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**Author**
Shugart, Howard A.

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Howard A. Shugart

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DIRECT MEASUREMENTS OF SPINS OF RADIOACTIVE NUCLEI

Howard A. Shugart

Department of Physics and Lawrence Radiation Laboratory,
University of California, Berkeley

## Abstract

This article contains a brief review of the principal optical and radio-frequency spectroscopic methods for determining spins of ground and long-lived-nuclear states. Some of the advantages and disadvantages of these techniques for radioactive isotope investigations are explained. A survey of the required sample sizes has been made to indicate the relative sensitivities of the various methods.

## Introduction

At present the nuclear spins of about 75 stable and 231 long-lived radioactive isotopes have been determined by techniques which produce a so-called direct measurement of the spin.[1] A breakdown of these measurements is given in Table I, where a classification into zero and nonzero spin has been made. This array of information on 406 isotopes has proved useful in the development of nuclear physics in several ways. These spins provide test data for models of nuclear ground states as well as a basis for level assignments in nuclear spectroscopy.

Although limitations will become clearer as the methods are described later, the concept of a "direct spin measurement" should be explored. In the generally accepted context these words refer to measurements obtained from techniques that yield a unique and unambiguous value for the nuclear spin, I, for a given energy level. The methods that have produced the bulk of these known spins include atomic-beam magnetic resonance, optical spectroscopy, paramagnetic resonance (electron spin resonance), microwave spectroscopy, nuclear magnetic resonance, and optical double resonance. Because it is the purpose here only to treat the most prolific methods, other techniques capable of ascertaining ground-state spins are not discussed. Figure 1 is a histogram of the number of spins obtained from these methods. Because a given

spin has often been observed by more than one method, the total number represented in the histogram is larger than the 406 individual determinations mentioned earlier. In addition the histogram shows the number of nuclear magnetic moments, $\mu$, and nuclear electric quadrupole moments, Q, obtained by these techniques. It is clear from the histogram that the facility of obtaining I, $\mu$, and Q varies from one technique to another. It is also true that the sensitivity and the accuracy of obtaining these quantities likewise varies from one technique to another.[2] Some of these aspects will be explored later.

As a general remark, it is important to recognize that none of the techniques considered here measures the nuclear spin very directly. Rather, in all cases the spin is deduced from observations by way of a theory of the system under investigation. The experiments provide signals that can be correlated with the presence of the sample in the measuring apparatus. These signals must then be interpreted and identified. This process involves, in all cases treated here, a well developed and tested theory of the observed system and a thorough knowledge of the interaction of the system with the measuring apparatus. When the results of a measurement are compared with the predictions of a theory, values of the parameters in the theory are obtained. The nuclear spin is frequently such a parameter.

The order of discussing various methods for determining spins has been chosen to be that of increasing generality, which seems well correlated with a decrease in sample size and a decrease in the restrictions on the system under investigation. Preliminary to discussing the individual methods, it is important to understand the properties of angular momentum. In the quantum theory of angular momentum a nucleus may possess a total angular momentum of $\sqrt{I(I+1)}\ \hbar$, where I is an integer or half integer and $\hbar$ is Planck's constant divided by $2\pi$. For different orientations this total angular momentum has $2I + 1$ measurable projections along a single axis in space. These measurable angular momentum components $m_I \hbar$ are labeled by the angular momentum projection quantum numbers $m_I$, which may assume the values I, I-1, I-2, .... -I+1, -I. Theory allows I and $m_I$ to be specified (measured) simultaneously. The nuclear spin, I, is obtainable from a knowledge of the largest measurable component of angular momentum, max $m_I \hbar = I\hbar$, along one direction or from a knowledge of the number $(2I+1)$ of possible projections. Thus the determination of a spin frequently results from counting the angular momentum components.

NUCLEAR SPIN-PARITY ASSIGNMENTS

## The Nuclear Magnetic Resonance Technique

Nuclei with $I \geq 1/2$ generally exhibit a magnetic dipole moment, of value $\mu$, which is the maximum measurable component along one direction. Because the coupling between nucleons by nuclear forces is far stronger than the perturbations on the nucleons by applied laboratory magnetic fields, it is possible to express the magnetic moment as proportional to the nuclear spin by $\vec{\mu} = g_I \mu_0 \vec{I}$, where $g_I$ is the nuclear g factor, given in terms of either the Bohr magneton or nuclear magneton depending upon whether $\mu_0$ is the Bohr magneton, $e\hbar/(2M_e c)$, or the nuclear magneton $e\hbar/(2M_p c)$, with $M_e$ and $M_p$ the masses of the electron and proton, respectively. For $I \geq 1$ the nucleus may also possess an observable electric quadrupole moment as well as rapidly diminishing, higher multipole moments.

In the absence of an external magnetic field the $2I + 1$ possible orientations of the angular momentum are degenerate in energy. However, upon application of an external magnetic field or a magnetic field due to atomic electrons, the degeneracy in energy is removed. For an externally applied field H, the energy Hamiltonian of the system is $\mathcal{H} = -\vec{\mu} \cdot \vec{H} = $ $= -g_I \mu_0 \vec{I} \cdot \vec{H}$. If H determines the quantization direction, this Hamiltonian gives $E(m_I) = -g_I \mu_0 m_I H$ for the energy levels of the system. As shown in Fig. 2, the $2I + 1$ possible values of $m_I$ have equally spaced energy levels. The difference in energy between any two adjacent levels is $E = g_I \mu_0 H$. The situation just described occurs for many nuclei in solutions or in suitable crystal lattices. Through relaxation processes, the magnetic sublevels are distributed according to the Boltzmann distribution function. The lowest energy level is most heavily populated and the next level contains fewer nuclei; the difference is given by $\Delta N \approx N(g_I \mu_0 H/kT)$. The factor $(g_I \mu_0 H/kT)$ is usually a few times $10^{-6}$ for most applications. In the nuclear magnetic resonance (NMR) technique,[3,4] this energy-level system is subjected to a radio-frequency magnetic field satisfying the Einstein relation $\Delta E = h\nu = g_I \mu_0 H$; transitions of the type $\Delta m_I = \pm 1$ are permitted in a suitably oriented oscillating rf field. With the radio-frequency field supplied by a coil of wire, the occurrence of transitions among the levels is detected in two ways. First, on resonance, power is absorbed by the system because upward and downward transitions are equally probable, but the lower energy levels are more highly populated. This net absorption, which ultimately heats the sample, can be sensed by observing minute changes in the electrical properties of the driving oscillator. This method is called nuclear magnetic resonance absorption.[5] Secondly, the resonance condition can be detected by the induction method.[6] If

the static field is along the z axis and the oscillating field along the x direction, on resonance a change in magnetization occurs in the y direction at the frequency $h\nu_0 = g_I \mu_0 H$ and can be detected by a suitably placed coil of wire and by a sensitive rf receiver. In both the absorption and induction experiments, $g_I$ results from a measurement of $\nu$ and H.

Thus far there is no mention of obtaining nuclear spins from this technique. Although several minor variations exist, only the most frequently employed method is mentioned here. From a detailed consideration of the expected signal as a function of $g_I$, I, and n (spins present), it can be shown[3,4] that the areas $A_1$ and $A_2$ under the unsaturated absorption curves for two species are related by

$$\frac{A_1}{A_2} = \frac{g_{I_1}}{g_{I_2}} \cdot \frac{n_1}{n_2} \cdot \frac{I_1(I_1+1)}{I_2(I_2+1)}$$

under the stringent assumptions that the line shapes are identical and the resonances are observed by varying the magnetic field while holding the radio-frequency magnetic field constant in frequency and in magnitude. Because of experimental difficulties, the ratio, $I_1(I_1+1)/I_2(I_2+1)$, cannot be determined with great precision. As a result the method works best for low spins where differences in this ratio are large for various possible values of $I_1$ and $I_2$.

In principle, about $10^{20}$ nuclei (I=1, $\mu$= 1 nm, and H= 10,000 gauss) are required to give a visible signal with standard narrow-bandwidth equipment.[5] With digital time-averaging techniques it should be possible to detect signals that are smaller by one or two orders of magnitude, but the data-gathering time becomes large. Because of the large-sample size restrictions, NMR studies are limited to long-half-life radioisotopes which can be prepared in abundance. Table 2 gives the sample sizes used in NMR investigations on several radioactive isotopes. The sample sizes are of the same order of magnitude as the calculated value quoted above.

As a variation of the NMR method, the technique of nuclear quadrupole resonance could in principle be employed for spin determinations; however, the sample size is somewhat greater than in NMR because of a smaller signal-to-noise ratio.[5] With the same equipment as used on magnetic resonance work, nuclear quadrupole resonances are observed between energy levels established by the nuclear electric quadrupole moment interacting with the electric field gradients in single crystals or powders and by the interaction of the nuclear moment with an external magnetic field. Because the energy separations between adjacent levels are no longer constant as they were in NMR, spin determinations are somewhat easier.

The procedure depends on observing and counting the number of resonance lines, which is a function of the spin, I, the crystal structure, and whether H is zero or nonzero.

## The Microwave Spectroscopy Method

Microwave spectroscopy[7,8] on gases and paramagnetic resonance in solids, liquids, or gases employ similar electronic equipment to observe microwave absorption in free molecules or in atoms in a crystal. The apparatus consists of a source of microwaves, a cavity or cell to contain the sample, and a detector to monitor the absorption in the sample. In practice the signal at the detector is modulated so that narrow-band, lock-in detection systems can be used to detect very small amounts of absorbed power. This modulation can be impressed by frequency modulating the microwave source or by modulating the resonant frequency of the sample with an impressed electric or magnetic field.

The determination of a nuclear spin by microwave spectroscopy involves comparison of an observed spectrum with the prediction of the resonance pattern from assumptions of the parameters involved. Both the frequency and height of resonance lines lend support to the correct assignment of the parameters. The energy levels of a molecule depend upon (a) electronic energy, (b) vibrational energy, (c) rotational energy, (d) hyperfine-structure energy, and (e) energy due to interaction with external fields. As an example, let us consider only a simple linear molecule $O^{16}C^{12}S^{33}$. In the ground electronic and vibrational states, each rotational state, quantum number J, is split by the interaction of the nuclear quadrupole moment, Q, of $S^{33}$ with the gradient of the electric field at the $S^{33}$ nucleus. This gradient $q_m$ is a property of the molecule and not of the state of rotation. (Magnetic hyperfine energy is usually negligible in molecular ground states with all electrons paired.)

Each rotational level of the molecule is thus split into a series of levels labeled by the total angular momentum quantum number $F = I + J, I + J - 1, \ldots, |I - J|$ . The number of F levels in a given J state is equal to the smaller of $(2I + 1)$ or $(2J + 1)$. All else remaining constant, the energy of this system is then a combination of the rotational energy and the quadrupole hyperfine energy. $W_{molecule} = BJ(J + 1) - e\, q_m\, Q\, f(F,I,J)$, where B is a rotational constant, $f(F,I,J)$ determines the relative positions of the energy levels, and $e\, q_m\, Q$ determines the scale for the shifts away from the pure rotational level. With the selection rules that $\Delta J = 0, \pm 1$, and $\Delta F = 0, \pm 1$ the possible transition energies are calculable. Including the additional information regarding transition probabilities, Fig. 3 shows the observed spectrum

of the transitions from the $J = 1$ to $J = 2$ levels in $O^{16}C^{12}S^{33}$ and the calculated spectra for $I = 3/2$, $I = 5/2$, and $I = 7/2$. Clearly the $I = 3/2$ pattern gives good agreement while the $I = 5/2$ and $I = 7/2$ do not. Considerations such as this can be extended to include more complex molecules and the effect of external fields on the spectrum. In addition to the nuclear spin a wide variety of molecular parameters result from these observations of the microwave spectrum.

In microwave spectroscopy the sample is a gas at a pressure of $10^{-2}$ to 1 mm of Hg. The low pressure is necessary so that pressure and collision broadening of the transitions do not mask the hyperfine structure sought. Because of limitations on the number of elements that can be incorporated into a gaseous molecule suitable for microwave absorption measurements, relatively few radioactive isotopes have been investigated. The principal ones are $S^{35}$, $Cl^{36}$, $Se^{75}$, $Se^{79}$, $I^{125}$, $I^{129}$, and $I^{131}$. Although good spectrometers can detect $10^{12}$ to $10^{13}$ spins, most experiments on radioactive isotopes start with $10^{15}$ to $10^{16}$ atoms (see Table 3).

## The Paramagnetic Resonance Method

Paramagnetic resonance (electron spin resonance)[8,9] utilizes transitions involving the spatial reorientation of an unpaired electron in a paramagnetic atom, molecule, or ion. The investigated sample may be in the form of a gas, liquid, or solid, but most of the effort in the field is devoted to studies of paramagnetic ions in crystals. As mentioned previously, the apparatus for observing electron spin resonance signals is similar to that employed in microwave spectroscopy. Resonances are observed by means of a change in microwave power absorbed when transitions occur between unequally populated levels in thermal equilibrium. For narrow band detection purposes the signal is usually modulated by a small sinusoidally varying magnetic field applied to the sample. A grosser, monotonic variation of the magnetic field will then cause the sample resonances to absorb power successively when the resonance conditions occur as the field is increased or decreased.

The energy-level spectrum of a paramagnetic ion in a crystal depends on parameters of the crystal, on the orientation of the crystal in the external magnetic field, on the paramagnetic ion electronic properties, and on the ion's nuclear properties. Because of the variety of possible crystal environments for the paramagnetic ion, the computation of the actual spectrum becomes rather specific. If the field-independent crystal parameters are small, the major energy contributions in a large applied field arise from the interaction of an unpaired electron with the externally applied

magnetic field. For an ion of spin S = 1/2, there would be two energy levels corresponding to $m_S$ = + 1/2 and $m_S$ = - 1/2, with an essentially linear dependence on H. If the ion possesses a nuclear spin, the nuclear magnetic moment causes a further splitting of each of these levels into 2I + 1 levels identified by the 2I + 1 values of $m_I$. The energy-level structure of such a system is shown in Fig. 4. Because of first-order selection rules $\Delta m_S$ = ± 1, $\Delta m_I$ = 0, only 2I + 1 high-frequency transitions occur among these levels. Transitions obeying these selection rules are labeled in Fig. 4. A count of these (2I + 1) regularly spaced resonances yields the nuclear spin.

Two similar variations in this technique have also been used to measure spins.[3] First, in the dynamic nuclear orientation method, the microwave rf power is increased enough that the populations of the two levels involved in a transition become equal or saturated. (Saturation of forbidden $\Delta m_S$ = ± 1, $\Delta m_I$ = ± 1 resonances yields even better ultimate orientations.) Under these conditions and with thermal paramagnetic relaxation mechanisms operating for the remaining $\Delta m_S$ = ± 1, $\Delta m_I$ = 0 transitions, the spins of the nuclei become partially aligned. The alignment is determined from a detailed consideration of the populations of the levels under the influence of the radio-frequency and thermal relaxation transitions. On resonance the small changes (< 10% for H $\approx$ 10,000 G and T = $1^\circ$ K) in alignment can be detected in radioactive isotopes by $\gamma$-ray anisotropy measurements in the directions parallel and perpendicular to the field. The alignment detectors in this way act to indicate the presence of the resonances, which might be too weak to detect by direct power absorption.

The second variation is the ENDOR (Electron Nuclear Double Resonance) technique,[10] in which transitions of the type $\Delta m_I$ = ± 1 are induced by lower radio frequencies (see Fig. 4) but detected by changes in amplitude of the ordinary $\Delta m_S$ = ± 1 paramagnetic resonance absorption or, for radioactive nuclei, by $\gamma$-ray anisotropy changes. Since the energy levels involved in the $\Delta m_I$ = ± 1 transition are nearly parallel, the associated resonance line is narrow because of the absence of field-inhomogeneity broadening. The nuclear spin is deduced from a detailed comparison of the behavior of the observed lines with the predictions of theory for the system.

The sensitivity of paramagnetic resonance absorption is far greater than that of NMR, and about the same as that of microwave spectroscopy. Table 4 lists the sample sizes used in various investigations. In most cases $10^{14}$ to $10^{15}$ atoms are needed, although spectrometers are advertised to be

sensitive enough to detect $10^{12}$ spins under the most favorable conditions. The smallest sample used was in an ENDOR experiment on $As^{76}$ using $\gamma$-ray anisotropy as a resonance indicator. In this case only $5 \times 10^{10}$ atoms were present. The greater sensitivity of nuclear radiation for indicating the resonance condition is here quite apparent. However, the $\gamma$-ray anisotropy method can be employed only when the change in alignment is greater than the uncertainties due to counting statistics.

Most of the samples investigated by paramagnetic resonance have half lives measured in days, months, or years. Because of the time required to grow suitable crystals and to prepare the sample in the spectrometer, and because of the number of atoms required, only isotopes with half lives greater than one day have proved manageable. A severe lower limit on the half life is set by the crystal growing time. It is likely, however, that the sensitivity of microwave absorption apparatuses can be improved by digital averaging techniques. In addition, the $\gamma$-ray anisotropy technique will likely be used successfully for less abundant samples and for cases in which high radiation levels might damage the crystal structure.

### The Optical Spectroscopic Method

Historically, high-resolution optical spectroscopy[11,12] was the first method used to detect nuclear spins (A. A. Michelson, 1891), but the explanation for the observed effect waited 33 years. In 1924, W. Pauli suggested that the hyperfine structure in spectral lines was due to the small, additional interaction energy between the nuclear moments and the fields established at the nucleus by the atomic electrons.[13] The optical spectral line resulting from a transition between two electronic states may contain many closely spaced components because of the original or final (or both) energy levels' being split into a series of closely spaced levels by the electron-nucleus interaction. This structure is observable if the light source has narrow enough spectral lines and if an instrument of high enough resolution is available to separate the spectral lines arising from transitions between the hyperfine-structure components. In practice, large diffraction-grating spectrometers and Fabry-Perot interferometers provide the required resolution to make hyperfine structures observable.

Each electronic energy level has associated with it a total angular momentum $J\hbar$. For $J \geq 1/2$ the electrons may produce an associated observable magnetic field at the nucleus, and for $J \geq 1$, a gradient of an electric field. The interaction of these fields with the nuclear moments depends upon

the relative orientation of $\vec{I}$ and $\vec{J}$. The electron J and the nuclear I can couple to give a total atomic angular momentum $F = I + J, I + J - 1, I + J - 2, \cdots, |I - J|$. The number of these F's is the smaller of $(2J + 1)$ or $(2I + 1)$. Under most circumstances this means each J level is split into a number of F levels, each of which has a distinct energy as shown in Fig. 5. The precise spacing and ordering of the F levels depends on the electronic state and the size of the nuclear multipole moments, as well as I, J, and F. For only a magnetic dipole interaction between the nucleus and electrons, the F levels are in numerical order and obey the interval rule, which states the separation between two adjacent F levels is proportional to the larger F value. Inclusion of the electric quadrupole interaction between the nucleus and the electrons can alter the spacing between F levels and rearrange the ordering. In optical transitions from one J state to another, there are several possible ways to determine spins:

(a)  If, as in Fig. 5, the one ($J = 2$) state has resolved hyperfine structure with $J > I$ and the other state has unresolved structure, the nuclear spin results from counting the $2I + 1$ component lines. Many more complicated situations can arise, but are amenable to analysis.

(b)  When the interval rule holds (small quadrupole interaction and lack of perturbations from neighboring J states), a measurement of the spacing of three adjacent hyperfine lines of a complete pattern allows F for the levels to be established. If J is known, the spin may be determined from $F_{max} = I + J$. This method does not work for I or $J = 1/2$, since only one interval occurs between two lines.

(c)  If the relative intensities of the hyperfine lines are known, the spin can be obtained; the intensities are well-defined functions of the initial and final states. For the simple case of Fig. 5, the intensities of the lines are proportional to $2F + 1$ of the upper state only. Therefore, a measurement of the ratio of the two most intense lines should be $(2 F_{max} + 1)/[2(F_{max} - 1) + 1]$, from which $F_{max}$ may be obtained. Then I can be deduced from a knowledge of J, from the expression $F_{max} = I + J$. Errors in intensity measurements may arise owing to perturbation from nearby states, causing the transition probabilities to change, or from self-reversal (self-absorption) in the light source.

(d)  If an external magnetic field is applied to the atom whose energy levels are shown in Fig. 5, each F level splits into $2F + 1$ components whose energy depends on the strength of the applied magnetic field; then counting these components arising from a single F level determines F, and the spin follows as in previous cases. At a sufficiently high field,

where all lines are resolved and with the lower state again left out of the discussion, the total number of lines resulting from a given J level is $(2J + 1) \cdot (2I + 1)$. The spin, I, may be determined from the count of the total number of lines and a knowledge of J.

In actual spectroscopic analyses the spin is usually deduced from considerations of more than one of the above-mentioned procedures. As a result of the various cross checks, high reliability is characteristic, but a few examples are known of errors in first measurements.

In Table 5 the sample requirement of optical spectroscopic determinations is seen to vary from $10^{12}$ to $10^{20}$ atoms, depending somewhat on the availability of the sample and on the complexities of preparing suitable light sources. The half lives range down to 9.5 hours. The lower limit is determined by the time needed to perform chemical procedures, to construct the discharge lamp, and to record the spectrum. Spectroscopic work is presently under way on half lives of 2 to 3 hours. One of the major difficulties in preparing lamp sources is contamination of the source with the difficult-to-exclude stable elements. Since the stable-isotope electronic transitions are separated from the same transition in other isotopes by small "isotope shifts" and by a different hyperfine structure, the presence of a more abundant stable isotope can easily obscure a faint line due to a rare radioisotope.

Recently, optical double resonance experiments have given excellent results on a few radioisotopes. In this method[14] radiation from an optical resonance line passes through, or is scattered from, a cell containing the sample. Usually this resonance light is polarized so that only certain states in the sample cell are involved. By the application of a radio-frequency or microwave magnetic field, transitions are caused among the F levels or, when a large magnetic field is present, among the $m_J$ or $m_F$ levels of the sample. When the rf and optical transitions both involve a common energy level, changes in population of that level or other connected levels can be caused by either the light or the rf. The resulting redistribution of populations is indicated by a change in the intensity or polarization of the transmitted or scattered light.

Table 6 shows that radioactive sample sizes from $10^{11}$ to $10^{15}$ atoms have been used in optical double resonance experiments. Although the optical double resonance method has high sensitivity, resonance cells have so far been constructed only for a few gases and elements with high vapor pressures at moderate temperatures.

# NUCLEAR SPIN-PARITY ASSIGNMENTS

## The Atomic-Beam Magnetic-Resonance Method

For a large number of elements the atomic-beam magnetic-resonance method[15] offers a very precise and general approach to spin determinations. About 178 radioactive nuclei with half lives ranging from 0.8 sec to $6 \times 10^{14}$ years have been investigated to date. Spins have also been determined for an additional 27 stable isotopes.

In this method an atom in its atomic ground state (or low-lying electronic state) passes through a vacuum chamber from a source oven O to a detector D, as shown in Fig. 6. En route, the atom is subjected to three magnetic fields labeled A, C, and B, respectively. The A and B fields are inhomogeneous and serve to deflect atoms by a force $F = \mu_{eff} \nabla H$, which depends on the atom's effective magnetic moment. Thus, the A and B magnets may be thought of as devices that determine the state of an atom before it enters the C region and after it leaves the C region. The A and B magnets have their gradients in the same direction, so an atom remaining in one particular state experiences a force in the same direction in both the A and B magnets. Such an atom might follow trajectory 1. On the other hand, if in the homogeneous C-field region, the atom undergoes an rf-induced transition that reverses its effective magnetic moment, the atom would follow trajectory 2 in the B field and reach the detector D. The geometrical stop S is placed in the B region to prevent any fast atoms with small deflections from reaching the detector. Thus, the background at the detector is kept low and a resonance signal is indicated by an increase in flux of atoms arriving at the detector. The requirements of the technique are: (a) it must be possible to vaporize and form an atomic beam of the sample; (b) the atoms must posses a nonzero magnetic moment (preferably $\sim$ 1 Bohr magneton); and (c) the beam must be detectable at the detector.

Although not yet fully realized, condition (a) can probably be accomplished for all elements. Condition (b) is true for most elements except the noble gases and those in Group II of the periodic table. Detection of the beam [condition (c)] is perhaps the most difficult of the three to accomplish, since the beam density is usually smaller than the density of residual gas atoms in the vacuum system. As a result only very selective detectors produce signals that are high compared with background. Three types of detectors are commonly employed: (a) an electron-bombardment ionizer followed by a mass spectrometer; (b) a hot tungsten wire, which ionizes only atoms of low ionization potential; and (c) a surface to collect the beam for subsequent radioactive counting. Detection means (a) and (b) are applicable to stable and long-lived isotopes, while (c) is necessary for small samples of short-

lived radioisotopes.

In a homogeneous magnetic field the energy-level diagram for an atom with total electronic spin $J = 1/2$ and nuclear spin $I = 3/2$ is as appears in Fig. 7. This level scheme results from an energy Hamiltonian of the form $\mathcal{H} = ha\,\vec{I} \cdot \vec{J} - g_J\,\mu_0\,\vec{J} \cdot \vec{H} - g_I\,\mu_0\,\vec{I} \cdot \vec{H}$, where the first term expresses the magnetic dipole hyperfine interaction between the electrons and nucleus (a is the dipole interaction constant), the second term expresses the magnetic interaction between the electron magnetic moment and the applied magnetic field, and the third term expresses the magnetic interaction between the nuclear magnetic moment and the applied magnetic field. In low fields, when the contribution to the energy of the first term is larger than that of the second, the states of the atom for a particular F level follow the expression $E_F = E_F(H=0) - g_F\mu_0 m_F H$, in which

$$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} + g_I \frac{F(F+1) + I(I+1) - J(J+1)}{2F(F+1)} .$$

In this expression the second term is about 1/2000 as large as the first term. Whenever either or both I or $J = 1/2$, the exact solution for the energies is given by the Briet-Rabi formula. A Breit-Rabi diagram for $J = 1/2$ and $I = 3/2$ is shown in Fig. 7. When I and J are both greater than 1/2, a quadrupole interaction term is found in the Hamiltonian. In this case, the solution for the energy levels is usually performed by some numerical iteration technique. The two important features of the "example" energy-level diagram shown in Fig. 7 are (a) the linearity and equal spacing of the $m_F$ levels arising from a given F level at low field, and (b) the distinct grouping of the levels according to $m_J$ at high fields.

In the A and B magnets of the atomic beam apparatus, the atoms are in a field corresponding to the right side of Fig. 7. During their traversal of these deflecting field regions (A and B), the atoms have an effective magnet moment ($\mu_{eff} = - \partial W/\partial H$) which is negative for the $m_J = + 1/2$ group and positive for the $m_J = - 1/2$ group. Therefore, an atom which remains in the $m_J = + 1/2$ group of states will be deflected along trajectories similar to 1 in Fig. 6. The trajectories of the $m_J = - 1/2$ states are omitted from the diagram, but would follow paths given by reflecting 1 in a mirror which contains the beam axis and is perpendicular to the plane of the figure.

In low magnetic fields the allowed rf magnetic transitions have $F = 0, \pm 1$ and $m_F = 0, \pm 1$. Fig. 7 displays nine such allowed transitions, which also result in a change in the sign of the effective magnetic moment of the atom. When

any one of these transitions carries the atom from
$m_J$ = + 1/2 to $m_J$ = - 1/2 or vice versa, the force on the atom
in the B field is opposite to that previously exerted on it
in the A field, because of the change in effective magnetic
moment occurring in the C-field region. Thus, those atoms
which have made a transition obeying selection rules for the
rf ($\Delta F$ = 0, ± 1 and $\Delta m_F$ = 0, ± 1) and for the apparatus
($\Delta m_J$ = ± 1) follow path 2 or its reflection in Fig. 6 and
reach the detector.

For spin determinations the transition labeled i in Fig.
7 is the one most frequently used. In the low-field approxi-
mation for J = 1/2, the frequency of the transition i is given
by $\nu$ = -$g_J$ $\mu_0$ H/[(2I+1) h] . This formula merely expresses
the fact that the energy separation of the $m_F$ = + $|I + J|$ and
$m_F$ = - $|I + J|$ states is divided into 2I + 1 intervals. Since
all the quantities in the frequency formula are generally
known except $\nu$ and I, there is a one-to-one correspondence
between the resonance frequency and the spin. A search at a
discrete number of frequencies will reveal the presence of a
resonance at one frequency and hence indicate the spin. Fig. 8
shows the signal observed at the detector for various settings
of the rf transition frequency. A very distinct signal occurs
at the I = 6 setting. From a single Cs run, Fig. 9 shows the
decay curves of three spin samples taken at three different
frequencies corresponding to I = 1/2, 2, and 5/2. The back-
ground on all other spin samples was $\approx$ 3 to 6 cpm. The half-
life analysis in Fig. 9 identifies the isotope responsible
for the individual signals. The spin-search procedure is
always repeated at several field values to make sure of the
linear behavior of frequency with field. At higher fields
transitions depart from linearity in H and yield information
on the hyperfine-structure constants, on $g_I$, and on $g_J$.

Although the sensitivity of the atomic beam method varies
considerably for different apparatus designs and detection
systems, a rough analysis of one atomic beam apparatus with
radioactive detection has shown that about $10^{11}$ × $\tau_{1/2}$ (hr)
is the minimum number of atoms required in a single
sample to perform a spin determination.[16] The presence of the
half-life term in the sample size expression results from the
counting detection method of assaying the activity of the
collected sample. This estimate is based on the following:
(a) a minimum counting rate is 10 counts/min on resonance
(counter background $\approx$ 2 counts/min); (b) thirty resonance
points are taken; (c) only 4% of the available states parti-
cipate in a resonance (this factor varies with the spin of the
nucleus and with the electronic J); (d) the beam is collected
on spin samples during 2/3 of the beam time; (e) the counter
efficiency is $\approx$ 50%; (f) the apparatus transmission solid

angle is $\approx 10^{-5}$; and (g) there is $\approx 50\%$ loss due to decay and chemical handling. In most experimental work it is possible to start with samples in excess of this minimum amount, since the minimum size is well within the range of most production schemes using cyclotrons and reactors.

## The Problem of Zero-Spin Isotopes

From hyperfine-structure observations alone, it is not possible to distinguish between an isotope with I = 0 and one with I > 0 and unresolvably small hyperfine structure. This confusion exists because the relevant terms in the Hamiltonian are zero either if the spin is zero or if all the nuclear moments and hyperfine structure constants are equated to zero. Therefore, most spectroscopic methods mentioned thus far do not yield an unambiguous assignment of I = 0.

One band-spectra technique, however, does give an un-equivocal I = 0 assignment to eight even-even isotopes. In diatomic molecules having two identical nuclei, a definite intensity relation between adjacent components in a rotational band spectrum is predicted by considerations of the symmetry properties of the complete molecular wave function, of the statistics obeyed by the nuclei, of the statistical weights of the rotational levels due to the existence of spin, and of the transition selection rules. The band may originate from transitions from the rotational levels of one molecular electronic state to the rotational levels of another electronic state, for example. The general expression for the ratio of the stronger lines to the adjacent weaker ones is (I + 1)/I for all I. Thus for I = 0, the expression requires that the alternate lines be absent from the spectrum. With I = 1/2 or I = 1, the ratio of adjacent lines in the band is 3:1 and 2:1, respectively. For larger spins, it is progressively harder to correlate the measured intensity ratio of alternate lines with a definite spin value. It should be noted that this band-spectra technique does not rely on considerations of hyperfine structure, only on the statistical weights of the levels involved in allowed transitions.

In optical and rf spectroscopy a measurement of I = 0 is usually accompanied by the qualification (a) that no hyperfine structure was observed, or (b) that if one assumed I = 1, then the hyperfine structure and magnetic moment was less than given values set by the resolution of the measuring apparatus.

At present some 69 even-even isotopes have exhibited no hyperfine structure and are presumed to be spin zero. In addition, however, three odd-odd isotopes ($Ga^{66}$, $Eu^{152m}$, and $Ho^{166}$) have no detectable hyperfine structure. Under the assumption of I = 1 for these isotopes the magnetic moments would have to be equal to or less than $4 \times 10^{-5}$, $4 \times 10^{-3}$, and

$10^{-4}$ nm, respectively. Among the nonzero-spin isotopes some are known to have magnetic moments as small as these (e.g., $Tl^{198}$ 5.3 hr, I = 2, $\mu < 2 \times 10^{-3}$ nm).

## Conclusions

Of the 1717 isotopes contained in the June 1964 edition of the Chart of the Nuclides, only 406 isotopes (less than one quarter) have been investigated by techniques that yield an unambiguous spin value.

Except for isotopes which have too short a half life (< 10 sec) or cannot be produced in sufficient quantities [> $10^{11}$ $\tau_{1/2}$(hr)/sample], it is likely that most of the unknown spins and moments will eventually be measured by present techniques. The effort expended on measuring spins of nuclear ground states continues to increase, but this increase is also matched by an increasing difficulty in all aspects of the measurements on remaining isotopes. As a result the rate of new spin measurements appears to be fairly constant at about 10 to 30 isotopes per year for the past 10 years. The changes in activity of the ground-state spin and moment field are clearly shown in Fig. 10. It is seen that the total number of publications annually in the field of spins and moments has remained remarkably constant (70 to 100 per year) over the past 15 years. Unless major alterations occur in the techniques involved or in financial support of this work, this level of activity will presumably persist. It will in any event continue to yield valuable information toward the understanding of atomic and nuclear structure.

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NUCLEAR SPIN-PARITY ASSIGNMENTS

TABLE 1

Number of Spins Measured by "Direct" Methods

| | Definite I=0 | Probable I=0 No resolved hyperfine structure | I ≠ 0 |
|---|---|---|---|
| Stable isotopes | 7 | 61 | 107 |
| Radioactive isotopes | 1 | 11 (including 3 odd-odd isotopes) | 219 |
| | 8 | 72 | Total 406 |

TABLE 2

Sample sizes used for NMR studies on radioisotopes (See Ref. 17)

| Isotope | $\tau_{1/2}$ | Sample size, atoms |
|---|---|---|
| $H^3$ | 12 y | $6.8 \times 10^{20}$ |
| $Cl^{36}$ | 0.3 My | $1.2 \times 10^{20}$ |
| $Tc^{99}$ | 210 ky | $9 \times 10^{20}$ |

TABLE 3

Sample sizes used in microwave spectroscopy (See Ref. 17)

| Isotope | $\tau_{1/2}$ | Sample size, atoms |
|---|---|---|
| $Se^{75}$ | 170 d | $1.2 \times 10^{16}$ |
| $Se^{79}$ | 60 ky | $7.6 \times 10^{15}$ |
| $I^{125}$ | 60 d | $5 \times 10^{15}$ |
| $I^{131}$ | 8.1 d | $9 \times 10^{15}$ |

NUCLEAR SPIN-PARITY ASSIGNMENTS

TABLE 4

Sample Sizes Used in Paramagnetic Resonance Studies (See Ref. 17)

| Isotope | $\tau_{1/2}$ | | Sample size, atoms | |
|---|---|---|---|---|
| $P^{32}$ | 14 | d | $4 \times 10^{14}$ | ENDOR |
| $Co^{56}$ | 77 | d | $7 \times 10^{13}$, $1.4 \times 10^{15}$ | |
| $Co^{57}$ | 270 | d | $1 \times 10^{14}$ | |
| $Co^{58}$ | 71 | d | $1.3 \times 10^{15}$ | |
| $Co^{60}$ | 5.3 | y | $3 \times 10^{15}$ | |
| $As^{76}$ | 26.5 | hr | $5 \times 10^{10}$ | ENDOR |
| $Tc^{99}$ | 210 | ky | $3 \times 10^{16}$ | |
| $Ag^{110m}$ | 260 | d | $2 \times 10^{15}$ | |
| $Ce^{141}$ | 33 | d | $2 \times 10^{15}$ | |
| $Nd^{147}$ | 11 | d | $2 \times 10^{14}$ | |
| $Pm^{147}$ | 2.6 | y | $5 \times 10^{16}$ | |

TABLE 5

Sample Sizes Used in Optical Spectroscopic Studies (See Ref. 17)

| Isotope | $\tau_{1/2}$ | | Sample size, atoms |
|---|---|---|---|
| $Ar^{37}$ | 34 | d | $2.6 \times 10^{16}$ |
| $Kr^{85}$ | 11 | yr | $3.4 \times 10^{17}$ |
| $Tc^{99}$ | 210 | ky | $1 \times 10^{20}$ |
| $Pm^{147}$ | 2.6 | y | $2 \times 10^{19}$ |
| $Eu^{152}$ | 13 | y | $5.8 \times 10^{17}$ |
| $Hg^{195}$ | 9.5 | hr | $10^{13} - 10^{14}$ |
| $Hg^{195m}$ | 40 | hr | $10^{13} - 10^{14}$ |
| $Hg^{197}$ | 65 | hr | $2 \times 10^{15}$ |
| $Hg^{197m}$ | 24 | hr | $10^{12} \to 2 \times 10^{14}$ |
| $Hg^{203}$ | 47 | d | $10^{13}$ |
| $Tl^{199-202}$ | 7.4 hr-12 d | | $\geqq 10^{12}$ |
| $Po^{208}$ | 2.9 | yr | $1 \times 10^{17}$ |
| $Po^{209}$ | 103 | yr | $3 \times 10^{16}$ |

NUCLEAR SPIN-PARITY ASSIGNMENTS

TABLE 6

Sample Sizes Used in Optical Double Resonance Experiments
(See Ref. 17)

| Isotope | $\tau_{1/2}$ | | Sample size, atoms |
|---|---|---|---|
| $Zn^{65}$ | 245 | d | $2 \times 10^{15}$ |
| $Cd^{107}$ | 6.7 | hr | $10^{14}$ |
| $Cd^{109}$ | 470 | d | $5 \times 10^{14}$ |
| $Cd^{113m}$ | 14 | y | $10^{11}$ |
| $Cd^{115}$ | 2.3 | d | $7.8 \times 10^{15}$ |
| $Cd^{115m}$ | 43 | d | $1.5 \times 10^{11}$ |
| $Hg^{197}$ | 65 | hr | $3 \times 10^{12}$ |

Fig. 1  Histogram of the number of nuclear spins (I),
nuclear magnetic moments ($\mu$), and nuclear quadrupole moments
(Q) measured by six techniques:  ABR = atomic-beam magnetic
resonance, OS = optical spectroscopy, ESR = electron spin
resonance or paramagnetic resonance, MS = microwave spectros-
copy in gases, NMR = nuclear magnetic resonance, and ODR =
optical double resonance.

Fig. 2  Energy-level diagram for a nucleus with a posi-
tive magnetic moment and I = 3/2 in an external magnetic field.

Fig. 3  The observed microwave spectrum of hyperfine
transition from the J = 1 to J = 2 rotational states of
carbonyl sulfide ($O^{16}C^{12}S^{33}$) show that the nuclear spin of
$S^{33}$ is 3/2.  Similar work on the radioisotope, $S^{35}$, also
establishes its spin as I = 3/2.

Fig. 4  The energy levels of a paramagnetic system with
S = 1/2 and I = 3/2 shown in the high field approximation.

Fig. 5  Hyperfine-structure levels arising in two elec-
tronic states.  When the hyperfine structure of the
J = 2 (J > I) level is large and that of the J = 1 level is
unresolvably small, there are 2I + 1 closely spaced hyperfine
components in the optical line.  The intensities of these
components are proportional to the 2F + 1 multiplicity of the
upper state.

NUCLEAR SPIN-PARITY ASSIGNMENTS

Fig. 6   Schematic arrangement of components in an atomic-beam flop-in apparatus.   In the absence of suitable transitions the atoms follow trajectory 1.   When a transition occurring in the C region reverses the sign of the atomic magnetic moment, the atom follows trajectory 2 to the detector.

Fig. 7   The energy-level diagram of a free atom with $J = 1/2$, $I = 3/2$, $g_J = -2$, and $g_I > 0$ in an external magnetic field, H.   The transitions labeled "a" through "i" are allowed by selection rules and also change the sign of the magnetic moment $(-\partial W/\partial H)$ of the atom in the high-field region of the diagram.

Fig. 8   A spin search in $Ag^{110m}$ shows a definite signal corresponding to $I = 6$.

Fig. 9   From a sample containing all three isotopes, a clear separation of three spin samples was performed by setting the radio frequency to correspond to transitions for spins $I = 1/2$, 2, and 5/2.   The half life of each spin sample helps establish the isotope responsible for the signal.

Fig. 10   The number of articles published in the field of ground-state nuclear spins and moments shows the relatively constant activity in recent years.

Fig. 1

MUB-8535

MAGNETIC   FIELD

MUB-8536

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

MU-13185

Fig. 7

MU-17136

Fig. 8

I = $\frac{1}{2}$ , T$_{1/2}$ = 35 hr , Cs$^{129}$

I = 2 , T$_{1/2}$ = 6.3 days , Cs$^{132}$

I = $\frac{5}{2}$ , T$_{1/2}$ = 9.0 days , Cs$^{131}$

COUNTS PER MINUTE

DAYS

MU-12273

Fig. 9

Fig. 10