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Optical Pumping

Scattered resonance light can polarize atoms and provide a simple means of observing fine structure.

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The term *optical pumping* refers to the redistribution of atoms among their fine- or hyperfine-structure levels by means of light. The resonance radiation of the atom is usually the radiation used. This is selected in some way, specifically by being circularly polarized, anisotropic, filtered, or amplitude-modulated. By unusually simple experimental techniques it is possible to measure the fine and hyperfine structure of atoms, the magnetic moments of radioactive nuclei, the cross sections of a number of interesting processes, and the magnetic properties of free ions and electrons, and to produce useful polarization of atoms, nuclei, and electrons. The techniques have led to the development of two especially useful devices—atomic clocks of great simplicity and magnetometers of particular usefulness in measuring the weak magnetic fields of the earth and in space—and the techniques have been at least partly responsible for the development of the coherent light generator, or laser.

The research has been pursued with enthusiasm, partly because of the range of applicability of the simple techniques, and partly because of the fascination of work in a field in which the ideas are so obvious that one cannot but wonder why they were not exploited earlier. In the last two decades there have been a number of discoveries, such as magnetic resonance, the laser, and recoilless radiation of gamma rays, which have been of this nature. In the case of optical pumping, the resonance radiation of sodium light was well explored in the 1920's: most of the necessary quantum mechanical ideas of angular momentum were understood, and in fact some of the phenomena of optical pumping were observed. It is possible that if the techniques of optical pumping had been discovered in the 1930's, the atomic beam apparatus would never have been developed.

The Process

Optical pumping is usually done with circularly polarized light. Just as light exerts radiation pressure, circularly polarized light can transfer angular momentum and produce a torque. This was first demonstrated with a torsion pendulum in 1935 (*1*). Before considering the effect of circularly polarized light on atoms, I review briefly the selection rules of ordinary dipole radiation. Light from an ensemble of randomly oriented, radiating atomic dipoles is isotropic in intensity, but if a magnetic field is applied to the atoms, the angular distribution of radiation is not isotropic for the different polarizations. Also, angular momentum is conserved when the circular polarizations (σ radiation) are emitted in transitions in which the state of the radiating atom changes in angular momentum ($\Delta m = 1$) by 1 unit of Planck's constant ($\hbar$). This is shown in Fig. 1, where the arrows indicate the directions of the electric field vectors.

To understand the effect on the atoms, let us consider the spectra and the energy-level diagram (Fig. 2) of a typical alkali metal, which for simplicity we may think of as having an atom with a nucleus which has no nuclear spin and no magnetic moment. In the ground state (or S state) the electron has no orbital angular momentum, so the angular momentum of the entire structure is solely in the spin of the outer valence electron, which can be quantized in direction parallel ($m_J = 1/2$) or antiparallel ($m_J = -1/2$) to some direction supplied by an external magnetic field. The principal resonance radiation induces transitions from this S ground state to a P level which has one unit of orbital angular momentum. Through the spin-orbit interaction and shielding effects of the other electrons, this level is split into two levels in each of which the total angular momentum J is either 3/2 or 1/2, depending on the orientation of the electron spin with respect to its orbital motion. (In the case of sodium, this gives rise to the pair of strong yellow Fraunhofer D lines.)

Figure 3 shows in more detail the structure of the levels, with the m_J numbers which represent the components of the total angular momentum along the direction of a magnetic field. The different levels are shown slightly split, as they would be if such a magnetic field were applied to define a specific axis in space. The straight lines show the absorption process, which involves an increase of one unit of angular momentum when the atoms are irradiated with circularly polarized resonance radiation along the axis (σ_+), and the dotted lines indicate the re-emission process, which can occur primarily by spontaneous emission and is therefore mostly unaffected by the absorbed light, although to some extent there are interesting interference effects between absorbed and emitted light. After repeated fluorescence transitions of this

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kind, the atoms are stochastically shifted to occupy the higher quantum numbers (*m*) (or the lower ones, if the opposite direction of circular polarization is used); in the case of the *S*-state atom with no nuclear spin, this is equivalent to saying that the valence electron is polarized.

The effect of this fluorescence process may be computed without too much difficulty in simple cases, since it is only necessary to compute the relative rates of transition from the initial ground states to the excited states and back. These rates depend almost entirely on the properties of the angular momentum involved, whereas computation of the absolute rate requires more detailed knowledge of the charge distribution. One may write a "master equation" to describe the process (*2*):

$$\dot{\mathbf{N}} = (\mathbf{P} - \mathbf{1})\cdot\mathbf{A}\cdot\mathbf{N} - \frac{1}{\tau}(\mathbf{R} - \mathbf{1})\cdot\mathbf{N}$$

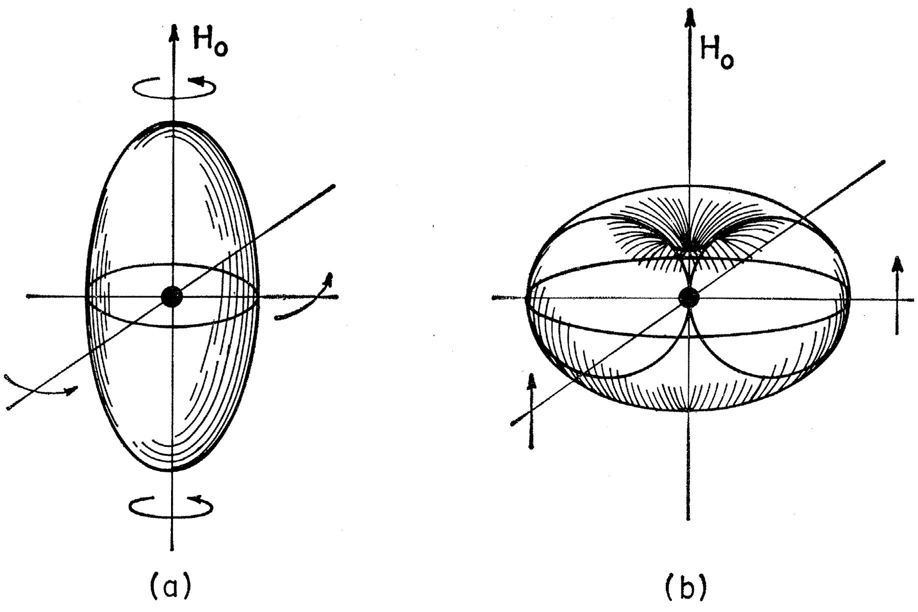
The components of the vector **N** represent the population distribution of the fine or hyperfine levels. The matrix **P** represents the complete probability of transition, up and down again, and is given in simple dipole radiation perturbation theory as

$$\mathbf{P}_{ik} = \sum_{j} |\langle i | \mathbf{A}^{a}\cdot\mathbf{p} | j \rangle|^{2}\cdot|\langle j | \mathbf{A}^{e}\cdot\mathbf{p} | k \rangle|^{2}$$

where **A** is the vector potential of the light used in absorption and emission; **p** is the momentum of the electron; and *i*, *j*, and *k* refer to initial, intermediate, and final states of the process. The matrix **A** is related to the oscillator strengths of the transitions, and the matrix **R** represents the effect of various relaxation processes which can depolarize the atoms. (An example is the spin-exchange process discussed later.) The size and rank of these vectors and matrices depends on the number of hyperfine levels in the ground and excited states. In the particularly simple case of the atom with nuclear spin of 1/2, the effect can be seen in Fig. 3, where the relative probabilities of transition are shown as numbers beside each of the transitions.

Method of Observation

The process may be observed in the manner indicated in Fig. 4. A beam of alkali metal atoms (sodium) is produced from an oven in a vacuum system with appropriate windows. Circularly



(a) (b)

Fig. 1. A plot of the angular distribution of the electric vector amplitude in electric dipole radiation for (*a*) σ or $\Delta m = 1$ transitions, and (*b*) π or $\Delta m = 0$ transitions, showing the direction of electric vector polarization of the emitted light.

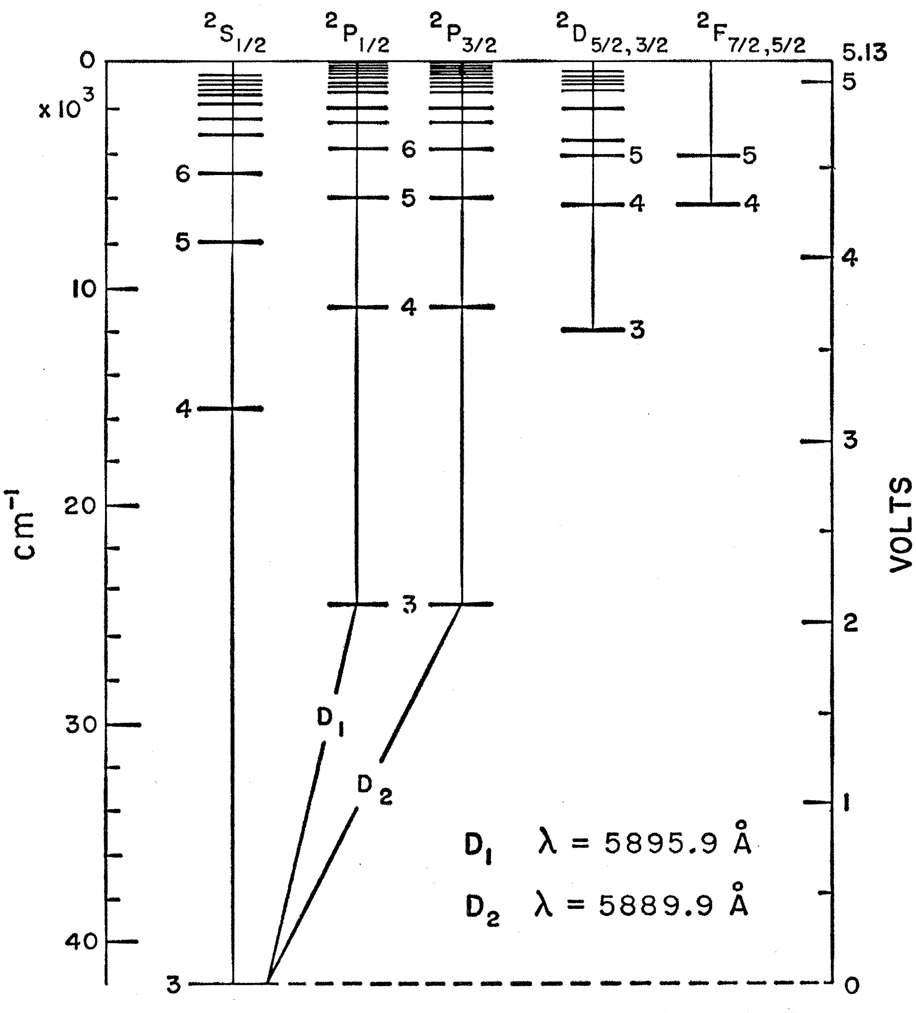


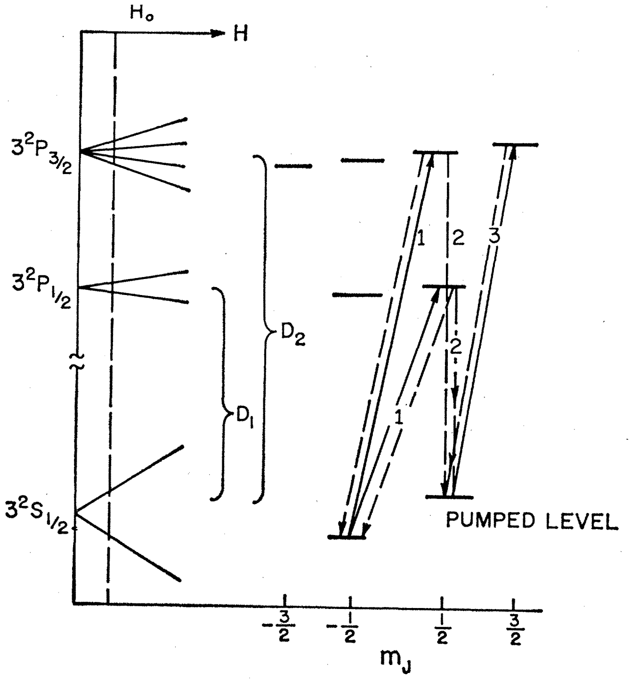
Fig. 2. Energy levels of neutral sodium, showing the origin of the D resonance radiation lines. If the principal quantum numbers are increased by −1, 1, 2, and 3, respectively, a qualitatively similar energy-level scheme can be pictured for lithium, potassium, rubidium, and cesium.

polarized light (sodium D light) is focused with considerable intensity on the beam along a direction which is parallel to a weak magnetic field (easily produced with Helmholtz coils). In the incident light, the Doppler width is such that the splitting of the energy levels by the magnetic field has very little effect unless the magnetic field has a strength of several thousand oersteds. The scattered light at right angles to this direction is analyzed in such a way as to determine the ratio of σ light to π light—that is, the ratio of the intensity of light polarized perpendicular to the magnetic field to the intensity of light polarized parallel to the field (see Fig. 1). As the atoms become polarized into the state $m_J = +1/2$, the light that is re-emitted is primarily σ_+ light which is re-emitted from the excited state $P_{3/2}$, $m_J = 3/2$, and this re-emitted light appears as an increase in the ratio σ/π. In order to avoid working with steady light intensities and direct-current amplifiers, the direction of the magnetic field may be varied, or its magnitude may be altered through zero field; the ratio σ/π will then vary and may be detected by an alternating-current synchronous amplifier or "lock-in" detector.

Optical pumping was first observed, in the manner described, by a group in Paris (*3*), following suggestions by Kastler, Bitter, and Brossel (*4*) of a way to measure the hyperfine splitting in the excited states of atoms where atomic-beam techniques cannot be used, and independently by R. H. Dicke and his students at Princeton (*5*), who were trying to produce polarized electrons in an effort to measure the magnetic moment of the electron. The methods were very similar; the experimental arrangement described is that of the Princeton experiments.

If the nucleus of the atom used in optical pumping has a spin (denoted by a quantum number I) and a magnetic moment, then, in fields that are not too large, the magnetic moment of the nucleus will couple to the total angular momentum of the electron to form a new quantum number F, which ranges in unit steps of $\hbar$ between the sum of, and the difference between, J and I. Figure 5 shows the resultant set of hyperfine levels, analogous to the levels of Fig. 3, but with the new F and m_F levels shown in the case of sodium-23, which has a nuclear spin of 3/2. The magnetic interaction between the nucleus and the electron gives rise to a so-called hyperfine splitting $\Delta\nu_h$ between the different F quantum numbers. (This splitting, in the case of atomic hydrogen, gives rise to the famous 21-centimeter radiation emitted by galactic hydrogen.) In spite of the added complexity, optical pumping proceeds in exactly the same fashion as it does for the atom with electronic angular momentum only. In the type of experiment described, the atoms would be pumped into the $F = 2$, $m_F = 2$ state, which would now represent the polarization of the electron and the nucleus as a coupled unit. It is therefore possible to do experiments with polarized nuclei as well as with polarized electrons. For example, the beta-decay asymmetry of polarized sodium-21 atoms produced by a (d,n) reaction in the neon-20 used as the buffer gas has been observed (*6*).

It is not possible to produce a high percentage of polarization in a beam or in a vacuum, because the atoms do not remain very long in the light path; frequently the atom remains for less than the time it requires to absorb one photon of light. It was soon found accidentally by the Paris group (*7*), and by the Princeton group through knowledge of methods of reducing the Doppler width of microwave and radiofrequency spectral lines (*8*), that a nonmagnetic gas, such as any of the noble gases or molecular hydrogen or nitrogen, could be used to prevent the atoms from diffusing rapidly out of the light path without disturbing the polarization. As long as the ground state is an S state



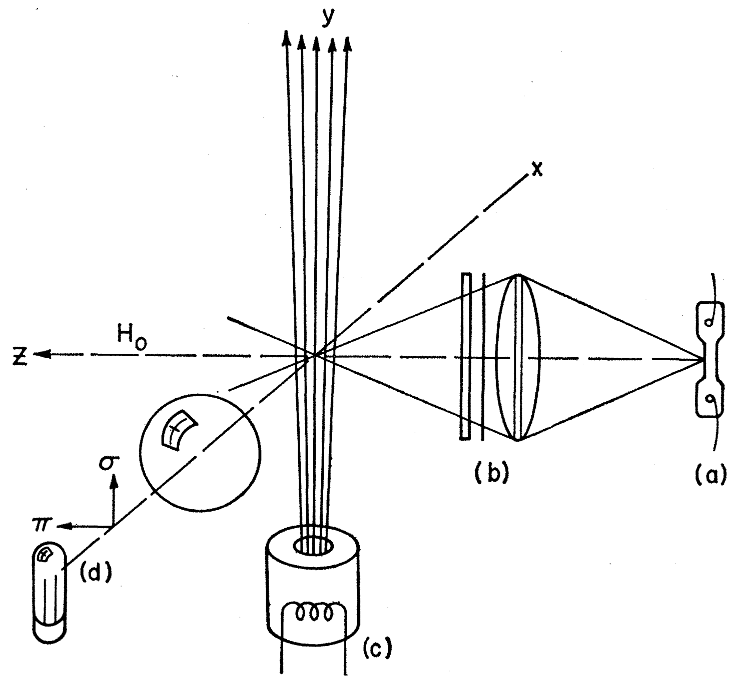


Fig. 3(left). Details of the fine structure of the resonance radiation states for sodium. (Solid arrows) Allowed absorption transitions for σ_+ radiation; (dotted arrows) allowed transitions for emission; (numbers) relative absorption probabilities for the different processes. Fig. 4(right). Schematic drawing of an optical-pumping fluorescence detector. (*a*) Resonance lamp; (*b*) illuminating lens, polarizer, and 1/4 wave plate of birefringent plastic sheeting; (*c*) sodium oven and beam; and (*d*) σ/π analyzer and photodetector.

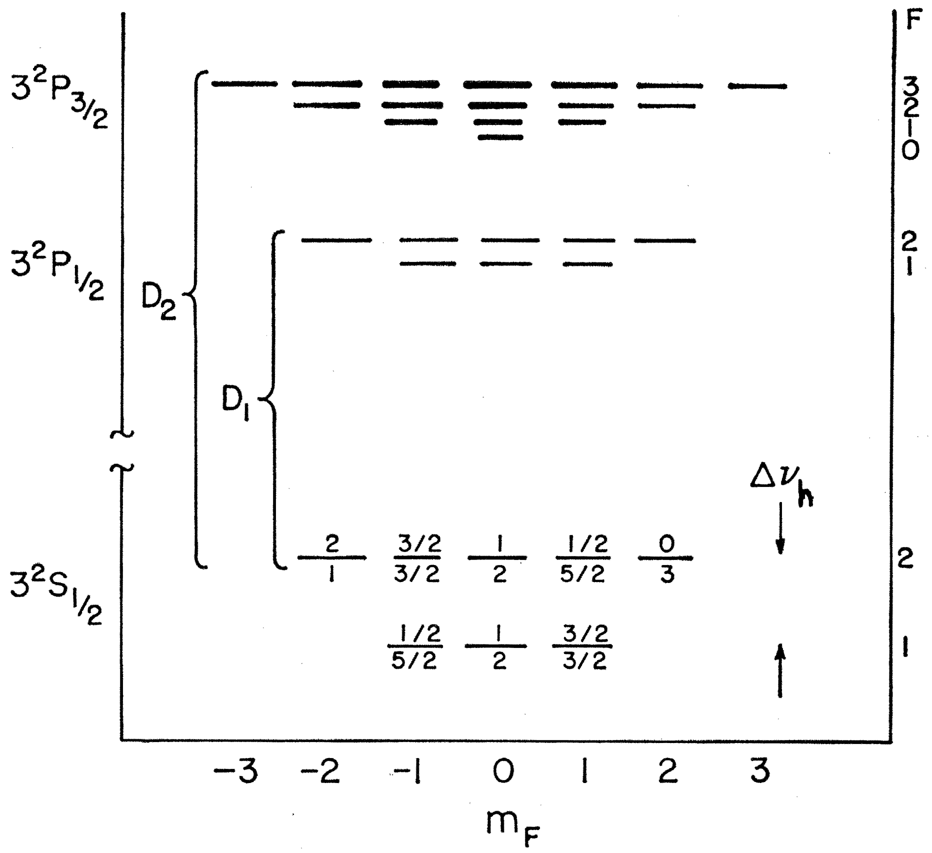


Fig. 5. Details of the hyperfine structure of the sodium-23 resonance radiation states of Fig. 3 when the nuclear spin $I = 3/2$ is coupled to the electron. (Numbers above line) Relative absorption probabilities for σ_+ D_1 radiation; (numbers below line) relative absorption probabilities for σ_+ D_2 radiation.

(that is, as long as the charge distribution of the electron is spherically symmetrical and there is no orbital angular momentum), the strong electric fields present in the collision of the atoms with the buffer gas will have no very strong way to disorient the angular momentum of the spin or nucleus. This is not true when the atoms are in the excited *P* states, but they do not spend so much time there. The use of buffer-gas pressures in excess of 1 torr mixes and destroys the information contained in the ratio of σ light to π light and makes it impossible to observe optical pumping by the methods described so far.

Intensity Pumping

Nevertheless, optical pumping in which buffer-gas pressures as high as many atmospheres are used may be carried out by a method, first developed by Dehmelt (*9*), which is quite different from the stochastic fluorescence pumping previously described and which might be better described as intensity or absorption pumping. If the buffer-gas pressure is sufficiently high to mix the states of the atoms while they are in the excited *P* levels, then no optical pumping will normally occur. The atoms still must absorb angular momentum from the circularly polarized radiation, but, after mixing in the excited state, the atoms will drop back down to any of the ground-state levels at random. Moreover, the sum of all the transitions which the atom can make from any particular initial state is constant. (This is not obvious but follows from fundamental symmetries in the angular momentum of the atom and can be seen to be necessary in order that an atomic ensemble will come to thermal equilibrium in a black-body cavity.) This means that all the hyperfine levels of the atomic ensemble are emptied at equal rates. However, if the incident light is not only circularly polarized but also filtered so that only one of the D lines is present, the absorption is not constant for each state of the atom. Let us consider specifically the case where the filter passes only the D_1 light which connects the $S_{1/2}$ level to the $P_{1/2}$ level. From Fig. 3 it may be seen that the absorption of σ_+ D_1 light by the state labeled $m_J = 1/2$ must necessarily be zero, since there is no $m_J = 3/2$ state in the $P_{1/2}$ state. On the other hand, the transition of the $m_J = -1/2$ level of the $S_{1/2}$ state to the $m_J = 1/2$ level of the $P_{1/2}$ state can occur. Hence, atoms which are pumped into the ground-level state 1/2 do not leave, and all the atoms are gradually pumped into this state and polarized, even if the atoms collide with buffer gas in the excited state. An opposite action takes place if only the D_2 light is present, but this action is not so effective, because the final population is inversely proportional to the probability of absorption and none of the probabilities of absorption are zero when the atom is exposed to D_2 light. An added advantage of the D_1 absorption pumping is that, as the atoms are pumped into the least absorbing state, the entire sample becomes more transparent and the radiation can be used to pump a "deeper" layer of alkali metal vapor (*10*). A similar effect occurs for the complete hyperfine structure. In Fig. 5 are shown the probabilities of absorption for the different levels; it can be seen that the probability of absorption for the state $F = 2$, $m_F = 2$ is zero for σ_+ D_1 light.

Pumping in this manner can readily be observed by means of the simple apparatus shown in schematic form in Fig. 6 and in the photographs of Fig. 7. Light from a sodium resonance radiation lamp is focused on a heated glass flask or bulb containing alkali metal which evaporates to a suitable density. The bulb may contain a buffer gas like helium, or it may be coated, at high vapor pressure, with paraffin or silicone, from which the atoms bounce without a long period of attachment to the wall, and thus without depolarizing. The light must pass through a circular polarizer and through a filter. Polaroid sheeting and 1/4 wave plate consisting of birefringent plastic sheeting is suitable for sodium, potassium, rubidium, and cesium pumping. For all but sodium pumping, interference filters of thin film can be used. The small separation of the D lines in sodium makes such a filter difficult to construct, but the D_2 light may be suppressed by passing the light through an extra filter cell of sodium vapor, placed between the poles of a magnet at a flux of several thousand gauss (*11*). The Zeeman splitting of the D_1 light is twice as great as that of the D_2 light, so the D_1 light from the line passes through a "gate" in the cell which is not wide enough to pass the D_2 light. Even if no filter is used it is still possible to obtain rejection of D_2 light at proper vapor densities. This occurs because the sum of possible transitions from the $S_{1/2}$ state to the $P_{3/2}$ state is twice as great as the sum of possible transitions from the $S_{1/2}$ state to the $P_{1/2}$ state, and so the D_2 light is scattered out of the sample flask more rapidly (especially since scattering increases exponentially with path length); this leaves the D_1 light strongest inside the cell and on the side where it eventually emerges.

The effect of optical pumping may be detected by measuring the light emerging from the optically pumped sample. If the output of the photodetector is observed as the direction of the magnetic field is reversed from parallel to the direction of incident light to antiparallel, the light output will temporarily decrease. The reason is simple. If the direction of the magnetic field is reversed adiabatically—that is, slowly enough for the atoms which precess at the gyromagnetic or Larmor frequency to follow the field change—then the atoms will remain in the same quantum states but their direction will be reversed with respect to the direction of the light. Polarization of the light will appear to proceed in a clockwise rather than a counterclockwise direction, and the polarization will pump the atoms to the opposite quantum level. Because the atoms had previously been pumped into the least-absorbing state, the change results in increased scattering of light from the atoms and in less transmission, during the time that the light is reestablishing equilibrium.

Resonance Transitions

A much more useful way to detect the optical pumping, and conversely to use the optical-pumping process as a detector in radio-frequency and microwave spectroscopy, is to irradiate the sample with light of a frequency which corresponds to that of one of the possible fine or hyperfine transitions of the atom in the magnetic field which is applied. The simplest method is to use the low-field Zeeman transition ($\Delta m_F = \pm 1$, $\Delta F = 0$) which occurs at the Larmor precession frequency for $S_{1/2}$ atoms of

$$\nu_L = 2.8/(2I + 1)$$

megacycles per second, where I is the nuclear spin. The effect of applying light of this frequency is to transfer atoms from one of the least absorptive m_F states into which they have been pumped into other states which absorb the light more strongly. In practice, one sweeps the magnetic field or the frequency range periodically with a synchronized oscilloscope or other monitor, and the resonance, shown by a dip in light transmission, is displayed. Figure 8 shows such resonances, and also shows two apparent line widths. One, when the field sweeps into the resonance from above or below, gives the true line width and the other, as

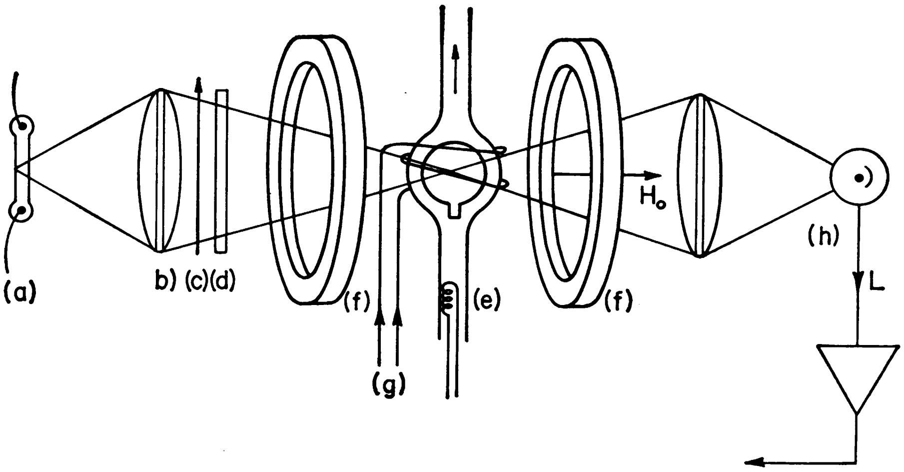


Fig. 6. Schematic drawing of intensity pumping apparatus. (*a*) Resonance lamp; (*b*) focusing lens; (*c*) polaroid sheeting; (*d*) 1/4 wave plate (and interference filter if used); (*e*) sodium vapor bulb and heater; (*f*) magnetic field coils or solenoid; (*g*) radio-frequency coil; and (*h*) photodetector.

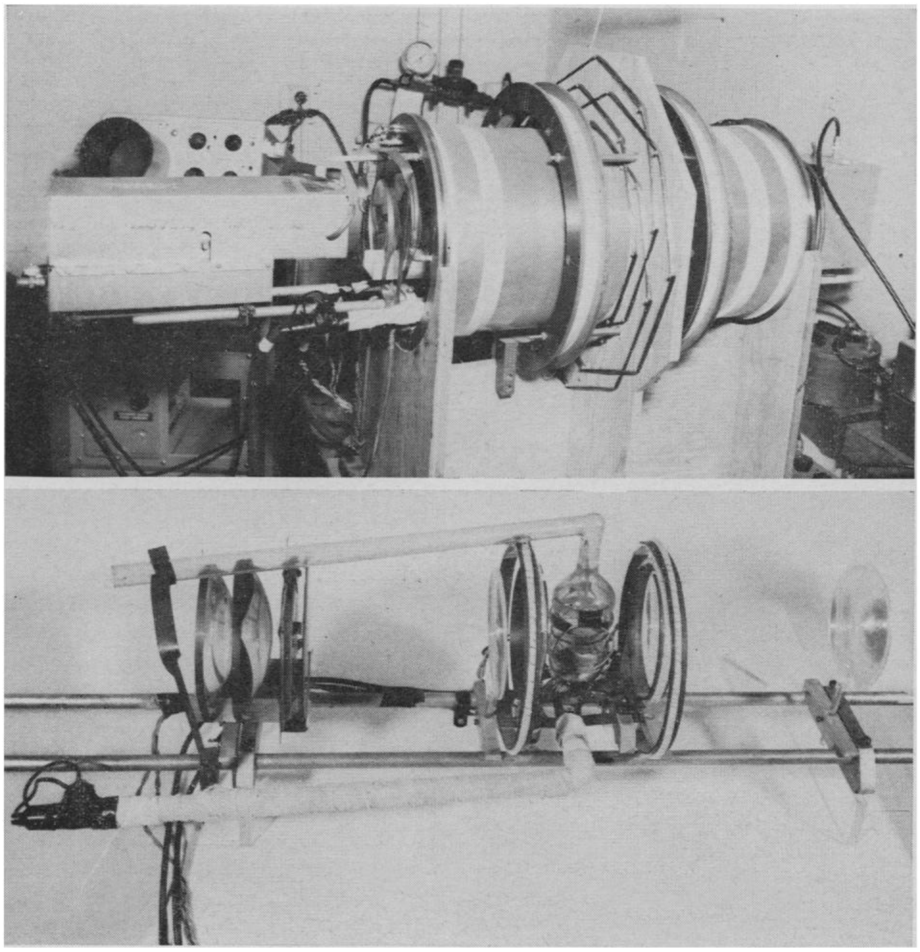


Fig. 7. (Top) Optical pumping apparatus in a homogeneous-field solenoid. The radio-frequency-excited resonance lamp is at left; the photodetector, at right. (Bottom) Internal optical arrangement, sample bulb, and heater.

the field passes out of the resonance, shows the time required for the light to re-establish equilibrium.

The use of magnetic dipole resonance transitions in connection with the optical-pumping process provides other possibilities of detection. When a coherent radio-frequency field is applied at resonance to an ensemble of atoms, the atoms precess coherently around the magnetic field, which is a combination of the static external field and the oscillating radio-frequency field. If a beam of linearly polarized resonance light is simultaneously transmitted at right angles to the axis in the experimental arrangement described earlier, the atoms will modulate the light at the Larmor frequency of precession, by virtue of the fact that their polarization is periodically wobbling. Thus, the radio-frequency may be directly observed as amplitude modulation of the light (*12*). If this radio-frequency signal from the photodetector is reapplied through an amplifier to a coil surrounding the sample, the whole device becomes a self-excited oscillator whose frequency is determined by the magnetic field on the sample. Such a magnetometer, because of its sharp lines and high-frequency response to low fields, has already sent back useful data on the magnetic fields in space; the information is obtained from the frequency of oscillation.

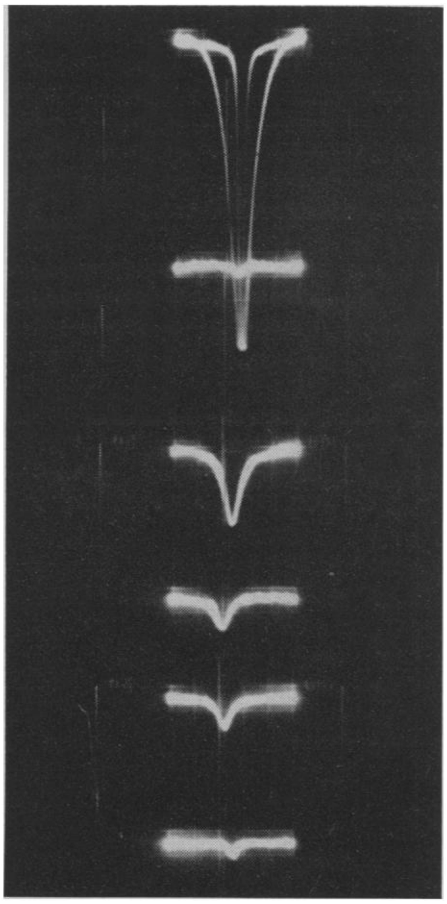


Fig. 8. Low-field Zeeman transitions in the ground state of rubidium-87. The magnetic-field-modulation sweep through the resonances is plotted on the x axis; the light signal at the photodetector, as displayed on the oscilloscope, is shown on the y axis. From top to bottom: $F = 2$, $m_F = 2 \rightarrow 1$; $F = 1$, $m_F = 1 \rightarrow 0$; $F = 2$, $m_F = 1 \rightarrow 0$; $F = 1$, $m_F = 0 \rightarrow -1$; $F = 2$, $m_F = 0 \rightarrow -1$; $F = 2$, $m_F = -1 \rightarrow -2$.

Such a light-modulation experiment has an inverse (*13*). A magnetic field is applied in a given direction, and circularly polarized light is applied at right angles to this direction. The light is amplitude-modulated (by a Kerr cell, perhaps) at the Larmor frequency of precession. The light produces a polarization of the atoms at right angles to the applied field, and this polarization precesses, as usual, by gyromagnetic coupling to the magnetic field. However, the light polarizes the atomic ensemble in phase with its precession, and the coherent-precession polarization grows. In effect, the magnetic dipole transition can be induced by amplitude-modulated light rather than by the oscillating magnetic fields usually used in paramagnetic or nuclear resonance experiments.

It is not necessary to use circularly polarized light at all. Figure 5 shows a splitting $\Delta\nu_h$, between the $F = 2$ and $F = 1$ states in an alkali metal atom. The splitting is caused by the magnetic interaction of nuclear and electronic magnetic moments. Some of these levels are affected by external fields, but the levels $F = 2$, $m_F = 0$ and $F = 1$, $m_F = 0$ are not affected, to a first order of magnitude, by fairly low fields. In the case of rubidium-87 whose nuclear spin (3/2) is the same as that of sodium, the frequency difference between these levels, which is also the frequency of precession of the electron and the nucleus in the coupled magnetic field, is 6834.682614 megacycles per second; this frequency will change by only about 5 cycles if the external magnetic field is a fluctuating field of 0.1 oersted.

Actually, it is easy to shield the field to reduce this value. Moreover, when the Rb^{87} atom is placed in a cell with a buffer gas to prevent rapid diffusion, the line width of the microwave transition is not determined by the normal Doppler width and can be made as narrow as 20 cycles per second.

To detect this narrow line, which can be made the flywheel of an atomic clock, it is only necessary to pass the resonance radiation of rubidium through the cell without polarization, detect it with a photocell on the other side, and apply radiation of microwave frequency harmonically generated from a crystal oscillator (*14*). Since there are more levels in the $F = 2$ state (*5*) than in the $F = 1$ state (*3*), the light causing transitions from the $F = 2$ states to the excited P states is reduced in intensity as it passes through the cell. The remaining light tends to pump the atoms from the $F = 1$ state to the $F = 2$ state, and the cell becomes more transparent. The application of radiation of the proper microwave frequency causes a resonant darkening of the photocell, as in the case of the low-frequency Zeeman transitions. The optical signal can be used to correct the crystal oscillator, or—better still, for certain purposes—because the populations are inverted, the device can be used as a self-oscillating maser. Use of an Rb^{85} isotope absorption cell before the light enters the Rb^{87} sample cell can further increase the population difference because the Rb^{85} has a different hyperfine splitting and an isotope shift which filters the light effectively. These devices are the simplest in the family of atomic clocks and have exhibited stabilities of $1:10^{11}$, equivalent to 1 second in 3000 years.

Mercury Pumping and Excited States

In the foregoing description, for the purpose of simplicity, the methods and techniques have been explained in terms of the alkali metals, primarily sodium and rubidium. Cesium, potassium, and lithium may also be used and, in principle, atomic hydrogen, although in practice the handling of Lyman α radiation at 1215 angstroms is very difficult. The most precise work in studying the actual shapes of the resonance lines has been done by the Paris group, using the isotopes of mercury (*15*). The electronic ground state of mercury is 6^1S_0, so there is no multiplicity of levels if the nucleus has no spin. In the simplest case the optical pumping may be studied by pumping to the 6^3P_1 level with the mercury resonance radiation at 2537 angstroms. If the pumping radiation is polarized parallel to the external field, the excited state populated will be an $m = 0$ state, and the scattered radiation must also be polarized in this direction. However, if magnetic dipole transitions are induced in the excited state between the levels $m = 0$ and $m = \pm 1$, then, when the atom reradiates, it may also emit radiation which is polarized perpendicular to the magnetic field, and this radiation may very readily be separated from the incident radiation and detected. Excited-state pumping of this general kind can be observed in other Group II metals also.

Measurement of the hyperfine structure in the excited state by this technique plays a unique role in the determination of the electric quadrupole moment of the nucleus. This property of the nucleus—that it is not a spatially symmetric charge distribution—manifests itself as a measurable quantity only when the nucleus is in a strong electric field gradient. The relative orientation of the symmetry axis of the nucleus with respect to the electric field gradient affects the energy and produces a measurable frequency shift in the hyperfine structure of the whole atom. For the class of atoms whose ground state is an S state, the spherically symmetric charge distribution produces no such gradient. However, the hyperfine structure can be seen by the optical method precisely with those atoms whose first excited resonance state is a P state. Such measurements cannot be made in the atomic beam apparatus in most cases, because the lifetime of the atom in its P state may be shorter than 10^{-8} second and is seldom longer than 10^{-4} second, so that the atom cannot travel farther than a few centimeters at most in the beam apparatus while it is excited.

If isotopes of mercury which have nuclear spins are pumped with circularly polarized light (*16*), then the ground state is polarized in a manner analogous to the polarization of the alkali metals. However, since the mercury atom has no electronic angular momentum, the polarization which results is only that of the nucleus. Moreover, since the magnetic moment of the nucleus is about 1/1000 that of the electron, the nuclear polarization which results is not relaxed rapidly by collisions. Nuclear relaxation times in the mercury atom may be longer than 100 seconds, especially when the walls of the flask are carefully prepared, whereas the depolarization time of atoms, like sodium, with electronic moments is less than 1 second.

Normally, the resonance line widths observed in optical pumping in the excited state are determined by the lifetime τ of the atoms in the excited state through the uncertainty principle $\Delta\nu \propto (1/\tau)$. If the vapor density of mercury is rather high (and a high vapor density can be achieved at reasonable temperatures), resonance light is actually "trapped" in the bulb. The resonance light can no longer be considered radiation from an individual atom but, rather, must be viewed as radiation from the entire assembly of atoms, which are passing the radiation back and forth. Curiously, it is observed that the line width is narrower under these circumstances (*17*), and it appears that the effective lifetime of radiation from the many-atom radiator is longer. This effect may be considered from the classic point of view which follows.

An atom presents a cross section of about λ^2 for a photon at the resonance radiation wavelength λ, and, if it is within λ of another atom, its reradiated fluorescence will cause interference. In other words, at sufficiently high densities a strongly radiating atom will be nearly surrounded by equally strong absorbers, and the light cannot travel far except by a process more akin to diffusion. Such effects should become important when there is more than one atom in each volume of λ^3, a situation that occurs at a pressure of about 10^{-4} torr. Such a pressure represents the approximate limit of sample pressure in direct optical pumping, and indeed is the range in which narrowing and coherence effects are seen.

Interesting "light-beat" effects may also be observed in emission of light from the excited state. If a beam with two resolved frequency components of optical wavelength is produced in a nonlinear detector, the two components will produce a beat-frequency signal in the same manner that any beat is formed. However, light emitted from mercury, for example, in the optically pumped excited state can be made to show light beats (*18*) even when the hyperfine levels of the excited state are themselves not separately resolved into distinct frequency components. The beating occurs when magnetic dipole transitions are caused to occur between the different hyperfine levels. A study of these beats has helped us understand that the emission of light is not radiation from a single atomic level to another but radiation from a "superposition" state of a many-level system.

Metastable States

In addition to optical pumping of atoms in the ground state to produce a long-life polarization, or application of the pumping techniques to spectroscopy, in the excited states of atoms, it is also possible to apply pumping techniques to atoms in metastable states (*19*), when the metastable state has its own resonance radiation and thus is a pseudo ground state. Helium has such a pseudo ground state, the $^3S_1$; the notation signifies that the electronic configuration is still spherically symmetric but that the two electrons are coupled together in parallel to give a total spin of 1 and a multiplicity of 3. This state lies 19.81 electron volts above the $^1S_0$ ground state but cannot radiate to the ground state without violating two dipole-selection rules of the Russell-Saunders coupling scheme, which require that the orbital angular momentum shall change by one unit of angular momentum and that the spin shall not change. Except through collisions with other atoms, electrons, or the walls, an atom in the metastable state has virtually no way to decay, and at optimum pressures of about 1 torr in ordinary small bulbs it may live for many milliseconds. This is sufficient time for it to absorb several of its resonance-radiation photons. The resonance radiation of this metastable state is light of 10,830-angstrom wavelength; thus, the metastable state is coupled to states denoted as $^3P_0$, $^3P_1$, and $^3P_2$. This resonance radiation is not far in the infrared, and thus no very special optical materials are required for detecting it, although it is not produced in a helium discharge lamp as strongly as resonance light of alkali metal is. The metastable helium is produced by a weak discharge, perhaps an electrodeless discharge, and for simplicity it can be produced in the same cell with the discharge which produces the light. In the latter case, of course, it is not possible to circularly polarize the light before it is absorbed and scattered by the metastable helium, but, when an external field is present, the lamp portion emits light which is partially polarized, and intensity pumping effects make it possible to observe the Zeeman transitions. The advantage of this system for simple magnetometers is the fact that the density of metastable helium may be controlled by the discharge current, rather than by temperature control of the vapor pressure.

If the stable isotope of helium, He^3, which is produced in some quantity from the decay of tritium, H^3, is optically pumped in the metastable state, this can cause the isotope in the ground state to become equally polarized by means of a "metastability exchange" (*20*), which may be represented by the process:

$$He^3 + He^{3*} \rightarrow He^{3*} + He^3.$$

The cross section for this effect is large because momentum and energy are conserved and, as we shall see later, because an electron exchange is essentially involved. If such a transfer of metastability were to occur for He^4, it would represent a collision of indistinguishable particles and would have no effect. In the case of He^3, however, the nucleus of the isotope has a spin of 1/2 and a magnetic moment. When the atom in the metastable state is polarized, the nucleus becomes polarized through hyperfine coupling with the electron spin, as in the case of the alkali metal nuclei, and the distinguishable characteristic is passed to the atom in the unexcited ground state after the metastability exchange has occurred. In a helium atom in the ground state, the nucleus does not relax rapidly, and the polarization produced through metastability exchange may persist for many minutes and perhaps hours. Although this process can be carried out only at pressures of less than a few torrs because of the difficulty of producing the metastable atom at higher pressures, the long period of nuclear relaxation is ample for mechanically pumping the polarized helium to high pressures and perhaps even for liquefying it. Even in liquid He^3 the nuclear relaxation period is about 10 minutes.

Spin-Exchange

It may appear that optical pumping can be used only when the density of particles is low, and only with alkali metals or Group II elements with strong resonance lines and *S* ground states, but the angular momentum produced in the pumped ensemble of atoms may in fact be transferred to other particles. The most effective transfer process is the spin-exchange process. The essentials of this process may be readily understood by those familiar with the nature of the bonding of the H_2 molecule. Figure 9 shows the potential energy of two hydrogen atoms as a function of the distance of separation of the nuclei. If the spins of the two *S*-state electrons are parallel, resulting in a total-spin *S* of 1 (the triplet state), according to the Pauli exclusion principle the electrons interfere and cannot overlap in the region between the two nuclei. Since this is where the charge must be in order to overcome the repulsion between the nuclei, the triplet state is repulsive. If the total-spin *S* is 0, however, the electrons can overlap and help to provide an attractive potential, at least until the nuclear repulsion becomes too great. Although sodium and rubidium atoms do not form such stable molecules in the usual sense, their valence *S*-state electrons give rise to similar potential functions. In fact, similar triplet-singlet differences exist in any two-electron system, including the interaction between a free electron and a hydrogen atom, although in this case there is no eventual repulsion as the particles approach in the singlet state. (Remember that an H^- atom is known to exist!)

When a hydrogen atom approaches a sodium atom, the two atoms cannot bind together, because, in a free collision, momentum and energy cannot be conserved. The energy of the system will be neither that of a singlet nor that of a triplet, but a mixture of the two; but the cross section will consist of a singlet cross section which is very large, because the system has a bound or nearly bound state, and a triplet cross section which is small. The effective exchange cross section is 1/4 of the singlet cross section, because, in the random collision, 1/2 of the particles arrive with spin antiparallel to that of the electron on the target atom, and because, after many spin exchanges have occurred during the time of collision, the chance that the spins have ultimately been exchanged is 1/2. Thus, a definite cross section exists for the process of interchanging the spin directions of the two electrons on the separate atoms, or the spin directions of an atom and a free electron. It is very much larger than the gas kinetic cross section, because the distance at which the two electrons begin to interact and exchange is much greater (see Fig. 9) than the distance at which strong repulsion effects bring about a strong transfer of momentum to the whole atom. Clearly, then, if an ensemble of unpolarized atoms or free electrons makes collisions with an optically pumped group of atoms, the polarization will be transferred to the unpolarized atoms and the pumped atoms will be depolarized but repumped by the light.

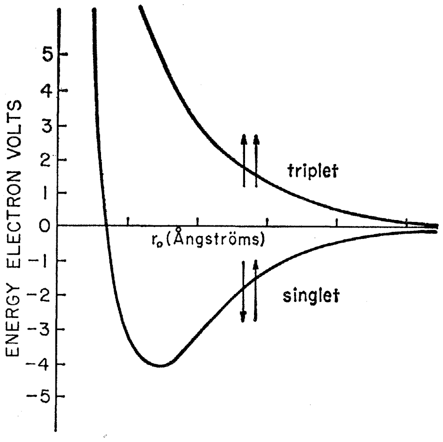


Fig. 9. Interaction energy of two hydrogen atoms as a function of the internuclear separation r_0.

The spin-exchange pumping was first shown to work (*21*) when it was used in measuring the magnetic moment of the electron. According to the Dirac theory, the electron particle should have a magnetic moment of exactly 1 Bohr magneton ($e\hbar/2mc$), and the fact that the magnetic moment differs from this value by about 0.1 percent was first discovered through careful atomic-beam measurement of the contribution of the electron bound to an atom to the total magnetic moment of the atom. The theoretical resolution of the discrepancy was accomplished through better understanding of quantum electrodynamics, and, in fact, efforts to account for the discrepancy were partly responsible for the developments in that field. The magnetic moment of the free electron

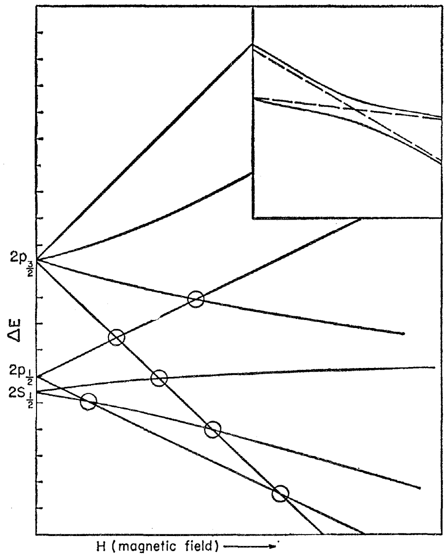


Fig. 10. Level crossings in the fine structure of the $n = 2$ *S* and *P* states of hydrogen. (Insert) The form of an "anti-crossing" which may occur in the hyperfine structure.

cannot, however, be observed in an atomic-beam experiment, because the inhomogeneous magnetic fields required to deflect the atom by means of their effect on the atom's magnetic moment will have a much greater deflecting effect on the charge of the atom. It was thought for some time that it was impossible to determine the magnetic moment of the free electron in any way. However, optical pumping and spin exchange have provided one of two methods by which this can be accomplished with great precision.

In the experiment, a conventional apparatus for optical pumping of sodium atoms (Fig. 6) is used. By using a pulsed discharge or by means of ultraviolet light or a steady continuous discharge, some of the optically pumped sodium atoms are ionized. The free electron may be depolarized through application of the Zeeman resonance frequency at 2.8 megacycles per gauss, and the resulting depolarization will be transferred back to the sodium atoms through spin exchange, producing the same effect of increased scattering and lowered transmission of the sodium resonance light that would have been produced if the sodium atoms had been directly depolarized. In a similar way, by using a discharge to dissociate molecular hydrogen or nitrogen, the hyperfine structures of these atoms have been studied by optical pumping (*22*), even though their resonance radiation in the extreme ultraviolet cannot easily be used for direct optical pumping. Heavy metals like silver may also be pumped in this fashion, even though the vapor pressure of such elements is rather low.

Angular momentum may be transferred to other atoms by another process, which is closely related to the Overhauser effect and is much slower than the spin-exchange process (*23*). If atoms of a noble gas which has a nuclear magnetic moment are used as the buffer gas in an optical-pumping experiment, the nuclei of the noble gas atoms will not be quickly relaxed and depolarized by collisions with other noble gas atoms, because there is little magnetic field present in such a collision, but will be strongly affected by collision with a sodium or rubidium atom which has the Bohr magneton of its unpaired electron. A detailed examination of the collision process shows that the sodium or rubidium atom and the spin nucleus of the noble gas atom will tend to make simultaneous spin flips in the same direction. As the sodium or rubidium atoms relax from an optically polarized condition they will tend to flip only in one direction and to cause the noble gas nuclei to flip in the same direction. The result, in principle, is polarization of the noble gas nuclei to the same order of polarization as that of the pumped alkali atoms. Although this method has not produced a high degree of polarization, it works at pressures of buffer gas which are above atmospheric pressure. The enhancement of the nuclear resonance of He^3 gas, for example, is so large as to make it possible to use this sharp nuclear resonance line as a very sensitive nuclear-spin gyroscope, and application of the method to studies of Ne^{21} may make it possible to determine very precisely the anisotropy of space, in somewhat the same sense as the Michelson-Morley experiment made this possible (*24*).

"Level-Crossing" Effect

Surprisingly enough, it is not necessary in all cases to apply radio frequencies or microwaves in order to observe and study the general hyperfine-structure parameters of atoms. In certain states of atoms (an example is the $n = 2$ states occurring in hydrogen, represented in Fig. 10), some of the fine-structure lines cross at particular values of the magnetic field. At the points where the levels are degenerate, the states mix, and the probability of absorption for one level is determined by the combined scattering from the two states. The effect is one of interference, and the light to the photodetector will increase at these points in a resonant manner. Since the phenomenon does not depend on polarized light or on producing population differences in the various levels, it may be used for studying atoms whose resonance radiation cannot be conveniently polarized, or where, even if it could be, the light intensity available would be too low to produce changes in the populations. It has therefore been useful in studying the excited-state fine structure in helium and the Group II elements (*25*). A recently discovered aspect of this "level-crossing" effect is the "anticrossing" signal (*26*) observed when two levels appear to cross but in fact repel one another. Such anticrossing appears in the detailed hyperfine structure at the places where the fine-structure lines cross. Such level crossings occur, of course, in zero magnetic field, as can be seen in Figs. 3 and 10. Hanle, in 1924, observed (*27*) the depolarization of resonance-radiation scattering in zero field, so this Hanle effect, very useful in measuring oscillator strengths, has essentially been rediscovered nearly 40 years later!

Optical pumping has been performed in solids, but the spectroscopy of ions in solids is well beyond the scope of this article. The use of optical pumping to produce a population inversion in ruby lasers is not a sophisticated process, but it involves the populating of excited states of the radiating impurity atoms, and the subsequent relaxation and de-excitation processes are the essential processes in causing a population inversion for the stimulated optical emission. The general developments in the field of optical pumping were undoubtedly important in hastening the development of the principle of lasers.

Although most of the suitable systems have now been studied by optical pumping, and although the basis of the dynamics has been established (*28*), it is obvious that active work will be continued, particularly to apply the techniques to the measurement of magnetic moments, fine and hyperfine splittings, and nuclear quadrupole moments in atoms in excited states and in radioactive isotopes where the small amounts of material and the ability to use sealed bulbs minimizes the radiation problem. Moreover, if optical pumping is used on beams of atoms in a vacuum system rather than in a closed bulb with a buffer gas, there is then no difficulty in optically pumping atoms whose ground state is a *P* state. Already work on calcium, carbon, and thallium beams has begun. We may also hope that the difficult problem of studying the precise fine and hyperfine structure of ions will be solved in the future.

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Cell Differentiation: Some Aspects of the Problem

The interaction of a temporal sequence of gene action and metabolic factors may direct differentiation.

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In a classical sense cytodifferentiation depends mainly upon the histological characteristics of cells. These morphological qualities, which provide a basis for classifying cells as differentiated, appear to be attributable primarily to structural properties of the proteins of the cells. For example, myosin of muscle and hemoglobin of erythrocytes are proteins which are end products of differentiation which typify these cells. The structural organization of proteins into cellular organelles is yet another facet of cytodifferentiation. Other cells may be characterized less easily by various cellular products which are synthesized under the control of specific enzymes or through certain physiological or biochemical activities having an enzymatic basis. Differentiation in an embryo involves the selective association of cells and tissues to form organs which attain a topographic pattern characterizing the organism, but this level of differentiation undoubtedly is also influenced by specific proteins of the cell membranes, which play a major role in the morphogenetic events. Since the properties of proteins are attributable to the activity of chromosomal genes, it would seem that the genes are the specific determinants of cytodifferentiation, although their activity may be modified by environmental factors.

According to the working definition of differentiation just given, the proteins that distinguish cells as differentiated are synthesized in significant amounts when the cells differentiate. For example, immunological studies have shown that myosin (*1*) and lens antigens (*2*) appear at the time of differentiation, and Boell and Shen (*3*) have demonstrated the onset of cholinesterase activity when the neural plate is formed. It is true that antigens with combining groups characteristic of myosin and actin (*4*), the globin portion of hemoglobin (*5*), and lens proteins (*6*) may be present in trace amounts before differentiation. This is of particular interest when the tissue-specific antigens are localized in cells that normally are directed into this type of differentiation. For instance, Ebert (*4*) has found that antigens which react with antisera against cardiac actin and myosin become localized in the prospective heart-forming areas of the early chick embryo.

Although specific proteins, when present, define or characterize cells as differentiated, it seems probable that the process of cell differentiation is allied with the mechanisms of directed or specific protein synthesis, rather than with the ultimate appearance of protein molecules. Schechtman (*7*) and Ebert (*8*) have emphasized that the appearance of tissue-specific antigens may reflect only the end point of differentiation. It appears profitable, therefore, to examine the role of DNA and of specific RNA's in directing protein synthesis, since their activities occur prior to protein synthesis and differentiation. This approach may be particularly fruitful in cases where the pathway of future differentiation of embryonic cells is set, or "determined," some time before the actual synthesis of the tissue-specific proteins occurring at the time of differentiation.

Recent studies in the field of molecular biology have revealed that a linear order of triplet combinations of nucleotides in RNA specifies the sequence of amino acids which are polymerized to form a polypeptide. The most convincing evidence for such a polynucleotide code was the demonstration by Nirenberg and Matthaei (*9*) that polyuridylic acid (polyU), a polynucleotide composed only of uridine, stimulated the formation of a polypeptide composed only of phenylalanine. In terms of a triplet coding unit, it appears that the triplet (UUU) codes for the utilization of phenylalanine in protein synthesis. This remarkable discovery tells us that a specific polyribonucleotide sequence can be transcribed into a specific sequence of amino acids. It does not, however, explain why certain gene-produced polyribonucleotide sequences operate in some cells whereas other sequences are transcribed in other cells, when the genetic constitution, and therefore the DNA makeup, of all cells in the organism is

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