

APPLIED PHYSICS

Editor

cal Mechanics

Physics

munication Theory

ysics

n to Modern Physics

Volume I
Volume II

Physics

tal Facts
y

he series from its inception in
iting Editor from 1939 to 1946,

Principles of Modern Physics

ROBERT B. LEIGHTON

Professor of Physics
California Institute of Technology

McGRAW-HILL BOOK COMPANY, INC.

NEW YORK TORONTO LONDON

1959

PC

Atomic Spectroscopy

Of all the tools that have been applied to the study of the detailed structure of matter, it can fairly be said that *spectroscopy* has been applied in more ways to more problems, and has produced more fundamental information, than any other. It has been used, and is still being used, not only to extend our knowledge of the ultimate properties of matter, but also to provide accurate measurements of many quantities of quite practical interest to physicists, chemists, and engineers. It is also an indispensable tool in the study of the chemical composition and the physical condition in which matter exists in certain situations which are inaccessible to more direct observation—such as in astrophysics and atmospheric physics—and in situations of a highly transient character, as in fast chemical reactions and electrical discharges.

In modern physics the term "spectroscopy" is used in connection with a great many quite different investigative techniques, e.g., optical spectroscopy (including infrared and ultraviolet atomic and molecular spectroscopy), microwave spectroscopy, β -ray spectroscopy, γ -ray spectroscopy. In each of these techniques the quantity that is directly measured is the energy, momentum, wavelength, or frequency of a photon or electron emitted or absorbed during a transition between two states of an atomic, molecular, or nuclear system. From this information the characteristics of the *energy levels* of the system are inferred, and from these characteristics (spacing, angular momentum, multiplicity, etc.) certain basic parameters of the system can often be determined with considerable precision. In this chapter we shall examine some of the more important aspects of the original form of spectroscopy—atomic spectroscopy.

8-1. General C

From what ha
should be aware
atomic spectrosc
quantum mecha
laws with the h
certain simple
*improve our un
more complicated*

In the preced
vides a beautif
and of the grou
visualized as o
lying of the var
in the field of
due to the ren
cussion was pu
requirement th
from the treatr
some finer det
the extent of tl
known feature

Before actu
delineate the
tatively the va
using for the j
ously. Thus
visualized as
of a number o
of the electro
The *most gen
importance*)
any of the en
range of the c
sion principle
that in which
when the ato
may be *comp
ionized*) and
Even with tl
may fall into
excitation w

8-1. General Considerations

From what has already been said in the preceding chapters, the student should be aware of some of the more important historical facts concerning atomic spectroscopy and the part it has played in the development of the quantum mechanics. Having thus arrived at the correct mechanical laws with the help of our knowledge of the spectroscopic properties of certain simple atoms, we may now properly seek to *use these laws to improve our understanding of the spectra and the detailed structure of the more complicated atoms.*

In the preceding chapter we have seen that quantum mechanics provides a beautiful interpretation of the periodic system of the elements and of the ground state of an atom, wherein the electrons of the atom are visualized as occupying—subject to the exclusion principle—the lowest-lying of the various energy states that would exist for an electron moving in the field of the nucleus and the spherically symmetric average field due to the remaining electrons. The approximation used for that discussion was purposely kept as simple as possible consistent with the requirement that the *main features* of atomic structure should emerge from the treatment. We now wish to utilize quantum mechanics to add some finer details to the above atomic model and to illustrate further the extent of the success of the Schroedinger theory in accounting for the known features of ordinary atomic processes.

Before actually embarking upon this procedure, it is desirable to delineate the present problem more clearly by first considering qualitatively the various types of excited states in which an atom might exist, using for the present the same approximate model that was used previously. Thus if, as indicated above, the ground state of an atom is visualized as corresponding to the electrons occupying the lowest-lying of a number of possible energy states, it is clear that, if any one or more of the electrons were to occupy a higher level, the atom would be excited. The *most general* state of excitation (which is of completely negligible importance) would then correspond to the various electrons being in *any* of the energy states—including the continuum which lies above the range of the discrete states—subject only to the limitations of the exclusion principle. By far the more common situation, on the other hand, is that in which most of the electrons are in the energy states they occupy when the atom is in its ground state, but in which one or more electrons may be *completely removed* from the atom (that is, the atom is perhaps *ionized*) and one or two of the electrons are in *bound* excited states. Even with this restriction the possible states of excitation of the atom may fall into several broad classes according to the manner in which the excitation was produced. For example, we shall see later that the

excitation of an atom by X-rays or by the impact of an energetic charged particle often results in the removal of electrons from an *inner shell*. This leaves the atom ionized and highly excited, and many interesting phenomena may occur in such a situation. On the other hand the atom may be excited by rather gentler means—as in an electric arc, spark, or glow discharge, or in a flame—in which case only the outermost of the electrons will be affected. Although *all* such states of excitation are in a sense a part of the same general problem, it is desirable to separate the discussion into several different categories upon the basis of the techniques used in the study of the excited states. Thus we shall study the states characteristic of *X-ray* and *microwave excitation* in later chapters. We are concerned at present only with the states of excitation in which the radiation involved falls in the visible or near-infrared or -ultraviolet regions of the spectrum; these are states of excitation in which only the outermost, *valence, electrons* are involved.

8-2. The Hamiltonian Function of a Complicated Atom

In order to deduce some of the finer details of the energy levels of a complicated atom, we proceed in a manner similar to that used in the case of the one-electron atom: namely, we consider first a problem which includes the major terms of the Hamiltonian function and whose energy levels are therefore very closely the same as for the complete problem. We then study the fine-structure splitting of these highly degenerate levels that results when the next most important terms are included as perturbations. For the extremely complicated problem now being considered, our treatment must remain rather qualitative throughout, even though a certain amount of quantitative information can be obtained by the use of advanced techniques. We shall thus be obliged to place heavy emphasis upon the similarities between the present problem and some of the features of the one-electron atom discussed in Chap. 5.

We first consider the various terms that should appear in the complete Hamiltonian function of an atom which has a nuclear charge Ze and is surrounded by N electrons. We assume for the present that $N \leq Z$; that is, the atom is not *negatively* ionized. The Hamiltonian function should thus be the sum of the following terms:

1. The kinetic energy of the electrons:

$$T = \sum_{i=1}^N \frac{p_i^2}{2m}$$

SEC. 8-2]

2. The electrostatic

3. The mutual elec

4. The spin-orbit e

5. The spin-spin i

$$V_{ss} =$$

6. Interactions be

7. Electron spin-

$$V_{eans}$$

8. Nuclear spin-

9. Other terms d
of the electri
nucleus, inter
orbital motio

In addition to
tions, the Hami
appreciable effe
action, such as

10. Terms to cc

2. The electrostatic interaction energy of the electrons with the nucleus:

$$V_{en} = - \sum_{i=1}^N \frac{Ze^2}{4\pi\epsilon_0 r_i}$$

3. The mutual electrostatic energy of the electrons:

$$V_{ee} = \sum_{i=1}^N \sum_{j=1}^{i-1} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

4. The spin-orbit energy of the electrons:

$$V_{so} = - \sum_{i=1}^N \frac{\mathbf{g}_i \cdot \mathbf{l}_i}{m^2 r_i c^2} \frac{dV}{dr_i}$$

5. The spin-spin interactions of the electrons:

$$V_{ss} = \frac{\mu_0}{4\pi} \sum_{i=1}^N \sum_{j=1}^{i-1} \frac{e^2}{m^2} \left[\frac{\mathbf{g}_i \cdot \mathbf{g}_j}{r_{ij}^3} - 3 \frac{(\mathbf{g}_i \cdot \mathbf{r}_{ij})(\mathbf{g}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right]$$

6. Interactions between the orbital magnetic moments of the electrons:

$$V_{oo} = \sum_{i=1}^N \sum_{j=1}^{i-1} C_{ij} \mathbf{l}_i \cdot \mathbf{l}_j$$

7. Electron spin-nuclear spin interactions

$$V_{eans} = \frac{\mu_0}{4\pi} \sum_{i=1}^N \frac{e}{m} \left[\frac{\mathbf{y}_{nuc} \cdot \mathbf{g}_i}{r_i^3} - 3 \frac{(\mathbf{y}_{nuc} \cdot \mathbf{r}_i)(\mathbf{g}_i \cdot \mathbf{r}_i)}{r_i^5} \right]$$

8. Nuclear spin-electron orbital moment interactions:

$$V_{nsso} = \frac{\mu_0}{4\pi} \sum_{i=1}^N \frac{e}{m} \left[\frac{\mathbf{y}_{nuc} \cdot \mathbf{l}_i}{2\pi r_i^3} \right]$$

9. Other terms due to nuclear electric-quadrupole moments, modification of the electric field near the nucleus owing to the finite size of the nucleus, interaction between the spin magnetic moments and the orbital motion of other electrons, etc.

In addition to the above terms which correspond to "true" interactions, the Hamiltonian function should also include terms to represent appreciable effects which do not correspond to a classical type of interaction, such as

10. Terms to correct for relativistic effects, e.g.,

$$R = \sum_{i=1}^N \frac{p_i^4}{8m^3 c^2}$$

The Hamiltonian function, when converted into an operator, will lead to certain wave functions for the energy states of the atom. According to the exchange-symmetry postulate of the preceding chapter, only those wave functions that are *antisymmetric with respect to the exchange of all pairs of electronic space and spin coordinates* are valid wave functions for the atom. This restriction upon the choice of acceptable wave functions has certain physically observable consequences, some of which have previously been described. For the atomic systems now being considered, the most important of these effects are, as was shown in the preceding chapter:

11. A tendency for electrons with parallel spins to avoid (or "repel") each other, and as a result of this and the electrostatic repulsion of the electrons, a strong "exchange correlation" between the spins *which tends to align electronic spins parallel to one another.*

The discussion of the preceding chapter was based upon a model which included terms (1) and (2) and a spherically symmetric "average" of term (3). We must now consider what effects the inclusion of the remaining terms will have upon the degenerate energy levels of that model. We are interested in two aspects of these effects—the *qualitative character* of each term in splitting a degenerate level into a number of distinct levels of smaller degeneracy, each characterized by a different quantized value of some "constant of the motion," and the *magnitude* of each effect.

On the basis of the perturbation theory, one can deduce the approximate magnitude of the various effects included in the above list. The analysis is too involved to be included here, but is quite straightforward for most of the effects. The final conclusion, which is in agreement with observation, is that there are two main categories into which most atoms should fall with regard to the relative magnitudes of the remaining effects:¹

1. For most atoms, the nonspherically symmetric residual electrostatic effects of term (3) and the spin correlations of (11) are the largest of the remaining terms; the spin-orbit term (4) is considerably smaller, and the remaining terms are quite negligible.
2. For some atoms, mainly the heavier ones, the spin-orbit term (4) predominates.

We shall now consider these two cases separately.

¹ Some of the effects, such as the relativistic correction terms, have a very large influence upon the lowest energy states, and much less upon the higher states. These corrections will thus appreciably affect the *total ground-state energy* of the atom, but not the energies of the states available to the valence electrons measured relative to the ground-state energy.

8-3. Russell-Saunders

The first of the effects of term (3), the remaining terms, we Russell-Saunders effect these terms simple central-field

We recall first that were degenerate with of the various electrostatic *central field* and no keeping device to that is, the *individual* as well as the *net orbital*, and the *total angular momentum*. Thus degenerate with respect equally well in terms of v valence electrons

- (a) (n_1, l_1, s_1, m_1)
- (b) (n_1, l_1, s_1, j_1)
- (c) (n_1, l_1, s_1, j_1)
- (d) (n_1, l_1, s_1) , (

The first two of these alternative quantum numbers for electron energy states are the natural choices for the quantized angular momentum of the electrons. In the numbers that define the total angular momentum of the electrons, the square of the total angular momentum, respectively used in the last two combinations of the same total angular momentum.

If we now consider we see that, since the nucleus, the orbital angular momentum will no longer be

¹ *Astrophys. J.*, 6

8-3. Russell-Saunders, or LS , Coupling

The first of the above situations, in which the residual electrostatic effects of term (3) and the spin-spin correlation (11) dominate the remaining terms, was first studied by Russell and Saunders¹ and is called Russell-Saunders coupling, or LS coupling. Let us now consider what effect these terms will have upon the degenerate energy levels of the simple central-field approximation.

We recall first that the various energy levels of the central-field model were degenerate with respect to the orbital angular momenta and spins of the various electrons, since each electron was assumed to move in a *central field* and no spin interactions were considered except as a book-keeping device to prevent two electrons from being in the same state; that is, the *individual orbital and spin* angular momenta of the electrons, as well as the *net orbital* angular momentum, the *net spin* angular momentum, and the *total* angular momentum of the electrons, *were constants of the motion*. Thus the various orthogonal states of given energy were degenerate with respect to all of these quantities and might be described equally well in terms of various possible sets of quantum numbers for the v valence electrons, such as

$$\begin{aligned}
 (a) \quad & (n_1, l_1, s_1, m_{l1}, m_{s1}), (n_2, l_2, s_2, m_{l2}, m_{s2}), \dots, (n_v, l_v, s_v, m_{lv}, m_{sv}) \\
 (b) \quad & (n_1, l_1, s_1, j_1, m_{j1}), (n_2, l_2, s_2, j_2, m_{j2}), \dots, (n_v, l_v, s_v, j_v, m_{jv}) \\
 (c) \quad & (n_1, l_1, s_1, j_1), (n_2, l_2, s_2, j_2), \dots, (n_v, l_v, s_v, j_v), J, M_J \\
 (d) \quad & (n_1, l_1, s_1), (n_2, l_2, s_2), \dots, (n_v, l_v, s_v), L, S, J, M_J
 \end{aligned} \tag{1}$$

The first two of these expressions will be recognized as being just the alternative quantum-number designations for the various individual one-electron energy states as described in Chap. 5, and the last two expressions the natural extension of the law of addition of independent quantized angular momenta given in that discussion to the case of several electrons. In the last two expressions, L , S , J , and M_J are the quantum numbers that define the square of the net *orbital* angular momentum of the electrons, the square of the net *spin* angular momentum, the square of the *total* angular momentum, and the z -component of the total angular momentum, respectively. (Note that, although fewer quantum numbers are used in the last two expressions than in the first two, the various possible *combinations* of quantum numbers in each expression necessarily define the same total number of substates of the degenerate state.)

If we now consider the effects of the residual electrostatic repulsions we see that, since these involve forces that are not directed toward the nucleus, the orbital angular momenta of the *individual* valence electrons *will no longer be constants of the motion*. Since the mutual repulsion

¹ *Astrophys. J.*, 61, 38 (1925).

between pairs of electrons is directed along the line joining them, however, the *total orbital angular momentum will remain constant*. Similarly, the spin-spin correlations given by (11) may cause the *individual spin angular-momentum vectors to change*, but the *total spin angular momentum will be constant*.

In the case of the spin-spin correlations, the individual spin angular momenta cannot change their *magnitudes*, since the spin is an intrinsic, unchangeable property of electrons. The *directions* of the spins may change, however. On the other hand, in the case of the electrostatic repulsions, the *individual orbital angular momenta could change in magnitude, but this is found seldom to occur*.

We thus find that the introduction of these two terms into the problem leads to a situation in which only the fourth of the alternative sets of quantum numbers given above is suitable for describing the substates of the perturbed system.

As to the quantitative effects of these two terms, the effect of the spin-spin correlation is usually greater than that of the electrostatic repulsion and, for the reason given in Exercise 7-13 of the previous chapter, gives the lowest energy for the state of *largest possible S*. Further, we can see that the electrostatic energy will be a minimum if the valence electrons remain as far as possible from one another. We thus expect that the state of lowest energy would be one in which the valence-electron orbits are arranged symmetrically around the periphery of the atom, and in which this symmetrical configuration "rotates" more or less as a "rigid body." Since the individual electrons would all then be revolving in the "same direction" about the nucleus, we might expect the state of lowest energy to be the one whose orbital quantum number L is *as large as can be formed* from the individual orbital angular-momentum quantum numbers. This is observed to be the case. The states are thus arranged in energy in the order of *decreasing L*, the largest L -value having the lowest-lying energy.

Finally, we must introduce the small spin-orbit term (4) as an additional perturbation upon the above separated but still individually degenerate levels. It is found that the total spin-orbit interaction may be represented with sufficient accuracy by an expression of the simple form

$$V_{so} = F(r_i)L \cdot S \quad (2)$$

Using this expression for the spin-orbit interaction, we can deduce an important semiquantitative rule governing the fine-structure splitting of a given level. We follow a procedure exactly similar to the case of the one-electron atom except that the r -dependence is now so complicated that it cannot be evaluated analytically. We represent it for each given

SEC. 8-3]

unperturbed level but in practice must be treated just as for the

and so that

Thus the average by the quantum nu

$$\langle L \cdot S \rangle =$$

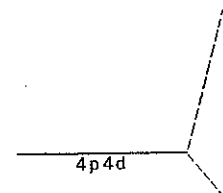
since $|J|^2$, $|L|^2$, and unperturbed system

We thus see that J , L , and S have discrete values, proportional to the quantum number of a multiplet is

$$E_{J+1} - E_J =$$

Thus the spacing between adjacent levels is proportional to the Landé interval rule of observed energy

To illustrate the specific case of an



Unperturbed state

+

FIG. 8-1. Schematic showing the splitting of a 4p and 4d level into sublevels. The spacings of the

unperturbed level by a constant C which can in principle be calculated but in practice must be evaluated empirically for all but the simplest cases. The angular part of the spin-orbit energy can, however, be evaluated just as for the one-electron atom by writing

$$J = L + S \tag{3}$$

and $|J|^2 = |L|^2 + |S|^2 + 2L \cdot S \tag{4}$

so that $L \cdot S = \frac{1}{2}(|J|^2 - |L|^2 - |S|^2) \tag{5}$

Thus the average of V_{so} over the unperturbed wave function described by the quantum numbers (ld) is equal to

$$\langle L \cdot S \rangle = \frac{1}{2}C'[J(J + 1) - L(L + 1) - S(S + 1)] \tag{6}$$

since $|J|^2$, $|L|^2$, and $|S|^2$ are all quantized constants of the motion in the unperturbed system ($C' = Ch^2$).

We thus see that, just as in the one-electron atom, states of different J , L , and S have different energy. The shift in energy is, for given L and S , proportional to $J(J + 1)$, and the spacing of consecutive levels within a multiplet is

$$E_{J+1} - E_J = \frac{1}{2}C'[(J + 1)(J + 2) - J(J + 1)] = C'(J + 1) \tag{7}$$

Thus the spacing between consecutive levels of a fine-structure multiplet is proportional to the larger of the two J -values involved. This is called the Landé interval rule. It can be of great help in determining the J -values of observed energy levels.

To illustrate the results of the discussion up to this point, consider the specific case of an atom having two valence electrons and suppose a

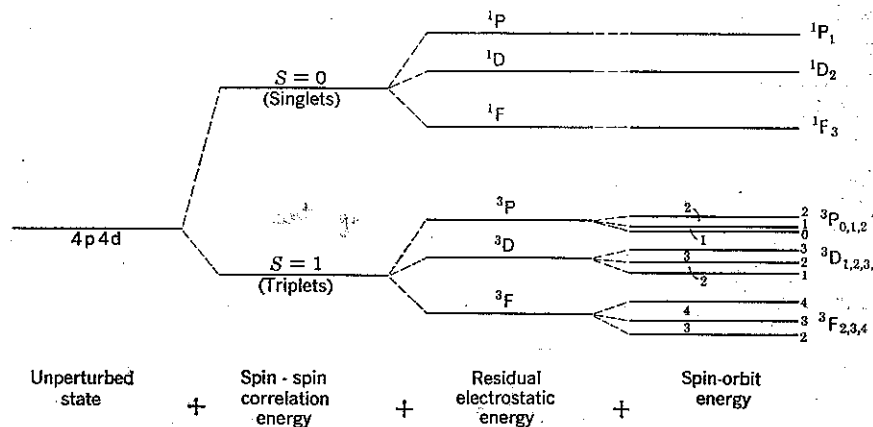


FIG. 8-1. Schematic diagram illustrating the fine-structure splitting of a level corresponding to a 4p and a 4d valence electron. The Landé-interval rule is illustrated in the spacings of the triplet levels.

ining them, how-
stant. Similarly,
e individual spin
angular momen-

ual spin angular
in is an intrinsic,
of the spins may
the electrostatic
change in magni-

into the problem
ternative sets of
ng the substates

the effect of the
the electrostatic
e previous chap-
S. Further, we
m if the valence

We thus expect
valence-electron
of the atom, and
ore or less as a
hen be revolving
pect the state of
as large as can be
antum numbers.
ranged in energy
the lowest-lying

(4) as an addi-
till individually
interaction may
m of the simple

(2)

can deduce an
ture splitting of
the case of the
so complicated
t for each given

certain unperturbed excited energy state of the atom corresponds to one of these electrons being in a 4p level and the other in a 4d level. The effect of the three perturbations is shown schematically in Fig. 8-1. At the left is the unperturbed level. The spin-spin correlation splits

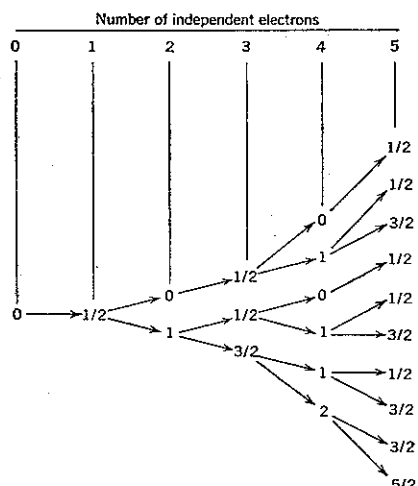


Fig. 8-2. A diagrammatic illustration of the resultant spin quantum numbers for 0, 1, 2, 3, 4, and 5 independent electrons. If a given subshell is more than half occupied, the exclusion principle will limit the number of spin combinations.

let their configuration be 2p 3p 4d. We first find *what spin combinations* will be present. This is most easily done by first combining the spins of two of the electrons and then combining the third spin with each of them. Figure 8-2 illustrates the possible spin quantum numbers which can be obtained by combining several independent electron spins. We thus find that there will be two sets of doublet states ($S = \frac{1}{2}$) and one set of quartet states ($S = \frac{3}{2}$).

Next, we must combine the three orbital angular momenta. If we first combine the two p states, we see that these will lead to an S-state ($L = 0$), a P-state ($L = 1$), and a D-state ($L = 2$). Combining the d state with each of these in succession then leads to

$$\begin{aligned} S + d &\rightarrow D \\ P + d &\rightarrow P, D, F \\ D + d &\rightarrow S, P, D, F, G \end{aligned}$$

Finally, the introduction of the $L \cdot S$ coupling splits each of these levels into an appropriate number of separate levels having different J -values.

The two sets of do

and the set of qua

$^4S_{3/2}$

to make a total of a spectrum can be name *doublet* or *q*ponents, respectiv

The fine-struct may be generaliz configuration is n

1. The unperturb a number of values of the electron spins. *subshell is more* filled, the possible number of electrons. Of these level
2. Each of the effects into a of different v L that can be of the v electrons *any two or more* the level having
3. Each of these into $2S + 1$ interval form of these multiplets *re* multiplet, the configuration the largest J

The above configuration level is

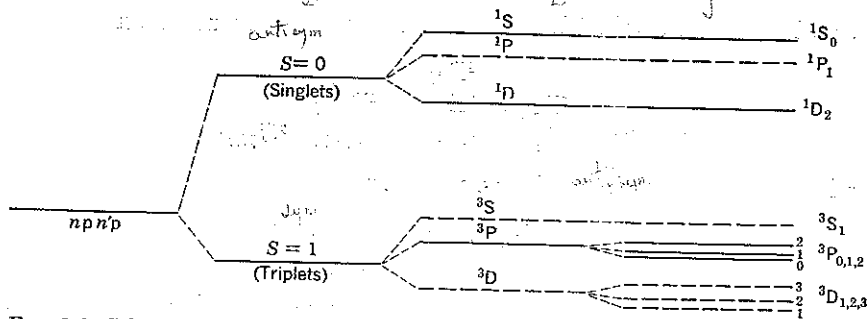


FIG. 8-3. Schematic illustration of the LS fine-structure splitting of a configuration involving two p electrons. The dashed levels are missing from the multiplet if the electrons are equivalent ($n = n'$).

valence electrons are involved. This complexity is somewhat reduced, of course, if some of these are in the same subshell. Electrons which are in the same subshell are called *equivalent electrons*; the exclusion principle must always be taken into account in analyzing the fine structure of a configuration involving equivalent electrons.

In case a subshell is more than half filled with electrons, the application of the exclusion principle leads to the important result that the combinations of L and S available to these electrons are exactly the same as if only a number of electrons equal to the number of unoccupied substates in the subshell were actually present. (Thus if five electrons were in a certain p subshell, the number of L and S combinations would be exactly the same as for one electron in this subshell, namely, $S = \frac{1}{2}$ and $L = 1$.) The most complicated fine structure therefore is associated with those elements having approximately half-filled subshells.

As an illustration of the effect of the exclusion principle upon the fine structure of a level, the fine-structure splitting is compared schematically in Fig. 8-3 for two equivalent and for two nonequivalent p electrons. The levels missing from the fine structure for the equivalent electrons are shown dotted.

This figure indicates that the 3D , 3S , and 1P terms that are found in the fine structure of a configuration of two nonequivalent p electrons are missing from the corresponding multiplet for equivalent electrons. These terms are eliminated because of the exclusion-principle requirement that no two electrons may have the same set of quantum numbers n, l, m_l , and m_s , and because only physically distinguishable states can be counted.

The general case of any number of equivalent electrons is best treated by the use of group theory, but unfortunately this method is beyond the scope of the present work. We can, however, deal with the particular case illustrated in Fig. 8-3 by a more elementary method. Let us tabu-

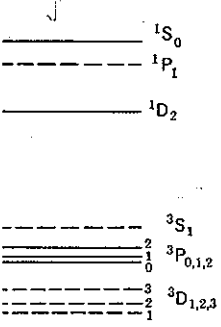
SEC. 8-3]

late the various possible combinations of M_L and M_S for two equivalent electrons, first treating the two electrons as nonequivalent and then taking account of the exclusion principle by striking out the combinations that are not allowed and by eliminating duplicate combinations. The possible combinations are 1, 4, 17, 20, 33, and

TABLE 8-1. m_{l1} AND m_{l2}

m_{l1}	m_{l2}	m_{s1}
+1	+1	$+\frac{1}{2}$
		+
		-
		-
+1	0	+
		+
		-
		-
+1	-1	+
		+
		-
		-
0	+1	+
		+
		-
		-
0	0	+
		+
		-
		-

pairs of states as 2 s numbers 1, 2, 3, etc combinations of M_L and M_S shown in Table 8-2 with the states excluded by the exclusion principle. Of these, only 15 are present, since this work rules out the presence of a given L and S combination if more than one combination is available. Of these, only 15 are present, since this work rules out the presence of a given L and S combination if more than one combination is available. Of these, only 15 are present, since this work rules out the presence of a given L and S combination if more than one combination is available.



late the various possible values of m_{l1} , m_{s1} , m_{l2} , and m_{s2} for the two electrons, first treating them as nonequivalent (Table 8-1). We then take account of the exclusion principle and the indistinguishability of the electrons by striking out those states for which $m_{l1} = m_{l2}$ and $m_{s1} = m_{s2}$, and by eliminating duplication of indistinguishable states. Thus states 1, 4, 17, 20, 33, and 36 are removed by the first criterion, and such

TABLE 8-1. m_l AND m_s VALUES FOR TWO EQUIVALENT p ELECTRONS

m_{l1}	m_{l2}	m_{s1}	m_{s2}	Label	m_{l1}	m_{l2}	m_{s1}	m_{s2}	Label
+1	+1	$+\frac{1}{2}$	$+\frac{1}{2}$	OUT	0	-1	+	+	11
		+	-	1			+	-	12
		-	+	1			-	+	13
		-	-	OUT			-	-	14
+1	0	+	+	2	-1	+1	+	+	6
		+	-	3			+	-	8
		-	+	4			-	+	7
		-	-	5			-	-	9
		-	-	6			-	-	11
+1	-1	+	+	7	-1	0	+	+	13
		+	-	8			+	-	12
		-	+	9			-	+	14
		-	-	2			-	-	OUT
0	+1	+	+	4	-1	-1	+	+	15
		+	-	3			+	-	15
		-	+	5			-	+	OUT
		-	-	OUT			-	-	OUT
0	0	+	+	10					
		+	-	10					
		-	+	10					
		-	-	OUT					

pairs of states as 2 and 3, 5 and 13, 6 and 15, etc., are labeled with new numbers 1, 2, 3, etc. For two equivalent p electrons, only the fifteen combinations of $M_L = m_{l1} + m_{l2}$, $M_S = m_{s1} + m_{s2}$, and $M_J = M_L + M_S$ shown in Table 8-2 are possible. We must now compare these states with the states expected in the LS multiplet: $1S_0$, $1P_1$, $1D_2$, $3S_1$, $3P_{0,1,2}$, $3D_{1,2,3}$. Of these, we can immediately see that the $3D_3$ state cannot be present, since this would require M_J values of $+3$ and -3 . This in turn rules out the presence of $3D_2$ and $3D_1$, since if one possible combination of a given L and S is present, all must be. On the other hand, state 2 requires the presence of an LS term with $L \geq 1$ and $S \geq 1$. Of the available combinations, this requires that $3P_{0,1,2}$ be present. Furthermore, state 1 can come only from an LS term having $L \geq 2$ and $S \geq 0$; from this we conclude that the $1D_2$ term must be present.

TABLE 8-2. M_L , M_S , AND M_J VALUES FOR TWO EQUIVALENT p ELECTRONS

Label	M_L	M_S	M_J	Label	M_L	M_S	M_J
1	+2	0	+2	9	0	-1	-1
2	+1	+1	+2	10	0	0	0
3	+1	0	+1	11	-1	+1	0
4	+1	0	+1	12	-1	0	-1
5	+1	-1	0	13	-1	0	-1
6	0	+1	+1	14	-1	-1	-2
7	0	0	0	15	-2	0	-2
8	0	0	0				

If we now count how many independent LS terms are known to be present, we have, from 3P_2 , 3P_1 , and 3P_0 , $5 + 3 + 1 = 9$ states; from 1D_2 , 5 states, or a total of 14. Furthermore, those states require M_J values of +2, +1, 0, -1, -2; +1, 0, -1, 0; and +2, +1, 0, -1, -2, respectively. These account for all of the M_J values in the table except for one, whose M_J value is zero. This then both permits and requires 1S_0 to be present.

By this procedure we have found that the fifteen independent states of two equivalent p electrons are to be identified with the fifteen LS states contained in 1S_0 , 1D_2 , and ${}^3P_{0,1,2}$. By a similar procedure one can deduce the fine-structure terms for other configurations involving equivalent electrons, with the results shown in Table 8-3.

If a given configuration contains both equivalent and nonequivalent electrons, one can analyze the LS coupling fine structure by starting with the equivalent electron terms and combining the other electrons, one by one, with them. Thus for the configuration $4p^2 5s$, the LS terms would be

$$\begin{aligned}
 {}^1S + s &\rightarrow {}^2S_{1/2} \\
 {}^1D + s &\rightarrow {}^2D_{3/2, 5/2} \\
 {}^3P + s &\rightarrow {}^2P_{1/2, 3/2}, {}^4P_{1/2, 3/2, 5/2}
 \end{aligned}$$

EXERCISES

8-1. Add up the degeneracies of the various LS terms appearing in Fig. 8-1 and thus verify that this is equal to the degeneracy of the $4p 4d$ level. *Ans.*: $g = 2^2 \times 3 \times 5 = 60$.

8-2. Add up the degeneracies of the various spin states appearing in Fig. 8-2 and thus verify that this is equal to 2^N , where N is the number of electrons whose spins are to be combined. (Each electron can independently have either of two orientations.) This expression is of course valid only if the exclusion principle does not limit the possible spin orientations.

TABLE 8-3. LS TERMS ARISING FROM EQUIVALENT ELECTRONS†

In this table the numbers in the first column are the total number of independent states corresponding to the configurations given in the second column. In the third column, the preceding superscripts are the multiplicities. The exponents that appear inside the parentheses for f-electrons are the number of distinct terms having the given multiplicity and L value. For example, f^5, f^6 : there are four 3P states, five 1D states, etc.

Equivalent p Electrons

f_s	M_J
-1	-1
0	0
-1	0
0	-1
0	-1
-1	-2
0	-2

are known to be 1 = 9 states; from states require M_J 2, +1, 0, -1, -2, in the table except permits and requires

independent states with the fifteen LS procedure one can variations involving 8-3.

and nonequivalent structure by starting the other electrons, $p^2 5s$, the LS terms

terms appearing in the energy of the $4p 4d$

states appearing in the N is the number of electron can independent of course the possible spin

TABLE 8-3. LS TERMS ARISING FROM EQUIVALENT ELECTRONS†

In this table the numbers in the first column are the total number of independent states corresponding to the configurations given in the second column. In the third column, the preceding superscripts are the multiplicities. The exponents that appear inside the parentheses for f-electrons are the number of distinct terms having the given multiplicity and L value. For example, f^5, f^6 : there are four 2P states, five 2D states, etc.

Indep states	Configuration	LS terms
(1)	s^2	1S
(6)	p^1, p^6	2P
(15)	p^2, p^4	$^1(SD) ^3P$
(20)	p^3	$^2(PD) ^4S$
(10)	d^1, d^9	2D
(45)	d^2, d^8	$^1(SDG) ^3(PF)$
(120)	d^3, d^7	$^2D ^2(PDFGH) ^4(PF)$
(210)	d^4, d^6	$^1(SDG) ^3(PF) ^1(SDFGI) ^2(PDFGH) ^6D$
(252)	d^5	$^2D ^2(PDFGH) ^4(PF) ^2(SDFGI) ^4(DG) ^5S$
(14)	f^1, f^{13}	2F
(91)	f^2, f^{12}	$^1(SDGI) ^3(PFH)$
(364)	f^3, f^{11}	$^2(PD^2 F^2 G^2 H^2 IKL) ^4(SDFGI)$
(1001)	f^4, f^{10}	$^1(S^2 D^4 FG^4 H^2 I^3 KL^2 N) ^3(P^2 D^2 F^4 G^3 H^4 I^2 K^2 LM) ^5(SDFGI)$
(2002)	f^5, f^9	$^2(P^4 D^6 F^7 G^6 H^7 I^5 K^5 L^3 M^2 NO) ^4(SP^2 D^3 F^4 G^4 H^3 I^3 K^2 LM) ^6(PFH)$
(3003)	f^6, f^8	$^1(S^4 PD^6 F^4 G^8 H^4 I^7 K^3 L^4 M^2 N^2 Q) ^3(P^6 D^5 F^9 G^7 H^5 I^6 K^6 L^3 M^3 NO) ^4(SPD^3 F^2 G^3 H^2 I^2 KL) ^7F$
(3432)	f^7	$^2(S^2 P^5 D^7 F^{10} G^{10} H^9 I^9 K^7 L^5 M^4 N^2 OQ) ^4(S^2 P^2 D^6 F^5 G^7 H^5 I^5 K^3 L^3 MN) ^6(PDFGHI) ^8S$

† Gibbs, Wilber, and White, *Phys. Rev.*, 29, 790 (1927).

8-3. By considering the combining properties of the spin angular momenta of a number of electrons, establish the *law of alternation of multiplicities* for LS coupling: "The spectral terms of successive elements in the periodic table alternate between even and odd multiplicities."

8-4. What spectral terms result from an electron configuration $3d\ 4f$, assuming LS coupling? Indicate on a sketch the expected spacing of the various components of the multiplets.

8-5. What spectral terms result from an electron configuration $2p\ 3p\ 4p$, assuming LS coupling? What degree of degeneracy is possessed by each of these levels?

8-6. What spectral terms should be present in the configuration $2p^2\ 3p$?

The foregoing description of LS coupling provides a basis for predicting the *spectroscopic character of the ground state of a given atom*. The ground state ought to possess the *highest* values of L and S —and if the valence subshell is less than half full, the *smallest* value of J —that are possible under the limitations of the exclusion principle. (If the valence subshell is more than half filled, the *largest* value of J will lie lowest.)

When the exclusion principle limits the possible combinations of L and S , the ground state is found to be a state of the *highest multiplicity* (largest value of S) that can be formed under the exclusion principle. If more than one value of L is possible for this multiplicity, the *largest* of these values determines the ground state. Then, depending upon whether the valence subshell is less than (or more than) half filled, the smallest (or largest) value of J for this combination of S and L completes the identification of the ground-state term. These rules, which almost without exception are observed to hold, show clearly that the spin-spin correlation effect which tends to make the spins line up parallel to one another is the largest of the perturbation terms, followed by the residual electrostatic effects which tend to line up the orbital angular momenta, and then by the spin-orbit term.

EXERCISE

8-7. Show that the following ground-state terms satisfy the above rules: $B(^2P_{1/2})$, $Sc(^2D_{3/2})$, $Se(^3P_2)$, $Zr(^3F_2)$, $Nb(^6D_{3/2})$, $Pr(^4I_{3/2})$, $Ta(^4F_{3/2})$.

8-4. j - j Coupling

Although the LS coupling scheme described above provides a suitable description of the fine-structure splitting of most of the energy levels of many atoms, there is another type of coupling which occurs for some atoms. In its ideal form, this second type represents an *opposite extreme* to ideal LS coupling in the sense that the fine-structure splitting of any

SEC. 8-4]

given level can be described as the *opposite extreme* of the two extreme types. It occurs in its ideal form in the case of the *residual electrostatic effects*. In this case the largest splitting is analogous, for each

4p4d

Unperturbed level

FIG. 8-4. Schematic illustration of j - j coupling.

Chap. 5 for the one type of splitting and the other for the other type.

1. The spin-orbit effect splits each of the $2S+1$ levels into $2S+1$ spaced levels, each of which is split into $2L+1$ possible j -values. According to Eq. 5-8(5) it follows that to all of the electrons in a level the number of levels is $(2S+1)(2L+1)$ by the orbital angular momentum principle, and it is $(2S+1)(2L+1)$ by the electrostatic effects.
2. The electrostatic effects split each of the $2S+1$ levels into $2S+1$ by different values of S and L by the exclusion principle.

We thus see that the splitting of the individual levels is of the *opposite extreme* type.

As an illustrative case as was described schematically above, the splitting produced by the j -values $1/2$ or $3/2$ spin-orbit effect

given level can be described in terms of a coupling which is a "mixture" of the two extreme types. The second type is called *j-j* coupling. It occurs in its ideal form if the spin-orbit energy [term (4)] greatly exceeds the residual electrostatic energy and the spin-spin correlation energy. In this case the largest part of the fine-structure splitting is exactly analogous, for each electron, to the spin-orbit splitting described in

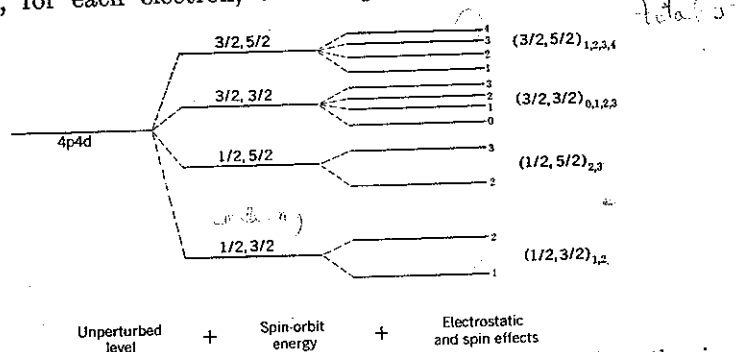


FIG. 8-4. Schematic illustration of the fine structure of a pd configuration in *j-j* coupling.

Chap. 5 for the one-electron atom. The effects of the various perturbations in splitting the unperturbed energy level can be described as follows:

1. The spin-orbit effects split the original level into a number of well-spaced levels, each of which corresponds to a different combination of the possible *j*-values for the individual valence electrons. From Eq. 5-8(5) it follows that the lowest-lying of these levels will correspond to all of the electrons having their smaller *j*-value ($j_i = l_i - 1/2$). The number of levels depends upon the number of valence electrons, their orbital angular momenta (only one *j* value if $l = 0$), and the exclusion principle, and it cannot exceed 2^n .
2. The electrostatic energy and spin-spin correlation energy then further split each of the above levels into a number of levels characterized by different values of the total angular momentum *J*. Here again the exclusion principle may act to limit the number of possible values of *J*.

We thus see that a given final level is characterized by the *j*-values of the individual valence electrons and by the total value of *J*. The various levels are commonly described by the notation $(j_1, j_2, \dots, j_n)_J$.

As an illustration of the *j-j* coupling scheme, let us consider the same case as was described in Fig. 8-1 for *LS* coupling. Figure 8-4 shows schematically how the expected fine structure for ideal *j-j* coupling is produced by the perturbation terms. The 4p electron can have the *j*-values $1/2$ or $3/2$, and the 4d electron the *j*-values $3/2$ or $5/2$. Thus the spin-orbit effect splits the unperturbed level into four levels, of which

spin angular
alternation of
five elements
licities."
ration 3d 4f,
d spacing of

ration 2p 3p
possessed by

ation 2p² 3p?
s for predict-
atom. The
J—and if the
J—that are
if the valence
ie lowest.)
ions of L and
at multiplicity
principle. If
y, the largest
pending upon
half filled, the
d L completes
which almost
the spin-spin
parallel to one
y the residual
ilar momenta,

sfy the above
, Ta(⁴F_{3/2}).

ides a suitable
energy levels
occurs for some
pposite extreme
plitting of any

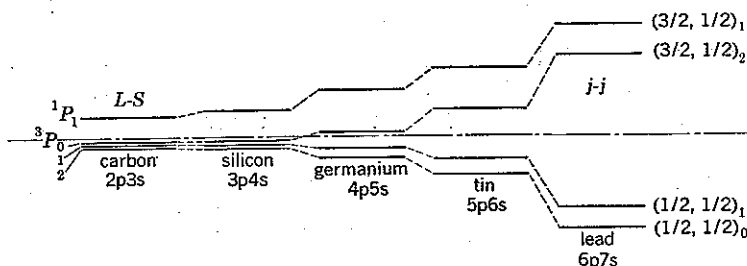


FIG. 8-5. Illustrating the gradual trend from ideal LS coupling in the light elements toward $j-j$ coupling in the heavy elements. (Adapted by permission from H. E. White, "Introduction to Atomic Spectra," McGraw-Hill Book Company, Inc., New York, 1934.)

$(\frac{1}{2}, \frac{3}{2})$ lies lowest and $(\frac{3}{2}, \frac{5}{2})$ highest. These four levels are then further split by the electrostatic and spin-spin correlation energies into the new levels shown. In each case the number of levels is equal to the number of integrally spaced values of J that can be formed out of the two j -values.

Note that the *total number* of final levels is the same as for the LS coupling scheme and that the J -value designations are also in one-to-one correspondence for the two schemes. Because of the highly schematic nature of the above example, it is not possible to define which of the above levels corresponds to each of the levels in the LS coupling scheme. The gradual shift in the coupling for certain levels from LS coupling for the light elements toward $j-j$ coupling for the heavy elements has been studied for several groups of elements. One of the best illustrations of this is provided by the carbon group of elements. Figure 8-5 shows schematically this change for the lowest-lying ps excited level in each of the members of this group.

In actual fact, one seldom finds that the fine structure of a given configuration is exactly describable in terms of ideal LS or $j-j$ coupling, because the relative magnitudes of the spin correlation, electrostatic, and spin-orbit energies do not satisfy the requirements of the idealized theory. Fortunately, by far the majority of cases are sufficiently close to ideal LS coupling that the LS notation is appropriate both qualitatively and quantitatively. Several cases falling between the ideal limits have been successfully treated, so that the observed departures from ideal LS or $j-j$ coupling are well understood theoretically. Accounts of such treatments can be found in advanced textbooks on spectroscopy.

8-5. Selection Rules

The two coupling schemes described above produce a quite satisfactory semiquantitative basis for interpreting the energy levels of multielectron

SEC. 8-5]

atoms. In order to understand transitions between these levels, selection rules govern the most probable transitions. The rules given below are those that can be derived by using the method of eigenfunctions and direct products. A few departures have only a weak intensity and are closely similar to those in the hydrogen atom.

A. Selection Rules

1. Transitions occur only when the atom changes its state.
2. The l -value of the final state must be equal to the l -value of the initial state or differ by one.

This is a special case of the selection rule for the *wave function* m arising from conservation of angular momentum, that is,

3. For the atom as a whole, the change in the total angular momentum S must be zero.

$$\begin{aligned} \Delta S &= 0 \\ \Delta J &= 0, \pm 1 \\ \Delta M_J &= 0, \pm 1 \end{aligned}$$

B. Selection Rules

1. Transitions occur only when the atom changes its state.
2. The l -value of the final state must be equal to the l -value of the initial state or differ by one.
3. $\Delta j = 0, \pm 1$ for each electron.
4. For the atom as a whole, the change in the total angular momentum J must be zero.

$$\begin{aligned} \Delta J &= 0, \pm 1 \\ \Delta M_J &= 0, \pm 1 \end{aligned}$$

The above selection rules involve transitions between states of the atom or (in LS coupling) between states of the individual electrons.

$(3/2, 1/2)_1$
 $(3/2, 1/2)_2$

$(1/2, 1/2)_1$
 $(1/2, 1/2)_0$

the light elements
 from H. E. White,
 Inc., New York,

levels are then
 energies into
 is equal to the
 out of the two

as for the LS
 in one-to-one
 gibly schematic
 sh of the above
 scheme. The
 upling for the
 as been studied
 ions of this is
 5 shows sche-
 in each of the

of a given con-
 r $j-j$ coupling,
 , electrostatic,
 f the idealized
 fficiently close
 e both qualita-
 the ideal limits
 epartures from
 . Accounts of
 pectroscopy.

ite satisfactory
 f multielectron

atoms. In order to understand the *spectral lines* that result from transitions between these levels, however, we must also know what *selection rules* govern the most common types of transition. The selection rules given below are those for *electric-dipole* transitions. Most of them can be derived by using only the general properties of the angular-momentum eigenfunctions and do not require a knowledge of the complete wave functions. A few depend upon the assumption that the valence electrons have only a weak interaction with each other. Note that they are very closely similar to the selection rules derived in Chap. 6 for the one-electron atom.

A. Selection Rules for LS Coupling

1. Transitions occur only between configurations in which *one electron* changes its state. (Only one electron "jumps" at a time.)
2. The l -value of the jumping electron must change by one unit

$$\Delta l = \pm 1$$

This is a special case of the general requirement that *the parity of the wave function must change in an electric-dipole transition*. Terms arising from configurations of odd parity are so designated by a superscript o , that is, ${}^3P_2^o$.

3. For the atom as a whole, the quantum numbers L , S , J , and M_J must change as follows:

$$\begin{array}{ll} \Delta S = 0 & \Delta L = 0, \pm 1 \\ \Delta J = 0, \pm 1 & \text{but } J = 0 \rightarrow J = 0 \text{ forbidden} \\ \Delta M_J = 0, \pm 1 & \text{but } M_J = 0 \rightarrow M_J = 0 \text{ forbidden if } \Delta J = 0 \end{array}$$

B. Selection Rules for $j-j$ Coupling

1. Transitions occur only between configurations in which *one electron* changes its state. (Only one electron "jumps" at a time.)
2. The l -value of the jumping electron must change by one unit; or, more generally, *the parity must change*.
3. $\Delta j = 0, \pm 1$ for the jumping electron, and $\Delta j = 0$ for all the other electrons.
4. For the atom as a whole,

$$\begin{array}{ll} \Delta J = 0, \pm 1 & \text{but } J = 0 \rightarrow J = 0 \text{ forbidden} \\ \Delta M_J = 0, \pm 1 & \text{but } M_J = 0 \rightarrow M_J = 0 \text{ forbidden if } \Delta J = 0 \end{array}$$

The above selection rules are observed to be in operation in the vast majority of transitions. The commonest violations of these selection rules involve transitions in which *more than one electron changes its state*, or (in LS coupling) in which *the spin changes by one unit*. In case more than one electron jumps, the selection rules still require that the *sum* of the individual orbital angular-momentum quantum numbers change by

one unit for an electric-dipole transition, since the parity of a state is just that of the sum of the l quantum numbers of the electrons.

8-6. Energy-level Diagrams for Complex Atoms

One of the most satisfactory ways of describing the character of the spectrum of a given atom is by means of an energy-level diagram similar to that used to illustrate the fine structure of hydrogen (Fig. 5-6). In

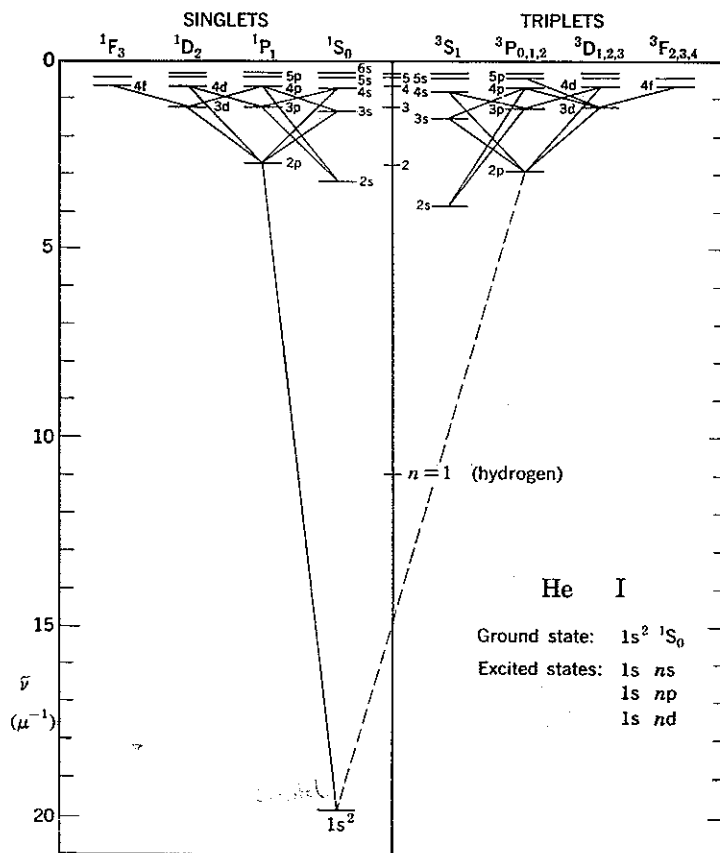
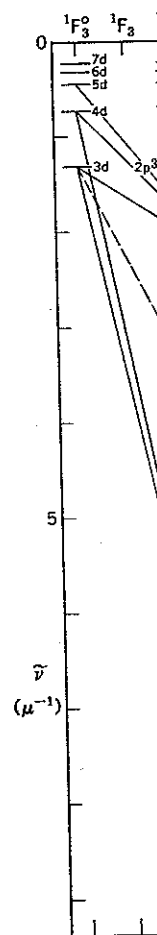


FIG. 8-6. Term diagram for neutral helium.

the following pages, diagrams are given for a number of atoms. A partial energy-level diagram for a relatively simple "complex" atom is shown in Fig. 8-6 for helium. This element has, in its ground state, two equivalent electrons in the $1s$ subshell. Thus from the foregoing considerations we expect the ground state to be a 1S_0 state. The lowest excited states involve the elevation of one of these electrons into a higher

shell, so that the ex two electrons only *si* selection rules $\Delta S =$ separate groups, with group. A transition



group to the other is shown in Fig. 8 in the spectrum of of one group may getting to the ground dipole or electric-

rity of a state is electrons.

shell, so that the exclusion principle does not affect these states. For two electrons only *singlet* and *triplet* states can occur; and because of the selection rules $\Delta S = 0$, it is convenient to represent these states in *two separate groups*, with permitted transitions occurring only within each group. A transition which violates this selection rule then goes from one

character of the *l* diagram similar n (Fig. 5-6). In

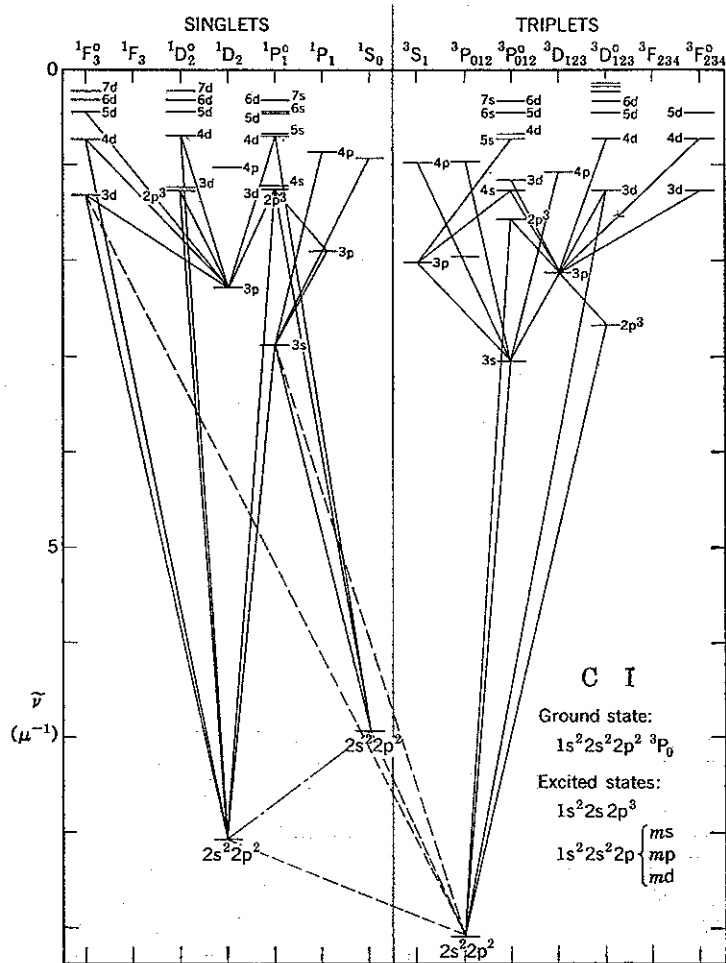
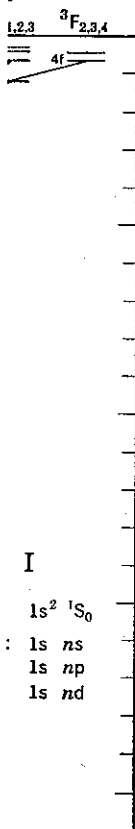


FIG. 8-7. Term diagram for neutral carbon.

er of atoms. A complex" atom is ground state, two ie foregoing con- ate. The lowest ons into a higher

group to the other and is called an *intersystem transition*. One of these is shown in Fig. 8-6. It often happens that some of the strongest lines in the spectrum of an atom are intersystem lines, because the lowest level of one group may lie above the ground-state level and the only means of getting to the ground state from this state may be through a magnetic-dipole or electric-quadrupole transition. Thus even though the probab-

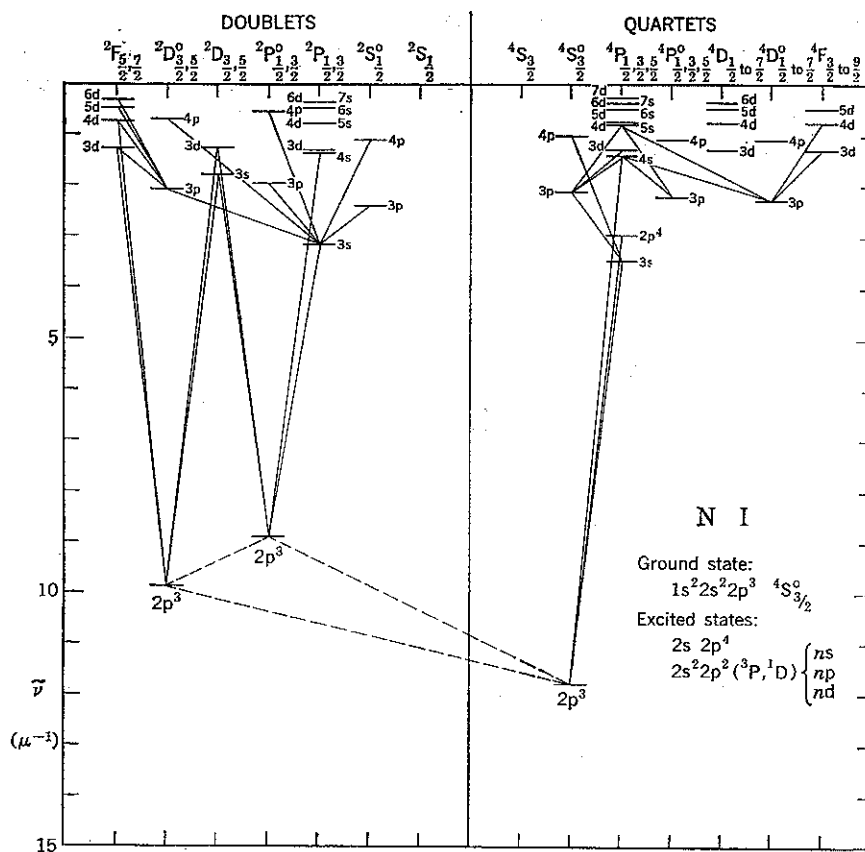


FIG. 8-8. Term diagram for neutral nitrogen.

ity of such a transition is many times smaller than that for an electric-dipole transition, it is still possible to have a strong spectral line, because atoms will continue to fall into this state from above until the number of atoms in it is so great that many transitions will occur per second in spite of the low transition probability per atom.

In Fig. 8-6, it should be noted that the higher excited levels approach those for neutral hydrogen quite closely. The transitions between these levels would thus approximate the corresponding transitions of hydrogen, except that the helium lines would show different fine structure. Energy-level diagrams for other complex atoms are shown in Figs. 8-7 and 8-8.

8-7. Regularities in Complex Spectra

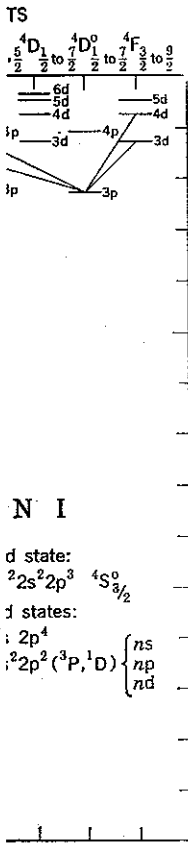
From the earliest investigations of atomic spectra great effort was spent to discover quantitative or qualitative spectral regularities and to

relate the spectra of spectral regularities v problem of determin various energy level vided an exceedingly and has itself aided elements. We have derived from the a atoms. There are s ined, however, and i principal regularities

A. *The Rydberg-s* tive relationships be were discovered by in Chap. 2, expresse from the Schroeding have a form similar able from the stan already been pointe electrons of a neutra an inverse-square fi excited states of a excited ought to a Fig. 8-6 for helium. of the spectra of th

Of course the lo hydrogen levels ve of small total angul nearly "circular" on the basis of th momentum toward electrons is small spectra.

B. *The Hartley* Rydberg's work in covered that the s plet line in the va measured in terms doublet or triplet ; This law is an obv Einstein condition energy difference c then all transition



relate the spectra of neighboring elements in the periodic table. Many spectral regularities were found empirically and were used as an aid in the problem of determining the correct spectroscopic designations of the various energy levels in an atom. Modern quantum theory has provided an exceedingly satisfactory theoretical basis for these relationships and has itself aided greatly in the task of mapping the spectra of the elements. We have already seen how some of these regularities can be derived from the application of the Schroedinger theory to complex atoms. There are several regularities that we have not explicitly examined, however, and it is thus worthwhile to tabulate in a single place the principal regularities that can be observed in atomic spectra.

A. *The Rydberg-series Relationships.* The earliest general quantitative relationships between certain lines in the spectrum of many elements were discovered by Rydberg. Rydberg's series, which were described in Chap. 2, expressed empirically a fact that can also be seen to follow from the Schroedinger theory, namely, that many atomic spectral series have a form similar to the Balmer series of hydrogen. This is reasonable from the standpoint of the Schroedinger theory because, as has already been pointed out, the electric field felt by a single one of the electrons of a neutral atom at large distances from the nucleus approaches an inverse-square field due to a *singly charged* nucleus. Thus the higher excited states of any neutral atom in which only a single electron is excited ought to approach those for hydrogen. This is illustrated in Fig. 8-6 for helium, and it constitutes one of the most striking features of the spectra of the alkali metals.

Of course the lower excited states of an atom do not approach the hydrogen levels very closely, especially in the cases of the lower orbits of small total angular momentum. This regular progression of the more nearly "circular" orbits toward the hydrogen levels can be explained on the basis of the greater penetration of the states of low angular momentum toward the nucleus, where the shielding effect of the inner electrons is smaller. This effect, too, is quite prominent in the alkali spectra.

B. *The Hartley Law of Constant Doublet Separation.* Even before Rydberg's work in expressing series in analytic form, Hartley (1883) discovered that the separation between corresponding members of a multiplet line in the various members of a spectral series was *constant* when measured in terms of *reciprocal wavelength*; that is, the components of a doublet or triplet series are separated by the same frequency difference. This law is an obvious consequence of the idea of energy levels with the Einstein condition relating the frequency of emitted radiation to the energy difference of two levels, since if one energy level is, say, a doublet, then all transitions that begin or end on this level will yield two sets of

t for an electric-
tral line, because
il the number of
r second in spite

l levels approach
ns between these
ions of hydrogen,
ecture. Energy-
gs. 8-7 and 8-8.

great effort was
gularities and to

lines, separated in frequency by just the energy difference of the level divided by h . Clearly, this law will also apply to widely spaced energy levels.

C. Similarities between Members of the Same Chemical Group. It was recognized very early in the study of spectra that close relationships exist between the spectra of chemically similar elements. As we have seen, the various groups of chemically similar elements are characterized by similar valence-electron configurations, and we can now appreciate that these elements will be characterized by similar electron configurations, and also by similar fine-structure splitting, for the various *excited levels*, with a possible gradual trend in the character of the coupling from one member of the group to the next.

D. The Alternation Law of Multiplicities. The alternation law of multiplicities states that spectral terms corresponding to successive (neutral) atoms in the periodic table alternate between even and odd multiplicities. This law was recognized empirically before the discovery of electron spin. As we have seen (Exercise 8-3), it is a consequence of the combining properties of the spins of the various valence electrons.

E. The Displacement Law. The displacement law was first stated by Kossel and Sommerfeld (1919): "The spectrum and energy levels of a neutral atom closely resemble the spectrum and energy levels of a *singly ionized* atom of one unit higher atomic number." This law clearly follows from the fact that the electron configurations of two such atoms would be the same. The main difference between the two cases results from the fact that one atom has one more unit of charge than the other, so that the field felt by an outer electron will be twice as great for the ionized atom as for the neutral one. We have already seen the consequences of this for the case of ionized He vs. neutral H: corresponding lines are systematically shifted toward the violet in the spectrum of the ion.

F. Isoelectronic Sequences. The displacement law can also be applied to a *series* of adjacent elements, each ionized to a successively greater degree. Such a series of atoms, whose electron configurations are identical, is called an *isoelectronic sequence*. The spectra of the various members of an isoelectronic sequence of atoms show the same type of fine-structure splitting, similar relative intensities for the various corresponding transitions, etc.

8-8. The Zeeman Effect

The analysis of the Zeeman effect given in Chap. 2 on the basis of the classical electron theory appeared to provide a valid theoretical basis for the "normal" Zeeman effect but was unable to explain the "anomalous" behavior of many spectral lines when the radiating atom is

located in a magnetic field. The theory lies in the beautiful entire Zeeman effect. on the basis of the Schrodinger theory.

The "Zeeman splitting" results from the interaction of the atom with an external magnetic field. The vector B is, from classical electrodynamics,

and since this energy is much smaller than the energy of the unperturbed atom, we can introduce this term into the energy as a *perturbation*.

In order to apply the perturbation theory in a suitable form for the Zeeman effect, we shall assume that the energy levels are done if we assume that the energy levels are described by LS coupling of the atom as the vector magnetic moments μ and μ_B are

$$\mu = -\frac{e\hbar}{2mc} \mathbf{L} - \frac{e\hbar}{mc} \mathbf{S}$$

$$= -\mu_B (L + 2S)$$

$$= -\mu_B (L + 2S)$$

Thus we see that the total angular momentum J is the sum of the orbital and spin angular momentum. The energy levels are split into different parts with the orbital angular momentum. The simplest mathematical argument: In the absence of an external magnetic field, the angular momentum J is a constant of motion depending upon the direction of the magnetic field. This precession is, divided by h . No external magnetic field is applied. The direct effect of the field is much slower than the precession.

located in a magnetic field. One of the greatest triumphs of the quantum theory lies in the beautiful quantitative interpretation it provides for the entire Zeeman effect. We shall now briefly analyze the Zeeman effect on the basis of the Schrodinger theory.

The "Zeeman splitting," as it is called, of the energy levels of an atom results from the interaction energy of the net *magnetic moment* of the atom with an external magnetic field. If we denote this magnetic moment by the vector \mathbf{u} , the orientation energy of \mathbf{u} in an external field \mathbf{B} is, from classical electromagnetic theory,

$$W = -\mathbf{u} \cdot \mathbf{B} \quad (1)$$

and since this energy is very small (that is, Zeeman splitting is ordinarily much smaller than ordinary fine-structure splitting) we may introduce this term into the Hamiltonian function of the atom as a *small perturbation*.

In order to apply the perturbation theory, we must now determine a suitable form for the *operator* corresponding to W . This is most easily done if we assume that the levels whose splittings are to be analyzed are described by *LS* coupling. We may express the net magnetic moment of the atom as the vector sum of the *orbital* magnetic moments and *spin* magnetic moments of the individual electrons [see Eqs. 5-5(3) and (5)]:

$$\begin{aligned} \mathbf{u} &= - \sum_{i=1}^v \left[\frac{1}{2} \left(\frac{e}{m} \right) \mathbf{l}_i + \left(\frac{e}{m} \right) \mathbf{s}_i \right] \\ &= - \frac{1}{2} \left(\frac{e}{m} \right) \sum_i \mathbf{l}_i - \left(\frac{e}{m} \right) \sum_i \mathbf{s}_i \\ &= - \frac{1}{2} \left(\frac{e}{m} \right) (\mathbf{L} + 2\mathbf{S}) = - \frac{1}{2} \left(\frac{e}{m} \right) (\mathbf{J} + \mathbf{S}) \end{aligned} \quad (2)$$

Thus we see that the net magnetic moment is *not necessarily parallel* to the total angular momentum \mathbf{J} of the atom. This is true because of the *different proportionality factors* connecting the magnetic moment with the orbital and spin angular momenta. To keep the analysis in the simplest mathematical form, we now make the following physical argument: In the absence of an external magnetic field, the total angular momentum \mathbf{J} is a constant, and \mathbf{L} , \mathbf{S} , and \mathbf{u} "precess" around \mathbf{J} at a rate depending upon the magnitude of the *LS* coupling. The frequency of this precession is, in a given case, just the energy shift due to $\mathbf{L} \cdot \mathbf{S}$, divided by h . Now, when an external field is applied, the total angular-momentum vector will no longer be constant but will precess about the applied-field direction. For a weak applied field this precession will be *much slower* than the $\mathbf{L} \cdot \mathbf{S}$ precession, so that the *time-average* component

on the basis of the
d theoretical basis
xplain the "anom-
radiating atom is

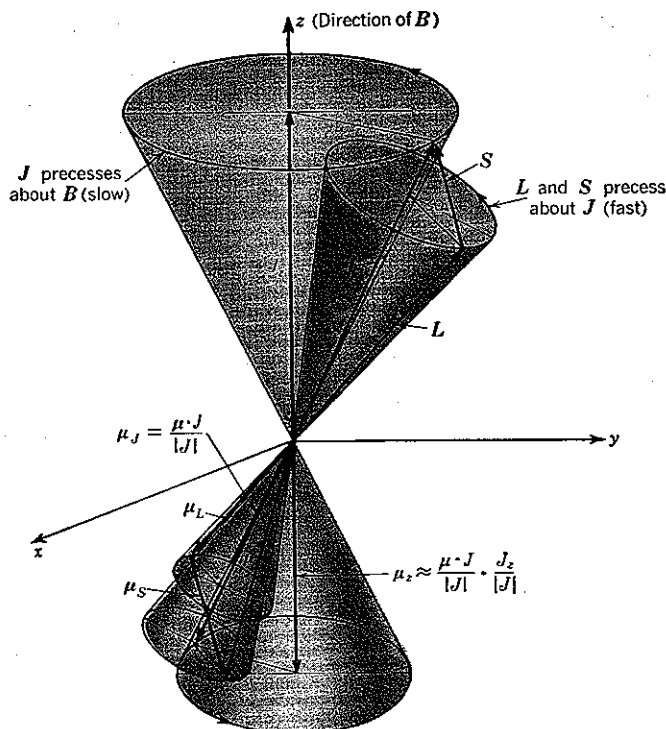


FIG. 8-9. Illustrating the approximations used in treating the Zeeman effect in relatively weak magnetic fields ($B < \sim 10^4$ gauss).

of μ along the field is very nearly equal to the component of μ along J multiplied by the component of J along the field. This is shown in Fig. 8-9. Thus we may write

$$\begin{aligned} W &= \frac{1}{2} \left(\frac{e}{m} \right) \frac{[(J + S) \cdot J](J \cdot B)}{|J|^2} \\ &= \frac{1}{2} \left(\frac{eB}{m} \right) \frac{(|J|^2 + J \cdot S)J_z}{|J|^2} \end{aligned} \quad (3)$$

By the same procedure as was used to arrive at Eq. 8-3(5) we now may write

$$J \cdot S = \frac{1}{2}(|J|^2 + |S|^2 - |L|^2) \quad (4)$$

so that we have for W ,

$$W = \frac{1}{2} \left(\frac{eB}{m} \right) \frac{[|J|^2 + \frac{1}{2}(|J|^2 + |S|^2 - |L|^2)]J_z}{|J|^2}$$

The operator for W is thus just the operator for the quantity on the right. Since $|J|^2$, $|L|^2$, $|S|^2$, and J_z all commute with one another, there is no problem regarding the order of appearance of the various quantities,

SEC. 8-8]

and we may write ΔE defined by the quantity

$$\begin{aligned} \Delta E = W &= + \frac{1}{2} \left(\frac{eB}{m} \right) \frac{J_z}{J(J+1)} \\ &= + \frac{1}{2} \left(\frac{eh}{m} \right) \frac{M}{J(J+1)} \\ &= + \frac{1}{2} \left(\frac{eh}{m} \right) \frac{M}{J(J+1)} \end{aligned}$$

This equation indicates that the energy levels L , S , and J will be split into equally spaced levels. The quantum number M takes on the integral values $-J, -J+1, \dots, J$. The effect removes the degeneracy. The quantity

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

is called the Landé g -factor. If the magnetic moments are equal, the g -factor is

The splitting of $2J + 1$ equally spaced levels into only $2L + 1$ levels because of the selection rule for the energy shift for

$$\Delta E_1 = \frac{1}{2} \left(\frac{eh}{m} \right) \frac{M}{J(J+1)}$$

so that the frequency

Thus if $g_1 = g_2$, the components $\pm \frac{1}{2} \left(\frac{eh}{m} \right) \frac{M}{J(J+1)}$ are in agreement with the

and we may write down immediately the first-order shift in the state defined by the quantum numbers L, S, J, M_J :

$$\begin{aligned}\Delta E = W &= + \frac{1}{2} \left(\frac{eB}{m} \right) \\ &\quad \frac{\{J(J+1) + \frac{1}{2}[J(J+1) + S(S+1) - L(L+1)]\} M_J \hbar}{J(J+1)} \\ &= + \frac{1}{2} \left(\frac{e\hbar B}{m} \right) \left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right] M_J \\ &= + \frac{1}{2} \left(\frac{e\hbar B}{m} \right) g M_J\end{aligned}\quad (5)$$

This equation indicates that a level described by quantum numbers L, S , and J will be split by the external magnetic field into a number of equally spaced levels corresponding to the various possible values of the quantum number M_J . The number of such values is $2J + 1$, since M_J takes on the integrally spaced values from $-J$ to $+J$. Thus the Zeeman effect removes the degeneracy of the levels with respect to M_J .

The quantity

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (6)$$

is called the *Landé g-factor*. If the proportionality factors connecting the magnetic moment with the orbital and spin angular momenta were equal, the g -factor would be a *constant*, independent of L, S , and J .

The splitting of the various LS levels as described by Eq. (5) into $2J + 1$ equally spaced components might still lead to a *spectral line* splitting into only *three* components as in the classical theory, if the g -factors of both of the levels involved in a transition were the same, because of the selection rule $\Delta M_J = 0, \pm 1$. This can be seen by writing the energy shift for two levels, 1 and 2, in the form

$$\Delta E_1 = \frac{1}{2} \left(\frac{e\hbar B}{m} \right) g_1 M_{J_1} \quad \text{and} \quad \Delta E_2 = \frac{1}{2} \left(\frac{e\hbar B}{m} \right) g_2 M_{J_2}$$

so that the frequency shift of a spectral transition from 1 to 2 would be

$$\begin{aligned}\Delta\omega_{12} &= \frac{\Delta E_1 - \Delta E_2}{\hbar} \\ &= \frac{1}{2} \left(\frac{eB}{m} \right) (g_1 M_{J_1} - g_2 M_{J_2})\end{aligned}\quad (7)$$

Thus if $g_1 = g_2$, then $\Delta\omega_{12} = \frac{1}{2}(eB/m)g_1 \Delta M_J$, giving just the three components $+\frac{1}{2}(eB/m)g_1, 0, -\frac{1}{2}(eB/m)g_1$ to the split line, in qualitative agreement with the classical theory.

It is therefore the fact that the *Landé g-factor varies* from one level to another, and not necessarily the fact that each level is split into $2J + 1$ components, that leads to an "anomalous" Zeeman pattern.

EXERCISES

8-8. Find the Zeeman structure of a spectral line which results from the transition ${}^4F_{3/2} - {}^4D_{3/2}$.

8-9. (a) By what factor will the total spread of the Zeeman pattern of the transition ${}^{10}H_{3/2} - {}^{10}G_{3/2}$ exceed the classical value? (b) How many lines will appear in the Zeeman pattern of this transition? *Ans.:* (a) $2^{11}/15$. (b) 6.

8-10. A certain spectral line is known to result from a transition from a 3D level to another level whose *LS* designation is unknown. The Zeeman pattern of the line is shown (to scale) in Fig. 8-10. Find (a) the *J*-value of the upper level and (b) the *LS* designation of the lower level.

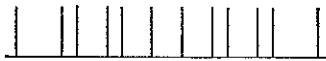


FIG. 8-10.

The Schrodinger theory of the Zeeman effect correctly predicts both qualitatively and quantitatively the pattern into which any given spectral line should be split by a magnetic field. Inasmuch as each different

transition possesses a characteristic pattern that may be quite complex, this fact strongly confirms the correctness of quantum mechanics, including electron spin. Indeed, much of what we now know of the spectroscopic designations of the various energy levels of atoms was either established by or checked against the observed Zeeman patterns of the spectral lines. As an illustrative example, Fig. 8-11 depicts the Zeeman splitting of the line ${}^3P_1 - {}^3D_2$.

8-9. The Excitation of Atoms

In our discussion of the spectroscopic transitions between the various excited levels of atoms we have almost completely ignored the question of the processes by which an atom is raised to an excited state. It is of course a familiar fact that emission spectra are observed whenever the atoms involved are in a flame or in an electric arc or spark, but we have not examined the *fundamental mechanism* by which excitation takes place in these cases. In order to give some idea of the mechanisms by which such excitation can take place, some of the commoner of these processes are listed below:

A. *Excitation by the Absorption of Light.* The analysis given in Chap. 6 concerning the effect of an electromagnetic field upon an atom has shown that an atom may be excited by absorbing a quantum from the electro-

magnetic field. In su ability any of the exci dipole transition, pro available to induce thi such an effect occurs i of excitation. The at states, and radiation f emitted as they return region and thus provi frequencies to induce "cool" atoms, thus ex but this reradiation ta loss of intensity of ra is the origin of the so

B. *Excitation by* (gaseous region, the a themselves or other a collision is an *inelas*

$$g = 1 +$$

M_{J1}	.
M_{J2}	.
$\Delta\omega_{12}$	$\left(\frac{3}{2}\right)$

$$\Delta = \frac{eB}{2m}$$

Spacing units of .

FIG. 8-11. Illustrating transition ${}^3P_1 - {}^3D_2$.

magnetic field. In such a process the atom may reach with high probability any of the excited levels related to its initial level by an electric-dipole transition, provided that light of the appropriate frequency is available to induce this absorptive transition. A familiar case in which such an effect occurs is at the cool boundary of a flame or other source of excitation. The atoms in such a region are generally in their ground states, and radiation from the excited atoms in the center of the flame, emitted as they return to their ground states, passes through this outer region and thus provides an intense source of radiation of just the right frequencies to induce absorptive transitions in the outer atoms. The "cool" atoms, thus excited, later reradiate the energy they have absorbed, but this reradiation takes place in all directions, so that there may be a net loss of intensity of radiation proceeding in the original direction. This is the origin of the so-called reversal spectrum of a cool vapor.

B. Excitation by Collision. In a flame or other high-temperature gaseous region, the atoms may have sufficient kinetic energies to raise themselves or other atoms into excited states when they collide. Such a collision is an inelastic collision in the mechanical sense, since kinetic

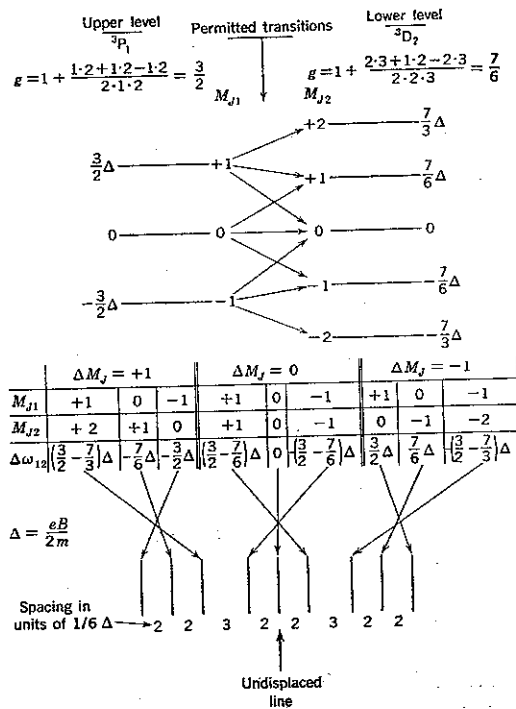


Fig. 8-11. Illustrating the Zeeman splitting of a spectral line corresponding to the transition $^3P_1 - ^3D_2$.

s from one level to s split into $2J + 1$ attern.

which results from

the Zeeman pattern value? (b) How transition? Ans.:

a transition from is unknown. The g. 8-10. Find (a) a of the lower level.

ory of the Zeeman both qualitatively pattern into which should be split by a h as each different be quite complex, mechanics, includ- ow of the spectro- atoms was either an patterns of the epects the Zeeman

etween the various ored the question ted state. It is of rved whenever the park, but we have itation takes place hanisms by which of these processes

sis given in Chap. 6 an atom has shown 1 from the electro-

energy of motion of the atom as a whole is transferred into "nonmechanical" energy of excitation of the atom. The transitions which can be induced by such means are not subject to the ordinary selection rules, of course, so that an atom may be left in a state of excitation from which it would be impossible to return to the ground state by electric-dipole transitions alone. Conversely, if an atom finds itself in a state of excitation whose mean lifetime is sufficiently long (i.e., one having a relatively small transition probability to leave this excited state) the atom may be removed from this state by collision before it can undergo a radiative transition. Certain transitions which have been observed spectroscopically (in gaseous nebulae) are so highly forbidden that their mean lives are *many seconds*. Such transitions cannot be observed in the laboratory because the atom would be removed from the excited state by collision long before it could radiate.

C. Excitation by Electron Bombardment. Somewhat related to the previous mechanism is that of excitation by electron bombardment. In this case, however, the temperature need not be very high, and the atoms need not be in equipartition equilibrium with the electrons. The electrons may themselves be produced independently of the atoms to be excited, e.g., by thermionic emission from a hot body, or may be produced as a by-product of the excitation process itself. In any case the electrons are usually accelerated by electric fields to high enough energy that they become capable of exciting an atom by colliding with it. This is one of the most important mechanisms of excitation in operation in an electric arc, spark, or low-pressure electric discharge.

Some of the early quantitative work on the excitation energies of atoms was done by bombarding gaseous atoms at low pressure with electrons of carefully controlled energy, and observing at what energies *inelastic scattering* of the electrons took place, as evidenced by a decrease in current to a collection electrode (Franck and Hertz, 1914).

D. Ionization. As a special case of some of the above mechanisms, an atom may be *ionized* by photoelectric absorption of a high-energy quantum or by an especially violent collision with another atom or particle. If a supply of free electrons is then available, one of these may come close enough to an atom to be captured into one of the higher bound states, and from there proceed downward toward the ground state in one or more "jumps."

8-10. The Breadth of Spectral Lines

In the discussion of the excited states of atoms so far, it has been assumed that each energy level is infinitely "sharp," that is, that each energy level corresponds to a state in which the energy of the atom is

precisely defined. The levels would yield a observed, however, "diffuse" lines, that defined, but vary or regarded as a device components, so that line is plotted vs. the ment of $\phi^* \phi$ for th some of the major c

A. Unresolved F_1 appear to be broad may not possess su fine-structure com importance, cannot in any fundamenta

B. Finite Lifetim source of line broad source is that due to excited state. Th electromagnetic fie spontaneous emissi of the "occupatic included. It is th with time, with a probabilities of tra measure the energ principle demands not limit the *time* system is so pertu state for a very lo in a *short time*, an of its energy. T energy, the great

The above sch the perturbation due to a given f "resonance" cur lifetime of the s energies between

precisely defined. Thus one would expect that a transition between these levels would yield a photon of *precisely defined wavelength.* It is actually observed, however, that some transitions lead to very "broad" or "diffuse" lines, that is, to photons whose wavelengths are not precisely defined, but vary over a range of wavelengths. A spectroscope may be regarded as a device which resolves a photon into its various wavelength components, so that a "line profile" in which the "brightness" of the line is plotted vs. the wavelength is actually an experimental measurement of $\phi^* \phi$ for the incoming photons. We shall now consider briefly some of the major causes of this so-called "line broadening."

A. Unresolved Fine Structure. One reason why some spectral lines appear to be broad rather than narrow and sharp is that the spectroscope may not possess sufficient power to resolve these lines into their several fine-structure components. This effect, although of great practical importance, cannot be regarded as an important cause of line broadening in any fundamental sense, and we shall not consider it further.

B. Finite Lifetimes of the Excited States. Probably the most important source of line broadening from the standpoint of its theoretical implications is that due to the finite time that an atom is likely to remain in an excited state. The analysis of the interaction of an atom with an electromagnetic field given in Chap. 6 can be extended for the case of spontaneous emission to apply to finite time intervals, for which the decay of the "occupation probability" $a_n^* a_n$, of the original state must be included. It is then found that this probability *decreases exponentially* with time, with a characteristic time constant which depends upon the probabilities of transition into all of the lower-lying states. In order to measure the energy of the system with *high precision,* the indeterminacy principle demands that we use some means of measurement which does not limit the *time interval* over which the measurement is made. If the system is so perturbed, however, that it is unlikely to remain in a given state for a very long time, we must make the measurement of its energy in a *short time,* and thus accept a certain *indeterminacy* in our knowledge of its energy. Thus the shorter the time available for measuring the energy, the greater is the uncertainty in the energy.

The above schematic analysis can be carried out analytically, using the perturbation theory, and it is found that the profile of a spectral line due to a given finite "decay lifetime" of a given state is a so-called "resonance" curve with a "width" inversely proportional to the decay lifetime of the state. That is, the intensity of light having quantum energies between E and $E + dE$ is

$$dI = I(E) dE = \frac{I_0 \Gamma \hbar^{-1} dE}{\Gamma^2/4 + (E - E_0)^2/\hbar^2} \quad (1)$$

ms so far, it has been
rp," that is, that each
energy of the atom is

where Γ is the reciprocal of the mean life of the state, E_0 is the average photon energy, and I_0 is the total rate of emission of energy in the transition.

EXERCISES

8-11. A similar formula can be derived classically for a "damped wave train" whose electric vector is, at a fixed point,

$$E = E_0 e^{-\Gamma t/2} \sin \omega_0 t \quad t > 0$$

and

$$E = 0 \quad t < 0$$

Analyze this wave train into its Fourier components, and thus show that such a wave train has a distribution of energy as a function of frequency similar to that of Eq. (1). *Hint:* Make use of the fact that Γ is ordinarily $\ll \omega_0$.

8-12. If the "width" $\Delta \bar{\nu}$ of a certain level is observed spectroscopically to be $10^{-4} \mu^{-1}$, what is the approximate lifetime of the state, in seconds?

C. Doppler Broadening. If the atoms of a gaseous source are at high temperature, a *spread* in the frequency of a given transition is produced by their randomly oriented velocities with respect to the spectrograph, as a result of the Doppler effect. This cause of line broadening is found to be sufficiently important that, for work requiring very high resolution, a low-temperature light source is used in order to keep the velocities as small as possible.

EXERCISES

8-13. The probability that the speed of a molecule of an ideal gas lies between v and $v + dv$ is given by the Maxwellian distribution

$$dP = 4\pi \left(\frac{\mu}{2\pi RT} \right)^{3/2} e^{-\mu v^2/2RT} v^2 dv \quad (2)$$

where μ is the molecular weight, R is the universal gas constant, and T is the absolute temperature (see Exercise 10-20). Find an expression for the intensity profile of a spectral line of central frequency ν_0 which originates in such a gas.

$$\text{Ans.:} \quad I(\nu) = \frac{I_0}{\nu_0} \left(\frac{\mu c^2}{2\pi RT} \right)^{1/2} \exp \frac{-\mu c^2 (\nu - \nu_0)^2}{2RT \nu_0^2} \quad (3)$$

8-14. Find the approximate magnitude of the Doppler broadening for an argon glow tube whose temperature is 300°K . Assume a wavelength of 0.5μ for the radiation.

SEC. 8-11]

D. Collision Broadening. The time between collisions of other atoms of a gas is not a single, continuous value. The width of the collisional broadening will correspond to the "natural" lifetime of the state. It is typically a series of sharp lines.

8-15. At what pressure will the Doppler broadening and Stark broadening be of the same order of magnitude for the argon source?

E. Stark Broadening. The Stark effect is a rather strong electric field causes a splitting of the spectral lines and thus produces a random nature of the spectral line. This effect is observed in the lamps—that the emission lines are split.

8-11. Conclusion

The material discussed in this section is a part of our understanding of the structure of the atom. Most of the phenomena discussed here are sufficiently advanced for the present state of our knowledge since our present understanding of the structure, rather than the most important one, is the feature of the electron of the Schrodinger equation, which is purely mathematical and nonrelativistic situations which involve individual particles. Furthermore, we should have no means limited to a single particle, but rather a complete system.

D. Collision Broadening. If the lifetime of a state is long compared to the time between successive collisions of the radiating atom with other atoms of a gaseous source, the atom may be disturbed sufficiently by the collisions that the successive "pieces" of the emitted photon do not form a single, coherent wave train. In this case the observed line breadth will correspond more nearly to the time between collisions than to the "natural" lifetime of the state, since the entire photon will effectively be a series of shorter, independent wave trains.

EXERCISE

8-15. At what pressure in centimeters of mercury should collision broadening and Doppler broadening become comparable in magnitude for the argon source of the previous problem?

E. Stark Broadening. In electric-discharge tubes, particularly those operating at high pressure and high voltage, an atom finds itself in the rather strong electric field due to a neighboring ionized atom. This electric field causes a perturbation of the energy levels of the radiating atom by the Stark effect (the electric analogue of the Zeeman effect) and thus produces a shift in the frequency of a given transition. The random nature of the situation leads to an average broadening of the spectral line. This effect can be so strong—as in high-pressure mercury lamps—that the emitted spectrum appears almost continuous.

8-11. Conclusion

The material discussed in this chapter may be regarded as the culmination of our understanding of the electronic structure of individual atoms. Most of the phenomena that have been treated here are actually in a sufficiently advanced state of development that they no longer merit great experimental or theoretical effort on the part of the physicist, but since our present objective is to examine what *is known* about atomic structure, rather than what is *not known*, these subjects are actually the most important ones for our purposes. It can be said that *every known feature of the electronic structure of atoms finds an interpretation in terms of the Schrodinger theory whose quantitative validity is limited only by purely mathematical difficulties or by the admitted limitation of the theory to nonrelativistic situations.* In view of the tremendous range of phenomena which involve individual atoms, this statement is a strong one indeed. Furthermore, we shall next find that the applicability of the theory is by no means limited to individual atoms but that it also provides an extraordinarily complete interpretation of chemical phenomena as well.

REFERENCES

- Herzberg, G.: "Atomic Spectra and Atomic Structure," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1937.
- Pauling, L., and E. B. Wilson, Jr.: "Introduction to Quantum Mechanics," McGraw-Hill Book Company, Inc., New York, 1935.
- Rojanski, V.: "Introductory Quantum Mechanics," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1938.
- Schiff, L. I.: "Quantum Mechanics," 2d ed., International Series in Pure and Applied Physics, McGraw-Hill Book Company, Inc., New York, 1955.
- White, H. E.: "Introduction to Atomic Spectra," International Series in Pure and Applied Physics, McGraw-Hill Book Company, Inc., New York, 1934.

The following tables are very useful in the quantitative analysis of spectra:

- Moore, C. E.: "Atomic Energy Levels," National Bureau of Standards Circular No. 467, Government Printing Office, Washington 25, D.C.
- Moore, C. E.: "A Multiplet Table of Astrophysical Interest," rev. ed., Princeton University Press, Princeton N.J., 1945.

Molecula

Having examined the of atoms, we turn to logical step in our st and more complicate cated type of system properties, is that of t another to form a *mc*

The study and sys ements has been, sinc active branches of ex ties of matter were l In spite of the great of the chemical prop elementary interacti chemical relationshi introduction of the that a certain degre understanding of th elements (e.g., NaCl for the interatomic by 1910, but the *fun* and the forces acti until about 1928.

The chemical binc