

when x-ray quanta are absorbed in matter. X-rays are, of course, ionizing radiations, and induce chemical reactions by formation of intermediate species, free radicals, and ions. These reactions may be used profitably for dosimetry, to produce mutations, and to irradiate selectively cancerous tissue, among many of the possible uses.

Because of space limitations, this review only sketchily refers to some of the numerous uses of x-rays. For further information it is suggested that the reader consult the references.

WILLIAM L. BAUN

#### References

- Compton, A. H., and Allison, S. K., "X-Rays in Theory and Experiment," 2nd Edition, New York, Van Nostrand Reinhold, 1935.
- Azaroff, Leonid, "X-Ray Diffraction," Vol. I, and "X-Ray Spectroscopy," Vol. II, New York, McGraw-Hill Book Co., Inc., 1974.
- Kaelble, E. F., "Handbook of X-Rays," New York, McGraw-Hill Book Co., Inc., 1974.
- Clark, G. L., "The Encyclopedia of X-Rays and Gamma Rays," New York, Van Nostrand Reinhold, 1963.
- Flugge, S., "Encyclopedia of Physics, X-Rays," Vol. XXX, Berlin, Springer-Verlag, 1957.
- Clark, G. L., "Applied X-Rays," 4th Edition, New York, McGraw-Hill Book Co., Inc., 1955.

Cross-references: ATOMIC SPECTRA, BIOMEDICAL INSTRUMENTATION, BIOPHYSICS, BREMSSTRAHLUNG, COMPTON EFFECT, CRYSTALLOGRAPHY, DIFFRACTION BY MATTER AND DIFFRACTION GRATINGS, ELECTRON, MEDICAL PHYSICS, X-RAY DIFFRACTION.

## ZEEMAN AND STARK EFFECTS

**Introduction** The Zeeman and Stark Effects refer, respectively, to effects of external magnetic and external electric fields on the structure of atoms or molecules. In most cases the effects are observed through the modification of spectral features such as strength, polarization, width and position of emission or absorption lines. The Zeeman effect is named after Pieter Zeeman, who in 1896 observed a magnetic-field-induced broadening of the *D* emission lines in sodium vapor. (Zeeman's observed broadening was later found to be a small splitting.) The Stark effect is named after Johannes Stark, who in 1913 observed the electric-field-induced splitting of the Balmer transitions in atomic hydrogen.

Both the Stark and Zeeman effects have received extensive study since their discoveries. During the period of the development of the early quantum theories the effects played an important role by helping to stimulate the development of new ideas and computational techniques. In modern times the effects have

enjoyed continued interest due to newly discovered aspects of the intermediate and strong field problems. To a degree, much of the recent interest is also connected with the technological developments of tunable lasers and digital computers.

This article will examine the effects of external magnetic and electric fields on hydrogen and hydrogenlike atoms. The discussion has been limited to such atoms for the sake of simplicity but not at the cost of completeness. All the essential features of external field effects are brought out by the discussion of this simple example. It will be shown that the Zeeman and Stark effects are traceable to the interaction between the magnetic and electric dipole moments of atoms and the external fields. Dipole moments in atoms occur naturally or are induced by external fields.

**Zeeman Effect Introduction.** The Zeeman effect is the result of the interaction between the magnetic moment of the atom and the external magnetic field. The leading term to the interaction energy is,

$$W = -\boldsymbol{\mu} \cdot \mathbf{B}, \quad (1)$$

where  $\boldsymbol{\mu}$  is the magnetic dipole moment and  $\mathbf{B}$  is the magnetic field. Magnetic dipole moments in atoms arise either from internal currents due to electron orbital motion, or from the natural (intrinsic) magnetism associated with the electron and the atomic nucleus. In the following discussions three well known cases of the Zeeman effect are considered: the normal effect, the anomalous effect, and the diamagnetic effect. (The terms "normal" and "anomalous" were coined before the Zeeman effect was well understood and unfortunately are misleading. The normal effect is actually a special case of the anomalous effect.) The magnetic moment associated with each case has a unique origin. The normal effect is caused by the interaction with the orbital magnetic moment. The anomalous effect is caused by the interaction with the combined orbital and intrinsic magnetic moments. The diamagnetic effect is caused by the interaction with the field-induced magnetic moment.

**Normal Zeeman Effect.** Figure 1 displays the simplest example of the normal Zeeman effect, that is, the effect on the *s-p* transition. (Spectroscopic notation is used to label quantum states. The letters *s*, *p*, *d*, *f*, ... designate the orbital angular momentum, *l*, corresponding to values of 0,  $\hbar$ ,  $2\hbar$ ,  $3\hbar$ , ...,  $2\pi\hbar$  is Planck's constant.) The *p* level splits into three equally spaced sublevels under the influence of the external field. The central *p* sublevel and the *s* level do not shift in response to the field. The energy spacings between the *p* sublevels increase linearly with the applied field. (An observation that applies to all normal-effect transitions is that the magnitude of the rate of separation between adjacent sublevels is a constant that is the same for all members of a Rydberg series. Thus, the

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induction. The Zeeman effect is the interaction between the atom and the external field leading term to the

$$\mathbf{L} \cdot \mathbf{B}, \quad (1)$$

magnetic dipole moment and  $\mathbf{B}$  is the external magnetic field. The magnetic dipole moments are due to internal currents due to the orbital motion, or from the natural magnetic moments associated with the electrons. In the following sections we discuss the normal Zeeman effect, the normal effect, the anomalous effect, and the "anomalous" effect. The normal effect was well understood and the anomalous effect was misleading. The normal effect is a special case of the Zeeman effect. The magnetic moment associated with the orbital motion is unique. The interaction with the external field is different. The anomalous effect is the interaction with the external magnetic field. The normal effect is the interaction with the external magnetic field.

Figure 1 displays the normal Zeeman effect for the  $1S-1P$  transition. (Specified to label quantum numbers  $l, f, \dots$  designate the  $1, l$ , corresponding to  $1, 2\pi\hbar$  is Planck's constant. The energy levels of the external field and the  $s$  level do not change. The energy levels increase linearly with the external field. An observation that the separation between the  $s$  and  $p$  levels is the same for all series. Thus, the

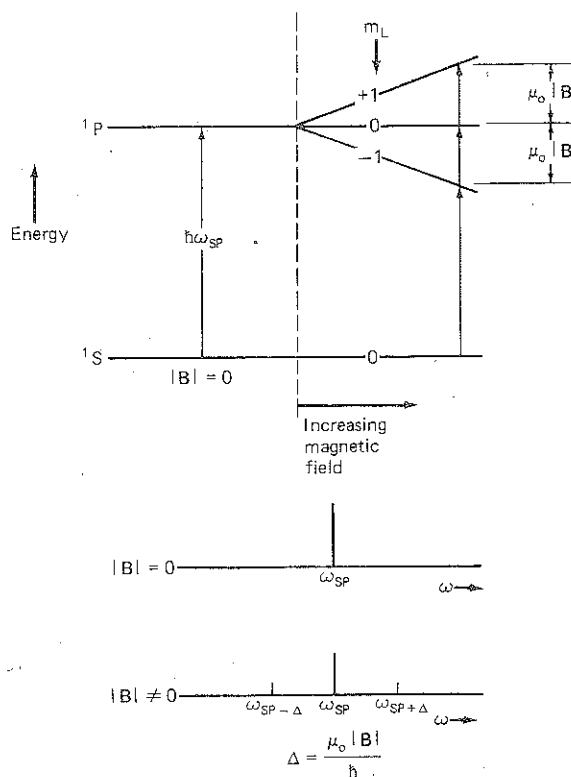


FIG. 1. Normal Zeeman effect for  $1S-1P$  transition. Above is energy level diagram; below is spectrum with and without an external field.

appearance of the effect does not depend upon the principal quantum numbers of the states in question. This last observation is Preston's rule.) The spectrum, which is due to transitions between the  $s$  and  $p$  states, appears as a triplet as indicated in the lower portion of Figure 1. (The normal-effect triplet for the  $s-p$  transition is named after Lorentz, who described the effect in terms of his theory of electrons. Lorentz's explanation helped to support the notion of orbiting electrons in atoms.)

As indicated in the introduction, the normal effect is the result of the interaction between the magnetic moment due to the orbiting electron and the external field. From electromagnetic theory, the magnetic moment due to an electron circulating in a closed loop and having angular momentum  $l$  is,

$$\mu_l = \frac{-e}{2m_e c} l, \quad (2)$$

where  $-e$  is the electron charge,  $m_e$  is the electron mass, and  $c$  is the speed of light. (Unless otherwise noted all quantities are expressed in cgs units.) The interaction energy follows from

Eq. (1),

$$W = \frac{e}{2m_e c} l \cdot B. \quad (3)$$

According to quantum mechanics the projection of  $l$  about an axis, here the magnetic field axis, assumes discrete values  $m_l \hbar$ , where  $m_l$  is an integer that ranges between  $+l$  and  $-l$ . The expression for the interaction energy is, thus,

$$W = m_l \mu_0 |B|, \quad (4)$$

where  $\mu_0$  is the Bohr magneton constant defined by,

$$\mu_0 = \frac{e\hbar}{2m_e c} \approx 1.4 \times 10^6 \text{ Hz/Gauss.}$$

The triplet spectrum in Figure 1 is thus completely described given that  $m_l$  for the  $p$  state has values  $+1$ ,  $0$ , and  $-1$ , while  $m_l$  for the  $s$  state has the value  $0$ .

It happens that the normal effect does not actually occur for ordinary one-electron atoms because of the complication of electron spin.

The discussion above is thus strictly correct only if one assumes that the electron has no intrinsic magnetic moment of its own. The triplet does occur, however, in certain many-electron atoms (e.g., helium) where because of pairing of spins, the effects of intrinsic moments can be ignored.

**Anomalous Zeeman Effect.** Figure 2 diagrams examples of the anomalous Zeeman effect on a number of different atomic transitions. (One-electron atoms fall into the doublet category.) It is evident that the structure of the anomalous effect is more complicated than that of the normal effect. In addition, the field dependence is also more complicated. In weak fields, the levels separate linearly with the strength of the applied field as they did for the normal effect; however, the rates of separation of levels are different than those observed for the normal effect. In moderate fields, the levels shift in a complicated way that is not easily described by any simple power law. In strong fields, the levels again shift in proportion to the field strength but this time with rates of separation that are the same as those of the normal effect.

The anomalous effect was a mystery until 1925 when S. Goudsmit and G. Uhlenbeck introduced the concept of electron spin. Electron spin was conceived to explain why the fine structure separation of the  $^2P$  levels of alkali metal atoms were so much larger than the corresponding levels of hydrogen. Goudsmit and Uhlenbeck suggested that electrons have both an intrinsic angular momentum and an intrinsic magnetic moment. Following this assumption, the fine structure splitting was shown to be the result of the magnetic interaction between the intrinsic magnetic moment of the electron and an internal magnetic field produced by the electron's orbital motion. This effect is referred to as the spin-orbit interaction. (Note that the spin-orbit effect in many-electron atoms is much more difficult to model because one must consider the magnetic couplings of all of the electrons with each other. These include, for example, the interaction between the magnetic field produced by the orbit of one electron with the magnetic moment of another electron. The problem is sufficiently complex that even sophisticated modern techniques have failed to reliably calculate the absolute magnitude and, in certain extreme cases, the sign of the spin-orbit interaction for the bulk of the atoms in the periodic table.)

Given the postulate of spin to explain fine structure, it became evident that spin could also be used to explain the anomalous effect. The only way that it was possible to reconcile both effects, however, was to assume that the maximum projection of the intrinsic angular momentum of an electron was  $\hbar/2$  and that the intrinsic electron magnetic moment was,

$$\mu_s = g_e \frac{-e}{2m_e C} s \quad (5)$$

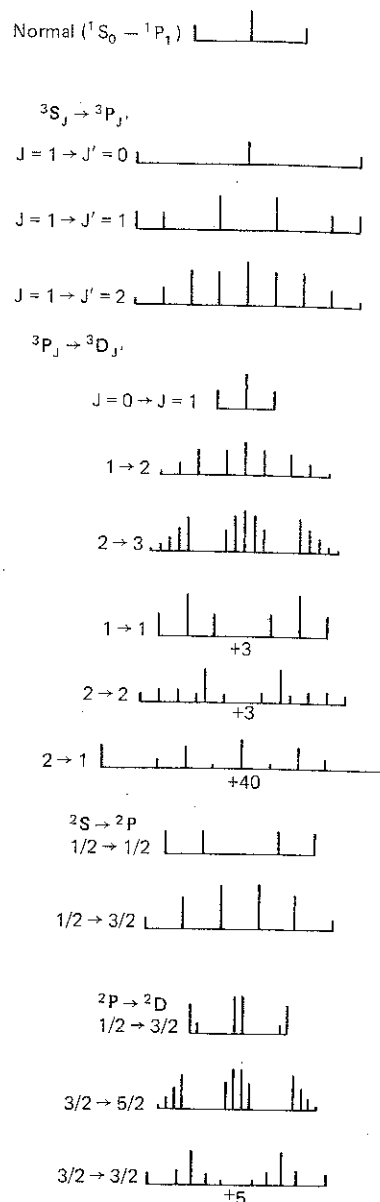
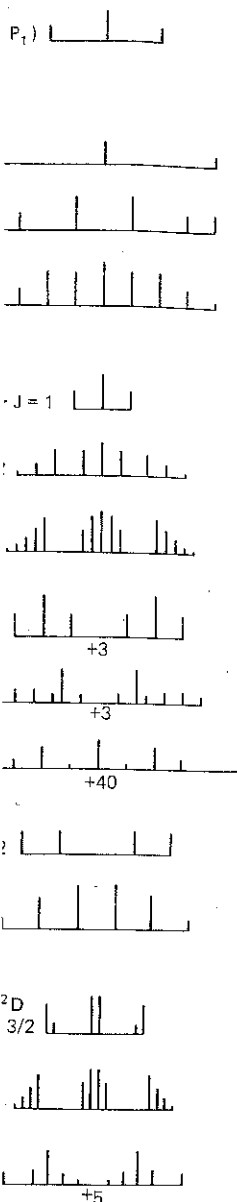


FIG. 2. Anomalous Zeeman spectra for numerous transitions. The normal Zeeman spectrum is shown for comparison. (After Condon and Shortley, 1971.)

where  $s$  is the electron spin angular momentum and  $g_e$  is an arbitrary factor added to preserve the form of the classical relationship between magnetic moment and angular momentum [Eq. (2)]. Early agreement with experiment was obtained by guessing that  $g_e = 2$ . (The Dirac equation, which combines quantum mechanics and relativity, justifies the ersatz of Eq. (5) and pre-



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dicts that  $g_e$  is exactly two. It is now known that  $g_e$  has a value that is a fraction of a percent larger than two. One of the important successes of modern quantum electrodynamic field theory, which treats both particles and fields quantum mechanically, is the correct prediction of this constant.)

With the introduction of electron spin it is straightforward, although nontrivial, to explain shifts associated with the anomalous effect. The energy of the quantum state of a one-electron atom follows from the expression for the interaction energy between a magnetic moment and an external field,

$$W = -(\mu_l + \mu_s) \cdot B + al \cdot s. \quad (6)$$

The additional term here,  $al \cdot s$ , represents the spin-orbit interaction. In the absence of external fields the spin and orbital angular momenta are coupled by the spin-orbit term such that the conserved quantity is  $j$ , which is defined as the sum of  $l$  and  $s$ , that is,

$$j \equiv l + s. \quad (7)$$

The complete characterization of the anomalous effect is complicated because the external field interaction affects the internal coupling of  $l$  and  $s$ . In light of this, only the weak and strong field cases, which are the two cases most easily described, are to be considered. These two cases represent the extreme situations where  $l$  and  $s$  are either completely coupled or completely decoupled.

In weak fields, where the interaction terms in Eq. (6) due to the external field are small compared with the spin-orbit term,  $l$  and  $s$  are completely coupled. In this case the dominant contribution of the magnetic moment is due to the portion of the moment that is parallel to  $j$ . (Since  $g_e \neq 1$ , the magnetic moment does not point along  $j$ . As a consequence of the coupling, however, the contribution of the portion not parallel to  $j$  is generally negligible.) Therefore the net effective magnetic moment is

$$\mu_j \simeq g_j \frac{-e}{2m_e C} j, \quad (8)$$

where the expression for  $g_j$ ,

$$g_j = 1 + \frac{j(j+1) + s(s+1) + l(l+1)}{2j(j+1)}, \quad (9)$$

is derived from angular momentum coupling relations assuming  $g_e = 2$ . Here  $j$ ,  $s$ , and  $l$  are the maximum projections of  $j$ ,  $s$ , and  $l$  in units of  $\hbar$ . Eq. (9) was obtained first empirically by Landé in 1921 based on studies of the experimental data of Back. (Landé's observations extended the earlier rule of Runge, which expressed the fact that the weak-field anomalous effect splittings are related to the normal effect splittings by a rational fraction.) With the above

value for  $\mu_j$ , the interaction energy for the weak-field anomalous effect according to Eq. (1) is,

$$W \simeq m_j g_j \mu_0 |B|, \quad (10)$$

where  $m_j$  is an integer or half-integer ranging from  $+j$  to  $-j$  in unit steps. (Besides explaining this aspect of the anomalous effect, the comparison between the quantum mechanical derivation of  $g_j$  and the empirical results of Landé served to show that the norms (lengths) of the vectors  $l$ ,  $s$  and  $j$  were  $\sqrt{l(l+1)}\hbar$ ,  $\sqrt{s(s+1)}\hbar$ , and  $\sqrt{j(j+1)}\hbar$  rather than  $l\hbar$ ,  $s\hbar$ , and  $j\hbar$  as predicted by the Bohr model.)

In strong fields, where the interaction terms in Eq. (6) due to the external field are large compared with the spin-orbit term,  $l$  and  $s$  are completely decoupled. The decoupling of  $l$  and  $s$  by the field is referred to as the *Paschen-Back effect*. As a result of the Paschen-Back decoupling,  $l$  and  $s$  are separately conserved so that the interactions associated with the orbital and spin moments contribute separately. Thus the expression for the strong-field anomalous effect is,

$$W \simeq (m_l + g_e m_s) \mu_0 |B|, \quad (11)$$

where  $m_s$  is an integer or half-integer that ranges from  $+s$  to  $-s$  in unit steps.

The weak and strong field cases are best summarized by means of an example. In Figure 3 the anomalous Zeeman effect of a  $^2P$  level is shown. In zero field, where  $l$  and  $s$  are coupled, there are two groupings of sublevels which correspond to states having  $j = \frac{3}{2}$  and  $j = \frac{1}{2}$ . In weak fields, all of the  $j$  groupings split up according to their  $m_j$  values. The relative slopes of the levels are governed by the values of  $g_j \mu_0$ , which for  $j = \frac{3}{2}$  is  $4\mu_0/3$ , and for  $j = \frac{1}{2}$  is  $2\mu_0/3$ . In strong fields there are five groupings of sublevels which separate with relative slopes of  $\mu_0$ . In intermediate fields the low and high field states connect smoothly with one another.

Up to this point the effect of the intrinsic magnetism of the atomic nucleus has been ignored. This is not a major omission, since nuclear moments are typically a few thousand times smaller than electronic moments. (This is due primarily to the differences in mass between nucleons and electrons.) The intrinsic nuclear moment enters into the anomalous effect in a way that is completely analogous to that in which the intrinsic electronic moment did. Here, instead of  $l$  and  $s$  coupling to form  $j$ , we have  $j$  and the nuclear spin angular momentum  $i$  coupling to form  $f$ . The coupling is the result of the interaction between the magnetic moment of the nucleus and the magnetic field produced both by the orbital motion and the intrinsic magnetism of the electrons. The so-called hyperfine splitting associated with this interaction leads to an energy term proportional to  $i \cdot j$ .



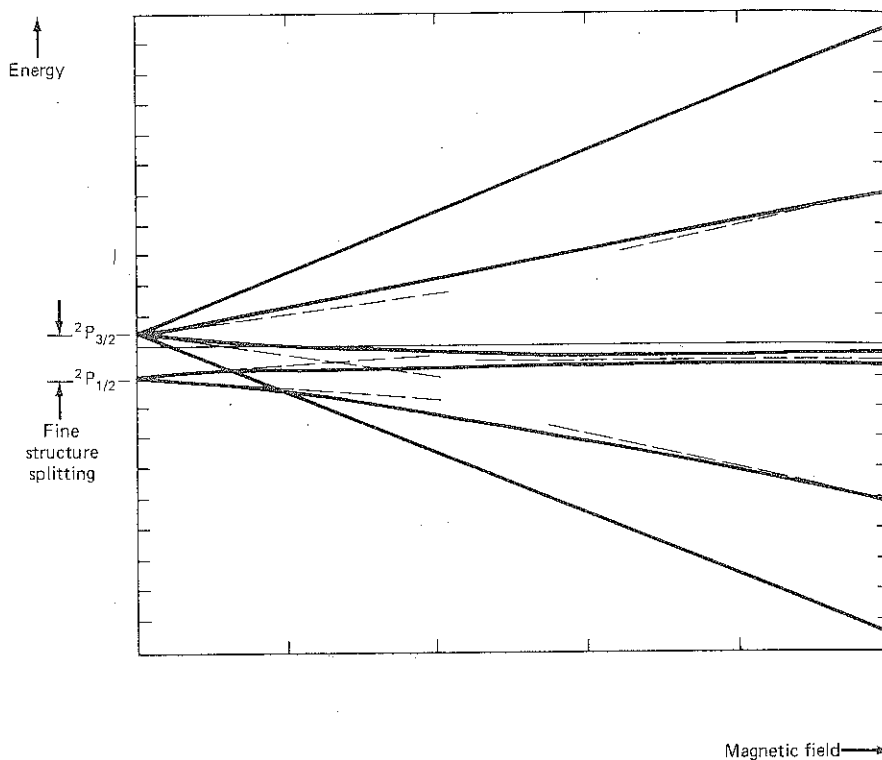


FIG. 3. The energy level diagram for  $^2P$  level, showing anomalous Zeeman effect in weak to strong external fields. (After Condon and Shortley, 1971.)

As with the case involving electron spin, there are two field regimes in which nuclear spin effects are easily described, that is, the weak field regime and the strong field regime. In weak fields a Landé-like  $g$ -factor is introduced,  $g_f$ , and the levels split up according to values  $g_f m_f$ . Likewise, in strong fields  $l$  and  $j$  are decoupled such that the interactions associated with the nuclear moment and the electron moment contribute separately and the levels shift according to their values of  $g_l m_l$  and  $g_s m_s$ . The strong field decoupling is the Paschen-Back effect, which is the analog of the Paschen-Back effect.

The complete picture of the anomalous effect now is that as the field increases from zero the contributions to the magnetic moment change from the case where  $l$ ,  $s$ , and  $i$  are completely coupled, to that where  $l$  and  $s$  are coupled but not  $i$ , to the final case where  $l$ ,  $s$ , and  $i$  are completely decoupled.

**Diamagnetic Effect.** Even when all the angular momenta are zero so that there is no orbital or intrinsic magnetic moment, there is still a shift due to external fields. The shift is quadratic in its dependence on field strength and corresponds to an increase in internal energy. The effect is due to an induced moment and the increased energy indicates that the moment opposes the

field. The opposition to the field means that this effect is inherently diamagnetic.

The diamagnetic shift can be understood simply as the result of the Larmor precession of an electron orbit when a magnetic field is applied. Here we consider the effect on an electron in a circular orbit. Larmor precession of the frame of reference due to the external field ( $\omega_L = eB/2 m_e c$ ) leads to a change in the orbital velocity of the electron when viewed in the laboratory frame. The changed orbital velocity results in a change in the net magnetic moment of an amount

$$\Delta \mu = -\frac{e^2 A}{4\pi m_e c^2} B. \quad (12)$$

where  $A$  is the orbital area projected on the plane perpendicular to  $B$ . It is a bit surprising that the change in the moment is not dependent on the direction of electron circulation. (This fact is actually connected with Lenz's law of electromagnetism which expresses the tendency of electrical conductors to set up countercurrents that produce fields which oppose an externally applied magnetic field.) The energy shift due to diamagnetism follows from Eq. (12) by integrating the differential form of Eq. (1) to

give,

$$W = \frac{1}{2} \frac{e^2 A}{4\pi m_e c^2} |B|^2. \quad (13)$$

The magnitude of the interaction energy associated with the diamagnetic effect can be estimated for an arbitrary state of principal quantum number  $n$ , by recognizing that the orbital area for a typical atom is  $\pi(n^2 a_0)^2$ , where  $a_0$  is the Bohr radius,  $0.5 \times 10^{-8}$  cm. Thus according to Eq. (13) a frequency shift of  $1.3 \times 10^{-4} n^4 |B|^2$  Hz is expected. (For 100 kG the  $n = 1$  level is expected to shift 1.4 MHz. For the ground  $^1S$  level of helium the observed shift is 2.4 MHz. Given that there are two  $n = 1$  electrons in helium, 2.8 MHz might be expected. The agreement here is remarkably good.) The  $n^4$  scaling of this effect means that for states of high  $n$ , the diamagnetic shift can be significant, especially in view of the fact that the Zeeman shifts due to the orbital and intrinsic moments are independent of  $n$ . The large relative size of the diamagnetic shift is one of the reasons that modern laser spectroscopists have studied this effect in the context of highly excited atoms.

**Current Status.** In recent years the Zeeman effect has received renewed interest due to the development of new experimental and theoretical techniques. One aspect of the problem that has received most of the recent attention is the case where the external fields cannot be considered as weak in comparison to the internal Coulomb field. This situation has been realized in the laboratory through the use of intense magnetic fields and high states of atomic excitation. It also occurs naturally in the atmospheres of certain collapsed stars for low states of excitation.

In a classic series of experiments on photoabsorption to the continuum (i.e., photoionization) by R. Garten and F. Thompson, the transition from weak fields, where the electron is bound to the atom, to strong fields, where the electron is bound to the field, has been observed. The experimental evidence for the changeover from one regime to the other has been seen through the emergence of the so-called quasi-Landau resonances in the energy region near the threshold for photoionization. (A free electron in a magnetic field is bound in the plane perpendicular to the field axis by the Lorentz force. This binding gives rise to cyclotron orbits. Quantized cyclotron orbits are the basis for the discrete Landau levels.)

Considerable attention has recently been focused on measurements of the diamagnetic effect for highly excited atoms. One of the potentially important findings observed by Kleppner and co-workers are sharp crossings of sublevels. Such sharp crossings suggest the possibility of the existence of an unidentified symmetry of the magnetic field problem.

Spurred on by experiments such as the ones

mentioned above, theorists have been making marked progress towards developing a general theory of magnetic effects in fields of arbitrary strength. The problem, however, is still far from being solved.

**Stark Effect Introduction.** The Stark effect is due to the interaction between the electric moment of the atom and the external electric field. The leading term to the interaction energy is,

$$W = -p \cdot E, \quad (14)$$

where  $p$  is the electric dipole moment and  $E$  is the external field. Electric dipole moments in atoms arise as a consequence of the way that charge is distributed within atoms. In the following discussions two aspects of the Stark effect are to be considered: the linear effect and the quadratic effect. It will be shown that the linear effect is due to a dipole moment that arises from a naturally occurring nonsymmetric distribution of electron charge, while the quadratic effect is due to a dipole moment that is induced by the external field. For simplicity the effects of fine and hyperfine structure will be ignored.

**Linear Stark Effect.** Figure 4 diagrams the simplest case of the linear effect, that is, the transition from the ground level ( $n = 1$ ) to the first excited level ( $n = 2$ ) of atomic hydrogen. The excited level splits into three equally spaced sublevels under the influence of the external field. The spacings between sublevels increase linearly with the applied field. The central sublevels of  $n = 2$  and the ground level do not shift in response to the field. (In the general case, an arbitrary  $n$  level splits into  $2n - 1$  sublevels that separate in the field at a rate that scales with  $n$ . Thus the higher  $n$  states are more sensitive to the external field.)

As indicated above, the linear effect is the result of the interaction between the electric dipole moment due to the distribution of charge within the atom and the external field. The dipole moment can be understood by considering an eccentric elliptical orbit as shown in Figure 5. Here the nucleus is at one focus and the electron follows a Kepler orbit that sweeps out equal areas in equal times. It is evident that the further the electron is from the nucleus the slower it moves, and as a result the electron's position averaged over an orbit is not centered on the nucleus. The separation between positive and negative charge centers here necessarily leads to a dipole moment.

The size of the naturally occurring dipole moment corresponding to a highly eccentric orbit can be estimated, given that the mean radius of an atom in a state of principal quantum number  $n$  is on the order of  $n^2 a_0$ , where  $a_0$  is the Bohr radius. Thus the dipole moment, which is the product of the charge and the charge separation, is  $en^2 a_0$ . This crude estimate is actually comparable with the observed moment

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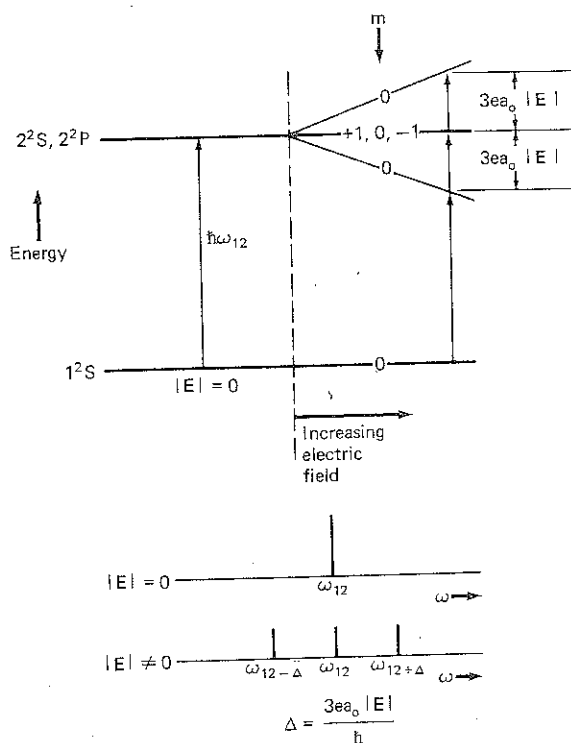


FIG. 4. Linear Stark effect for  $n=1$  to  $n=2$  transition. Above is energy level diagram; below is spectrum with and without external field.

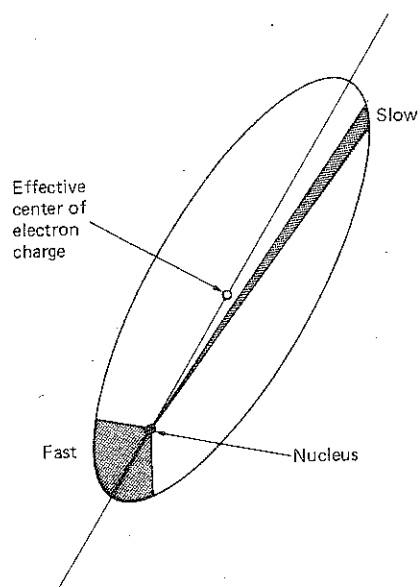


FIG. 5. Elliptical electron orbit. According to Kepler's law the electron is moving quickly when it is near the nucleus and slowly when it is far from the nucleus.

of the extreme-most Stark level,  $3en(n-1)a_0/2$ . The general result according to nonrelativistic quantum theory is that the linear shift is

$$W = \frac{3}{2} enka_0, \quad (15)$$

where  $k$  is the electric quantum number, which ranges in value from  $+(n-|m|-1)$  to  $-(n-|m|-1)$  for all possible values of  $m$ , which ranges from  $+(n-1)$  to  $-(n-1)$ .

The quantum mechanical predictions of charge distribution that correspond to the states described by Eq. (15) are most interesting. The charge distributions reveal parabolic symmetry. This symmetry is evident in Figure 6 from maps of the charge distributions corresponding to the eight  $m=0$  sublevels of the  $n=8$  level in atomic hydrogen. The ridges of charge are intersecting parabolas that open along and against the electric field axis. (This is most easily noted for the central states,  $k=\pm 1$ , which have the smallest dipole moments and correspond to nearly circular orbits.) The parabolic nature of the Stark problem is reflected in its usual analytical treatment, where the three-dimensional Schrödinger equation is separated into three one-dimensional equations in a parabolic coordinate system. (Incidentally, by comparison the magnetic field

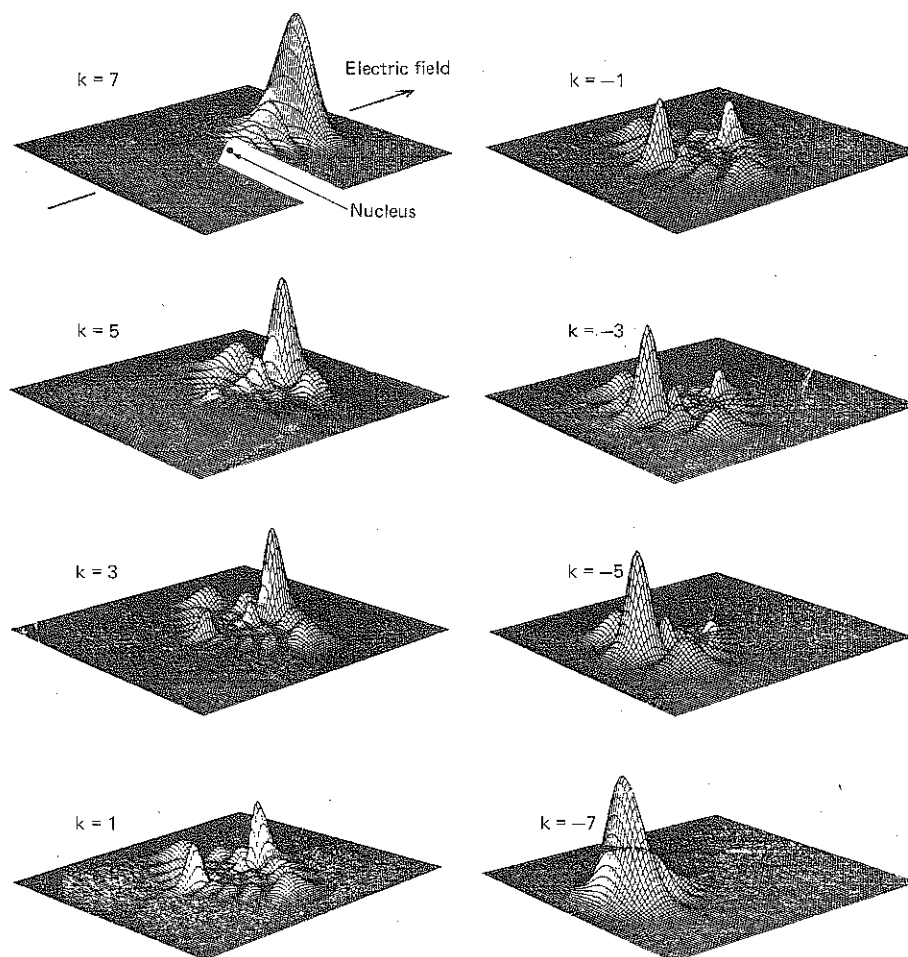


FIG. 6. Charge distribution for the eight  $m_L = 0$  sublevels of the  $n = 8$  level of hydrogen. The  $k = +7$  and  $k = -7$  sublevels are the extreme-most Stark states which display the largest dipole moments. The nucleus is in the center of the mesh. (Adapted from Kleppner, Littman, and Zimmerman, 1981.)

problem is more difficult to model analytically than the electric field problem because no similar separation of variables has ever been accomplished.)

Up to this point the discussion has concerned the linear effect for atomic hydrogen. More complex atoms also display linear effects, however, they can only do so when two or more states of different angular momentum have the same energy in zero field. Because of the high level of degeneracy in hydrogen this condition is met for all excited levels. In complex atoms, this condition is usually met only for the high angular momentum states. Isolated angular momentum states of a well defined parity cannot display linear shifts because of their inversion symmetry. (This is because the charge distribution must be the same when  $\mathbf{r}$  is replaced by

$-\mathbf{r}$  so that the center of electron charge for these states must coincide with the nucleus.)

The linear Stark effect has the distinction of being the first problem to which the well known perturbation method was applied. (Perturbation theory allows for the approximation of a solution of one problem in terms of an expansion of the solutions of another.) In this first application, the wavefunction for an atom in an electric field was expressed in terms of an expansion of wavefunctions for an atom in the absence of external fields. The linear shift was given by the first order term in the expansion for the energy.

**Quadratic Stark Effect.** For states with no linear shift, such as the ground state of hydrogen, there is still a shift due to external fields. The shift is quadratic in its dependence on field strength.

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scribed above are most interesting. The  
charge distributions have parabolic symmetry.  
in Figure 6 from maps  
of the charge distribution corresponding to the  
 $n = 8$  level in atomic hydrogen. The  
charge distributions are intersecting  
and against the electric field.  
The most easily noted for the  
states which have the smallest  
dipole moments respond to nearly cir-  
cular nature of the Stark effect.  
usual analytical treatment of the  
three-dimensional Schrödinger equation  
in a three-dimensional coordinate system.  
In comparison the magnetic field



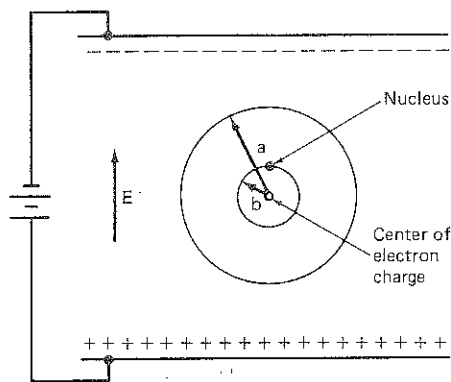


FIG. 7. The idealized effect of an external field on a uniform spherical charge distribution of radius  $a$ . The electron cloud and the nucleus separate by distance  $b$ . (After Purcell, 1965.)

As was the case with the quadratic shift in magnetic fields, the quadratic shift in electric fields is due to an induced moment. The induced moment can be understood by considering the external field effect on a uniform sphere of negative charge centered on a positive nucleus. The external field pulls the positive and negative charges in opposite directions which sets up an opposing force due to the displacement of charge centers. The magnitude of the displacement can be estimated by imposing the condition that the two forces be balanced. Figure 7 depicts the situation here. The charge outside of the inner sphere of radius  $b$  does not contribute to the net attractive force because the field inside a uniform spherical shell is zero. (This is the same phenomenon that causes the gravitational field at the center of the earth to be zero.) Thus, only the charge inside the inner sphere contributes. The amount of charge inside is  $e(b^3/a^3)$ , so that the force balancing condition is

$$e|E| = \left( e \frac{b^3}{a^3} \right) \frac{e}{b^2}, \quad (16)$$

or alternatively,

$$|\Delta p| \equiv eb = a^3 |E|. \quad (17)$$

Thus the strength of the induced dipole moment is roughly proportional to the field strength times the volume of the charge cloud. (The constant of proportionality is known as the *scalar polarizability*.) Given this expression for the induced moment, the interaction energy is obtained by integrating the differential form of Eq. (14), which gives

$$W = \frac{1}{2} a^3 |E|^2. \quad (18)$$

The magnitude of the interaction energy associated with the quadratic effect can be estimated given that the mean radius for an arbitrary state of principal quantum number  $n$  is  $n^2 a_0$ . Thus, according to Eq. (18), a frequency shift of  $11.2n^6 |E|^2$  Hz is expected, where  $|E|$  is in units of stat-Volt/cm. For the ground state of hydrogen this estimate is low by a factor of 5, but for highly excited states it is correct to within a few percent.

At this point an example is appropriate. The linear and quadratic shifts that have been discussed thus far are evident in the laser spectroscopic data of sodium excited states near  $n = 15$ , as shown in Figure 8. The levels which enter from above and below here correspond to states from neighboring  $n = 14$  and  $n = 16$  levels. The grouping of states near the  $15d$  level corresponds to the  $n = 15$  high-angular-momentum states, and these display linear shifts. The  $16p$  level, on the other hand, is far from any other states of differing angular momentum, and so it displays a quadratic shift.

**Current Status.** In recent years the Stark effect has received renewed interest due to the development of new experimental and theoretical techniques. Much of the recent interest has been in the situation where the external fields are comparable or stronger than the internal fields that hold the atom together. This condition has been realized in the laboratory through the use of fields of moderate strength and high states of excitation.

One of the interesting effects of intense fields on atoms that has received recent study is the field-induced ionization of the neutral atom. Field ionization is interesting because the purely quantum mechanical effect of tunneling is known to play an important role. One of the significant observations of recent field ionization studies is that the ionization threshold for virtually all complex atoms occurs near the threshold energy that one would predict classically.

Another topic that has received recent attention is the lack of rigorous convergence of the Stark perturbation expansion. The convergence difficulty is connected to the fact that, in the presence of an electric field, bound states do not strictly exist because of a finite probability that any given state will spontaneously ionize via tunneling. (This problem is most important in strong fields.) Using a technique developed by Leibnitz and a digital computer, H. Silverstone and co-workers have calculated the perturbation expansion to 150th order and demonstrated explicitly the nature of the divergence. They also have shown how the convergence can be improved using the technique of Padé approximants.

Yet another topic that has drawn much attention is the observation of oscillations in the photoionization spectrum of an atom in an electric field. Here R. Freeman and co-workers have

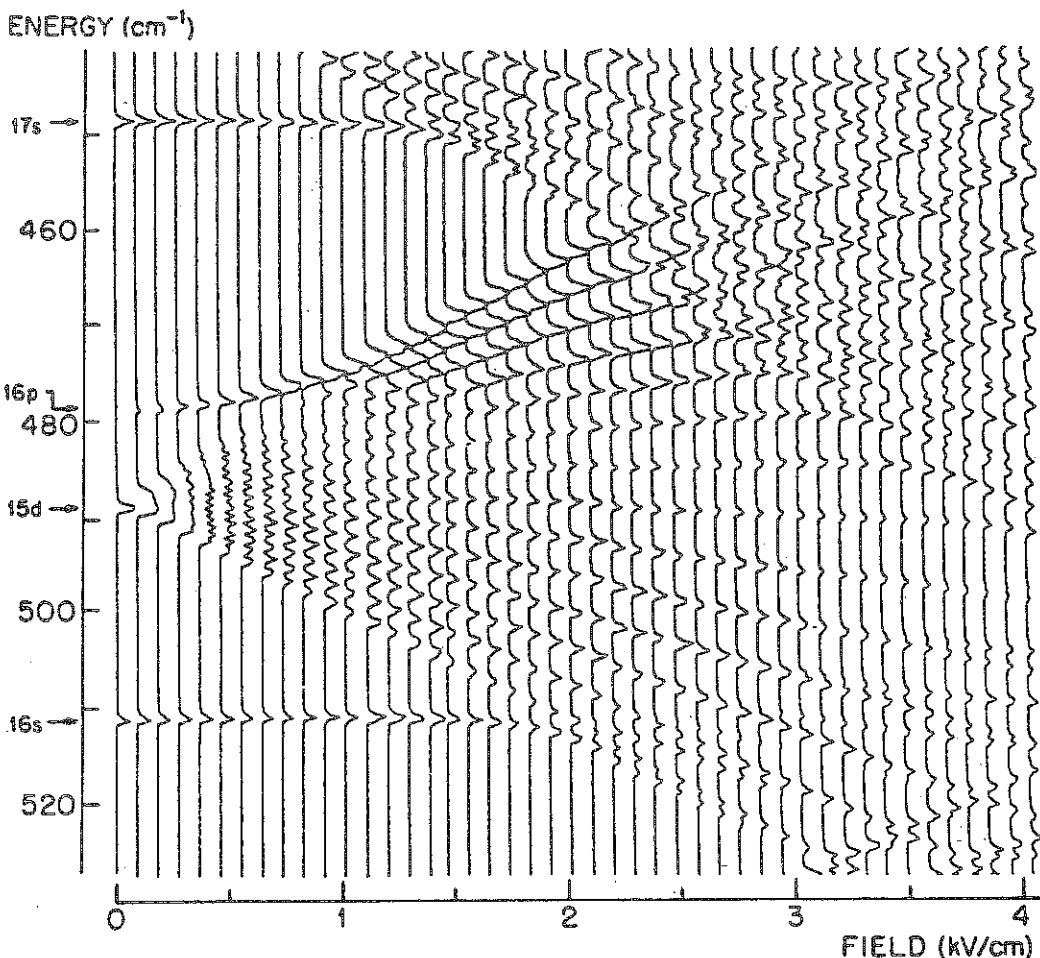


FIG. 8. Spectroscopic study of Stark effect on excited levels of sodium near  $n = 15$ . This is a composite map of data accumulated at many different values of applied field. [From M. G. Littman, M. L. Zimmerman, T. W. Ducas, R. R. Freeman, and D. Kleppner, *Phys. Rev. Lett.* 36, 788 (1976).]

studied what appears to be the electrical analog of the quasi-Landau levels discussed previously (see the section of this article on Zeeman Effect—Current Status).

In spite of the fact that the Stark effect is an old topic, recent activity has shown that the area is indeed still vital.

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#### References

Bethe, H. A., and Salpeter, E. W., "Quantum Mechanics of One and Two Electron Atoms," Berlin, Springer-Verlag, 1957.

Ramsey, N. F., "Molecular Beams," Oxford, Clarendon Press, 1969.

Purcell, E. M., "Electricity and Magnetism," Berkeley Physics Course, Vol. 2, New York, McGraw-Hill, 1965.

Condon, E. V., and Shortley, G. H., "The Theory of Atomic Spectra," Cambridge, U.K., Cambridge Univ. Press, 1970.

Kleppner, D., Littman, M. G., and Zimmerman, M. L., "Highly Excited Atoms," *Sci. Amer.* 244, 130 May (1981).

Cross-references: ATOMIC SPECTRA, DIPOLE MOMENTS, ELECTROMAGNETIC THEORY, FARADAY EFFECT, KERR EFFECTS, POLARIZED LIGHT, QUANTUM ELECTRODYNAMICS, QUANTUM THEORY, SPECTROSCOPY.

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The levels which enter here correspond to states  $4$  and  $n = 16$  levels. The  $15d$  level corresponds to high-angular-momentum linear shifts. The  $16p$  level, is far from any other angular momentum, and so shifts.

In recent years the Stark effect has received interest due to the experimental and theoretical of the recent interest has been where the external fields are longer than the internal fields together. This condition is the laboratory through moderate strength and high

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