and 34.

Iron-57 isomer shifts have been measured in many compounds and only a few general features are mentioned here. For ionic configurations in which the electrons of iron follow Hund's rule, the isomer shifts are the reverse type. The $3s$ electron density is increased as $3d$ electrons are withdrawn from iron, thereby lessening their shielding effect.[35] In spin-paired complexes $3d$ electrons may be delocalized by d_π bonding. As the strength of d_π bonding increases (on changing ligands), the shielding by $3d$ electrons is decreased and again the $3s$-electron contribution

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[31] R. B. Frankel, H. H. Wickman, and D. A. Shirley (unpublished data).

[32] C. A. Coulson, L. B. Redei, and D. Stocker, Proc. Roy. Soc. (London) **A270**, 357 (1962).

[33] R. W. Grant, D. A. Keller, and D. A. Shirley (unpublished data).

[34] L. D. Roberts, H. Pomerance, J. O. Thomson, and C. F. Dam, Bull. Am. Phys. Soc. **7**, 565 (1962).

[35] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).

to $\psi^2(0)$ goes up. Danon has analyzed the isomer shifts for several iron complexes on this basis.[36]

B. Metals

It is possible to measure the contribution of outer s electrons to $\psi^2(0)$ in metals using isomer shifts, but rather careful calibration with compounds is first necessary. It has been found that the 4s electron density in metallic iron is approximately equal to that from one free-atom 4s electron. Gray tin has a 5s electron density about equal to that of one 5s electron, as does white tin. As discussed above, europium has the equivalent of about one 6s electron. With careful measurements and more sophisticated interpretations it should be possible to improve the accuracy of these figures and to extend them to several other metals.

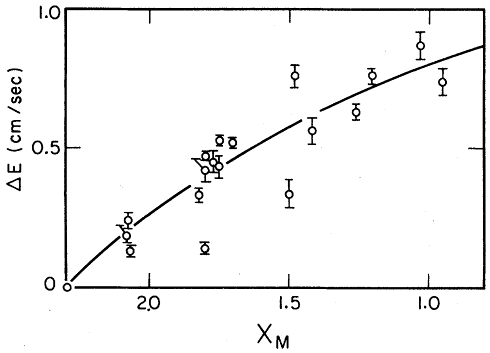

Fig. 5. Isomer shifts relative to a gold metal absorber, of sources of gold dissolved in various metals, in very dilute solution. After Barrett *et al.* (Ref. 37).

Another interesting area is the study of electron densities at impurity atoms in metals. The assumption has often been made that impurity atoms have substantially the same "conduction" electron densities (with possibly a slight renormalization for cell size) in other hosts as they do in the pure metals. However, Barrett *et al.*[37] have shown that the isomer shifts for Au^{197} in nineteen metallic hosts are very substantial, corresponding to the transfer of up to 0.5–1.0 6s electron in such electropositive hosts as Li and Ca. In fact, the shifts are strongly correlated with electronegativity, indicating the existence of specifically chemical effects in metals (Fig. 5). More data along these lines might add substantially to the understanding of the outer electrons on impurities in metals.

C. Intermetallic Compounds

When two metals differ substantially in electronegativity they often form stoichiometric compounds rather than solid solutions. This is attributed to the transfer of electrons in the formation of chemical bonds. These bonds may be quite similar to those in molecules, although there are few data available, apart from "bond lengths" and "bond angles," with which to decide.

Pauling has stated a "principle of electroneutrality" for intermetallic compounds, according to which bond polarity is compensated by transfer of electrons from the more electronegative metal to the less electronegative one and the net charge on each atom is zero.[20] Coulson *et al.*[32] have performed molecular-orbital calculations on intermetallic compounds and find that atoms of the more electropositive metal always have a net positive charge. It should be possible to decide this point with isomer shifts, although great care must be taken to decide what a given theory predicts about s electrons. A large shift of 0.7 cm/sec was found for Au^{197} in Al_2Au, for example,[37] indicating transfer of ~0.4 or more 6s electron. While it is tempting to conclude that this compound is somewhat ionic, this is not established. Future isomer shift work will almost certainly yield insights into the nature of intermetallic bonding.

IV. NUCLEAR STRUCTURE INFORMATION FROM ISOMER SHIFTS

Interpretation of isomer shifts in terms of nuclear structure is rather difficult because one is given only one datum for an isomeric pair, and even this datum is usually not known to better than 50% accuracy. Nuclear models are often too crude to provide sufficient sensitivity to details such as differential 2ρth moments of radial charge, and there are enough models available to fit almost any isomer shift data. With all these qualifications isomer shifts can still yield very useful information in cases where a particular nuclear model is fairly well established. It is possible, for example, to obtain a measure of the mean-square deformation for vibrational nuclei[18] and thus set a constraint on a parameter in the theory.

The charge distribution for a nucleus in the ground state may be written as

$$P(\theta,\varphi) = \sum_{L,M} a_{LM} R_L(r) Y_{LM}(\theta,\varphi) .$$

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[36] J. Danon, J. Chem. Phys. **39**, 236 (1963).

[37] P. H. Barrett, R. W. Grant, M. Kaplan, D. A. Keller, and D. A. Shirley, J. Chem. Phys. **39**, 1035 (1963).

Clearly a quantity which measures any radial moment will depend on the a_{LM}. Thus we can only measure some function of all of these parameters and comparison of theory with experiment becomes a very implicit process. Fortunately only the $L = 0$ and $L = 2$ terms need usually be considered as making a large contribution to $\Delta\langle r^{2\rho}\rangle$. There are four nuclear models to which isomer shifts may be relevant. These models are, of course, applicable in different parts of the periodic table. For a particular isotope only one of these models will be applicable, although it is not always easy to decide between two. The models are:

(1) *The extreme single-particle shell model.* Here the isomeric states are assumed to differ in configuration by only one nucleon. (It is clear that only the configuration, and not the type of coupling, is important, because only the radial integrals contribute to radial moments.) For the cases of interest the second moment gives a very good approximation to $\langle r^{2\rho}\rangle$; for uniform charge distribution the correction factor is $5/(2\rho + 3)$. (This is the ratio of $\langle X^{2\rho}\rangle/\langle X^2\rangle$, where $x = r/R$.) Even for Au^{197} this correction is less than 10%. For the "top slice" model,[4] with the charge concentrated on the nuclear surface, the ratio is unity. Inner nucleons will have larger correction factors, but they are not involved in transitions between the lowest two isomeric states. In the harmonic-oscillator approximation $\Delta\langle r^2\rangle$ between two states in the same oscillator shell vanishes; $\Delta\langle r^{2\rho}\rangle$ does not. The oscillator potential however, is only a good approximation for light nuclei, for which $2\rho - 2$, and consequently $\Delta\langle r^{2\rho}\rangle$, are very small.

These shell-model calculations are only applicable to odd-proton nuclei. For odd-neutron nuclei the radial charge moment differences will be reduced by a factor of $\sim Z/A^2$ (the recoil contribution) in this approximation. Using very approximate reasoning it is easily shown[38] that core polarization may be estimated by attributing an "effective charge" of order $\approx +Ze/A$ to the odd neutron. One might then proceed to evaluate $\Delta\langle r^{2\rho}\rangle$ for the neutron as above and treat $\approx Z/A$ as a correction factor. Such a procedure is not very convincing, although it should usually give the right sign, because it is used only in lieu of a configuration-mixing calculation or another more comprehensive theoretical model which predicts other properties as well. The effective charge for isomer shifts will not be simply related, in general, to the "effective charge" for $E2$ transitions, because one involves diagonal, and the other off-diagonal, matrix elements of r^2, and the basis functions are unknown. It is preferable to use one of the three models below. It should be noted from the examples given below that real isomeric pairs are very rarely simple enough to justify use of the simple shell model as described above. It is curious that the effective charge approximation gives a value of $\delta R/R$ of the right sign for Sn^{119}, Te^{125}, and Hg^{197}. In the first two cases the magnitude is too large by factors of 2 to 3. For Hg^{197} the magnitude of $\delta R/R$ is a factor of 6 too high, and the measured quadrupole moment of the excited state is not large enough to account for the shift. These cases and others are discussed in detail below.

(2) *The collective nuclear model.* In the region of the periodic table where nuclear deformation is large and well established, the nuclear surface can be approximated by an equation of the form

$$R'(\theta) = R[1 + \alpha P_2(\cos\theta)] .$$

Here $P_2(\cos\theta)$ is a Legendre polynomial and R and α are constants, though the isomeric states may have different values of α. The deformation can contribute substantially to the isomer shift even though the nuclear volume may not change because, for $\alpha > 0$, the polar regions contribute heavily to $\langle r^2\rangle$ (or $\langle r^{2\rho}\rangle$). This larger contribution for a deformed nucleus more than compensates for the smaller contributions from the equatorial regions for a moment as high as 2ρ. It is easily shown that the ratio of (the total shift in electron energy from deformation) to (the total shift due to finite nuclear volume) is α^2 in the nonrelativistic limit. Thus one takes $\delta(\alpha^2R^2) = 2\alpha R^2\delta\alpha$ rather than $\delta R^2 = 2R^2(\delta R/R)$ in deriving Eq. (1), and the nuclear factor $\delta R/R$ is replaced by $\alpha\delta\alpha$. For the reasonable values $\alpha = 0.20$, $\delta\alpha = 0.01$ the nuclear factor becomes 0.002 as opposed to 10^{-3}–10^{-4} for spherical nuclei. It is worth noting that isomer shift experiments are probably quite feasible in the heavy rare earths and refractories, even with very large linewidths. Shifts of 10 or more cm/sec seem quite possible in some cases.

Wilets, Hill, and Ford[39] have studied deformation effects on isotope shifts for relativistic electrons. They found the ratio of this contribution to that of the normal volume effect to be, in perturbation theory approximation,

$$\rho\left(\frac{2\rho+3}{5}\right)\alpha^2\left[1 + \frac{2}{21}(2\rho+3)\alpha\right],$$

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[38] D. A. Shirley, in *Proceedings of the Second International Conference on the Mössbauer Effect* (John Wiley & Sons, Inc., New York, 1962), p. 258.

[39] L. Wilets, D. L. Hill, and K. W. Ford, Phys. Rev. **91**, 1488 (1953).

to terms in α^3. Thus we may take account of deformation by replacing $\delta R/R$ in Eqs. (8) and (9) by

$$\frac{2\rho+3}{5}\alpha\delta\alpha\left[1+\frac{1}{7}(2\rho+3)\alpha\right].$$

Bodmer has also discussed this problem.[40] Boyle has suggested the very interesting possibility of studying $\Delta\alpha^2$ for the two lowest members of a ground-state rotational band.[41]

(3) *The pairing model.* Kisslinger and Sorensen[42] have treated pairing forces in single-closed-shell spherical nuclei such as tin, and one can calculate, using their results, the mean-square amplitude of zero-point vibration of the core. Physically this corresponds to a time-dependent deformation α, and an angle θ which is undefined because the core no longer has a symmetry axis of deformation.

Some contribution to α^2 may still arise from the quadrupole moment. This must be considered separately. In some cases, as in the case of Sn^{119} which Boyle *et al.*[18] analyzed on this model, the quadrupole moments may be known and their contribution to $\Delta\alpha^2$ can be evaluated.

(4) *The core-excitation model.* In an odd-A nucleus an alternative to particle excitation is collective excitation of the even–even core. Braunstein and de-Shalit have recently analyzed Au^{197} on this basis[43] and several isotopes of Cu, Hg, and Tl may show core excitation. The model is quite empirical, and the nature of the excitation is not understood. It is, however, possible in some cases to calculate the quadrupole moment of the *core* from $E2$ transition probabilities. The isomer shift measures the time average of $\Delta\alpha^2$, however, and one must be careful in comparing data with this model to account for zero point vibrational contribution to α^2.

Several isomeric pairs are discussed separately below.

Fe^{57}. Walker, Wertheim, and Jaccarino[35] obtained $\delta R/R = -1.8\times10^{-3}$ for the 14.4-keV ground-state isomeric pair. This nucleus is very difficult to understand theoretically, as it doesn't fit any simple model well. Perhaps the large value of $\delta R/R$ can be attributed to zero-point oscillation.

Sn^{119}. Boyle *et al.*[18] have analyzed this case. They found $\delta R/R = 1.1\times10^{-4}$ and attributed this to zero-point oscillation, showing that the pairing theory of Kisslinger and Sorensen fits the data very well. They obtained a value of $\Delta\beta^2 = +6\times10^{-4}$ for the differential mean-square time-averaged oscillation amplitude. This corresponds to $\Delta\alpha^2 = 2.4\times10^{-4}$.

It is interesting to see what a crude "effective charge" calculation gives for $\delta R/R$. Using second radial charge moments obtained by multiplying the finite square well second radial moments of Eisinger and Jaccarino[10] for a $3s_{1/2}$ and a $2d_{3/2}$ neutron by Ze/A, we find $\delta R/R \cong 2\times10^{-4}$.

Te^{125}. The shifts have not yet been carefully calibrated, but we can calibrate roughly. Buyrn and Grodzins[44] found a shift of -1.5 mm/sec for a tellurate absorber, relative to a tellurium source. If these two environments differ by about one $5s$ electron per Te atom the situation is not very different from Sn^{119}, and we may calculate $\delta R/R \approx +0.7\times10^{-4}$. Violet *et al.* have given the quadrupole moment of the 35.5-keV state as 0.20 b.[45] If this represented only deformation and there were no zero-point core vibration, this would lead to $\Delta\alpha^2 \cong +19\times10^{-4}$ or $\delta R/R \cong +9\times10^{-4}$. Probably zero-point vibration is important in this case, however. Unlike tin this nucleus does not have a single closed shell, and a pairing calculation is quite involved. An "effective charge" estimate gives $\delta R/R \cong 2\times10^{-4}$.

I^{129}. De Waard, De Pasquali, and Hafemeister have reported large isomer shifts in iodine compounds and have concluded that $\delta R/R$ is positive.[27] The shell model may be appropriate here, although, as noted by De Waard *et al.*, it is necessary to invoke "hole" states to obtain the right sign for $\delta R/R$. If the range of the observed shifts (from $\mathrm{KIO_3}$ to $\mathrm{KIO_4}$), which is 0.40 cm/sec, is taken to correspond approximately to the transfer of ($\leqslant 1$) $5s$ electron, one can derive a lower limit of -1×10^{-4} for $\delta R/R$. If the isomeric states differed by a $d_{5/2}-g_{7/2}$ proton pair, $\delta R/R$ would be approximately -3×10^{-3}, using the moments given by Eisinger and Jaccarino.[10]

Eu^{151}. Barrett and Shirley[46] found a large shift in Eu metal, relative to $\mathrm{Eu_2O_3}$ and interpreted this shift using an approximate formula. In light of the even larger shifts in EuO relative to $\mathrm{Eu_2O_3}$ it is worthwhile to re-interpret the shifts. The calibration in terms of $\psi^2(0)$ is still not known accurately, but a good estimate is that 1 cm/sec is roughly equivalent to one

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[40] A. R. Bodmer, Proc. Phys. Soc. (London) **A67**, 622 (1954).

[41] A. J. F. Boyle and H. E. Hall, Rept. Progr. Phys. **25**, 441 (1962). This article gives an interesting discussion of isomer shifts.

[42] L. S. Kisslinger and R. A. Sorensen, Kgl. Danske Videnskab. Selskab Mat. Fys. Medd. **32**, No. 9 (1960).

[43] A. Braunstein and A. de Shalit, Phys. Letters **1**, 264 (1962).

[44] A. E. Buyrn and L. Grodzins, Bull. Am. Phys. Soc. **8**, 43 (1963).

[45] C. E. Violet, R. Booth, and F. Wooten, Phys. Letters **5**, 230 (1963).

[46] P. H. Barrett and D. A. Shirley, Phys. Rev. **131**, 123 (1963).

$6s$ electron, with $\psi^2(0) = 0.4 \times 10^{26}$. From Eq. (9), we find $\delta R/R = +5 \times 10^{-4}$. In this odd-proton nucleus the $\frac{7}{2}+$ 21.7-keV state and the $\frac{5}{2}+$ ground state would be the $g_{7/2}$ and $d_{5/2}$ proton states in the nuclear shell model, but Eu^{151} is near the collective region, and the Nilsson orbitals $\frac{7}{2}+(404)$ and $\frac{5}{2}+(402)$ may provide a better description. These orbitals have radial moments which differ little from the shell-model states at small deformations, however, and taken by themselves they give a much larger value for $\delta R/R$.

A possible explanation of the smallness of $\delta R/R$ is that the 21.7-keV state is essentially undeformed and that a contribution to the shift from $\Delta\alpha^2$ counteracts that from $\delta R/R$ due to the odd proton. We could write

$$\left(\frac{\delta R}{R}\right)_{\mathrm{exp}} = \left(\frac{\delta R}{R}\right)_{\mathrm{particle}} + \frac{1}{2}\,\Delta(\alpha^2)_{\mathrm{core}}.$$

Here the observed $\delta R/R = +5 \times 10^{-4}$ is the sum of the particle contribution and that due to deformation. Using the finite-square-well values of $\langle r^2\rangle$ for a $d_{5/2}$ and a $g_{7/2}$ proton ($\langle r^2\rangle = 0.58\ R^2$ and $\langle r^2\rangle = 0.80\ R^2$, respectively), we find $(\delta R/R)_{\mathrm{particle}} = +0.0030$. Thus $\Delta\alpha^2 = -5 \times 10^{-3}$. If the excited state is spherical, $\alpha_1 = 0$ and $\alpha_0 = 0.07$. In fact, the ground-state deformation is $+0.08$.[47]

Au^{197}. An early interpretation of the isomer shifts in this nucleus was given by Shirley using the shell model.[47] While approximate agreement with experiment was obtained with the shifts then available, the much larger shifts reported by Barrett *et al.*[37] seemed to render any interpretation based on the single-particle shell model untenable. An approximate expression for isomer shift, without the relativistic correction factors, was used by these workers to derive radial moments. With the relativity factor properly accounted for, we find the results once again are in agreement with shell-model estimates. To obtain $\delta R/R$ from Eq. (9) we assume that 1.5 cm/sec is equivalent to a transfer of the $6s$ electron, with $\psi^2(0) = 1.4 \times 10^{26}$. This yields $\delta R/R = +3 \times 10^{-4}$. If the isomeric states differed by a $2d_{3/2} - 3s_{1/2}$ proton transition, a $\delta R/R$ of up to 7×10^{-4} could be obtained from the nuclear potential giving the largest shift, a finite square well.

This nucleus is very difficult to understand theoretically, but the core excitation model[43] seems to fit it rather well. Solving for $\Delta\alpha^2 = 2\delta R/R$, we find $\Delta\alpha^2 = +6 \times 10^{-4}$. We may attribute this change in mean-square deformation to excitation of the core. From the entire ground-state quadrupole moment of $+0.60$ b we may calculate $\alpha_0 = +0.065$ in the strong-coupling limit. Combining this with $\Delta\alpha^2$ gives $\alpha_1 = +0.069$ for the excited core. This would correspond to a deformation parameter $\delta = +0.1$ or to an intrinsic quadrupole moment of $Q_0 \cong 3$ b for the excited core. Of course, the shifts in α^2 may arise from differences in zero-point oscillation rather than from static quadrupole moments.

Hg^{197}. Isomeric shifts were first observed in this nucleus by Melissinos and Davis,[48] using optical spectroscopy. Lardinois[49] has suggested that the experimental shift of 0.021 cm^{-1} can arise from the known quadrupole moment of the excited state, $Q_{13/2} = 1.5$ b, if any similar contribution from the ground-state core is neglected. This assumption is questionable in view of the complexity of nuclei in this region, and zero-point oscillation may not be negligible.

TABLE II. Nuclear factors.

Isotope	Isomeric energy, keV	$\delta R/R$
Fe^{57}	14.4	-1.8×10^{-3}
Sn^{119}	23.8	$+1.2 \times 10^{-4}$
Te^{125}	35.5	$\sim +.7 \times 10^{-4}$
I^{129}	26.8	-1×10^{-4} or larger
Eu^{151}	21.7	$+5 \times 10^{-4}$
Au^{197}	77.5	$(+)\,3 \times 10^{-4}$
Hg^{197}	297	$+1.6 \times 10^{-4}$

From the experimental shift of 0.021 cm^{-1} arising from the difference of one $6s$ electron we obtain, using Eq. (8), $\delta R/R = +1.6 \times 10^{-4}$. This corresponds to $\Delta\alpha^2 = 3.2 \times 10^{-4}$. Thus if we assume, with Lardinois, that $\alpha_{13/2} = 0.032$ (i.e., that the excited state α arises only from the quadrupole moment), we obtain $\alpha_{1/2}^2 = 7.0 \times 10^{-4}$, or $\alpha_{1/2} = 0.026$. This is probably to be interpreted as zero-point vibration. We have used a value of $\psi_{6s}^2(0) = 1.6 \times 10^{26}$ in deriving these results. This is somewhat higher than the value used by Lardinois. An effective charge of Ze/A for the odd neutron would give a $\delta R/R$ of $\sim +10^{-3}$, much larger than the experimental value.

The derived values of $\delta R/R$ are tabulated in Table II.

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[47] D. A. Shirley, Phys. Rev. **124**, 354 (1961).

[48] A. C. Melissinos and S. P. Davis, Phys. Rev. **115**, 130 (1959).

[49] J. Lardinois, Nucl. Phys. **15**, 522 (1960).

V. CONCLUSIONS

(1) The theory for isomer shifts is essentially that for isotope shifts, and is well understood. Relativistic effects are very important in isomer shifts for heavy elements.

(2) Qualitative or semiquantitative chemical information, including the validity of "ionic character" in certain bonds, is readily available from isomer shifts. Relative values of $\Delta\psi^2(0)$ may be determined with high accuracy. Absolute values are unlikely to be obtainable to better than about 10% even in the most favorable cases and most cases will probably be considerably less accurate.

(3) Isomer shifts offer a useful method for obtaining conduction electron densities in metals. They should also prove very useful in studying bonding in intermetallic compounds.

(4) Derivation of the nuclear parameter $\delta R/R$ from isomer shifts can be quite useful in understanding nuclear structure, although great care must be taken in the interpretation. This parameter is most useful in cases where the level structure is already fairly well understood.

(5) Very large isomer shifts seem quite likely in the heavy rare earths and refractories. The large $\psi^2(0)$ from $6s$ electrons, the large relativity factors, and large and varying nuclear deformation combine to enhance the shifts here.

CONTRIBUTED PAPERS FOR SESSION I

Electric Quadrupole Splittings in Ferrous Compounds[*]

R. Ingalls,[†] *Carnegie Institute of Technology*

The various problems associated with interpretation of electric quadrupole splittings, obtained from Mössbauer experiments, are discussed. An attempt is made to express the electric field gradient tensor in ferrous compounds in terms of the d_ϵ energy splittings and the covalency factor, which roughly governs the values of $\langle r^{-3}\rangle$ and spin-orbit coupling constant, λ. In doing so, a detailed study of the problem, ferrous ion + ligands, is somewhat sidestepped. At the same time, however, one gains some insight concerning the behavior of the quadrupole splitting as a function of axial and rhombic crystalline field strengths and temperature. As a result of this study, one obtains an estimate of the quadrupole moment of Fe^{57m}, which agrees with that obtained from ferric Mössbauer experiments. Estimates, based upon Mössbauer results, are also made of the d_ϵ energy splittings in, $FeSiF_6\cdot6H_2O$, $FeSO_4\cdot7H_2O$, $FeC_2O_4\cdot2H_2O$, $Fe(NH_4SO_4)_2\cdot6H_2O$, $FeSO_4$, $FeCl_2\cdot4H_2O$, and FeF_2.

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Electric Field Gradient Measurements in Ferrous Compounds[*]

Peter Zory, *Carnegie Institute of Technology*

The nuclear electric field gradient (EFG) tensor parameters[1] in paramagnetic ferrous compounds may be adequately determined by transmitting monoenergetic, unpolarized Mössbauer radiation through "thin" single crystal absorbers. The EFG asymmetry N and the Euler angles connecting the EFG principal axes with the crystal axes are obtained from measurements of the orientation dependent ratio of the two absorption peak areas. The parameter q is then determined from the observed splitting. The analysis of $FeCl_2\cdot4H_2O$ is presented.

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[*] T. P. Das and E. L. Hahn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Suppl. 1.

[1] Supported by the Office of Naval Research and the National Science Foundation.

Determination of the Sign of the Electric Field Gradient in Randomly Oriented Samples

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If single crystals are available, the determination of the sign and magnitude of the electric field gradient at Mössbauer nuclei is relatively straightforward. When the γ-ray direction is along the direction of the principal axis of the EFG tensor, then the intensity of the $\frac{3}{2}$ line is 3 times that of the $\frac{1}{2}$ line; in a perpendicular direction this ratio changes to 0.6. If only powdered crystals are available, and the direction of observation is therefore random with respect to the axis of the EFG, the amplitude of the two quadrupole peaks become equal (unless the thermal vibrations are markedly anisotropic) and other methods must be employed to determine the sign of q.

We have calculated the spectra resulting from the application of a magnetic field, both parallel and perpendicular to the γ-ray direction, to a randomly oriented sample with an axially symmetric EFG. We have chosen the size of the EFG to correspond to a total splitting (2ϵ) of 2.4 mm/sec; the magnetic field strengths are 16, 42, and 84 kOe. Our experimental linewidths have been folded into the computation.

The results indicate that the shapes of the two quadrupole peaks become distinguishable at less than 50 kOe applied field.

Mössbauer Study of Fe^{2+} in Ionic Crystals

Kazuo Ôno and Atsuko Ito, *University of Tokyo*

The data obtained in several ionic divalent iron crystals are listed in Table I. From obtained values of these parameters, we will discuss the ground states of Fe^{2+} in these crystals. It is noted that

(1) The ratio $q(FeSiF_6\cdot6H_2O)/q(FeCO_3)$ is $=1.8 \approx -2.0$. This confirms that the ground state of $FeSiF_6\cdot6H_2O$ is an orbital singlet (ψ_0), while that of $FeCO_3$ is an orbital doublet $(\frac{2}{3})^{\frac{1}{2}}\psi_{-2} + (\frac{1}{3})^{\frac{1}{2}}\psi_1,\ (\frac{2}{3})^{\frac{1}{2}}\psi_2 = (\frac{1}{3})^{\frac{1}{2}}\psi_{-1})$.

(2) Two forbidden lines were observed in $Fe_3(PO_4)_2\cdot8H_2O$ because of the existence of the large electric quadrupole interaction perpendicular to the internal magnetic field.