way from the $6s6p$ configuration in mercury are shown in Fig. 81. This configuration, with $l = 0$ and $l = 1$, gives rise by electrostatic interaction to singlet and triplet P terms, which are then split by the spin-orbit effect into $^1P_1$ and $^3P_0$, $^3P_1$ and $^3P_2$ levels. A $7p6p$ configuration would produce 10 final levels: $^1S_0$, $^1P_1$, $^1D_2$; $^3S_1$, $^3P_0$, $^3P_1$, $^3P_2$; $^3D_1$, $^3D_2$, $^3D_3$.

All allowed transitions between two multiplets of levels, taken together, give rise to a group of spectral lines which may be called a *spectral multiplet*. The student should distinguish carefully between multiplets of levels and multiplets of lines. Often one can tell only from the context whether the word "triplet," for example, refers to three energy levels or to three lines.

125. Spacing of the LS Multiplet Levels. For the spacing of the levels in an LS multiplet, wave mechanics furnishes a simple and useful formula, which holds quite accurately so long as the entire width of the multiplet is small relative to its difference in energy from all other energy levels. The increase in the atomic energy due to the spin-orbit effect, for any one of the J levels of a given multiplet, is ΔW where

$$\Delta W = \tfrac{1}{2}B[J(J + 1) - L(L + 1) - S(S + 1)] \tag{165}$$

Here B is a constant that varies from one multiplet to another.

The relative spacing of the levels in a given multiplet is determined by the term $\tfrac{1}{2}BJ(J + 1)$. The difference between the energies of a level for J and that for $J + 1$ is the difference in the corresponding values of ΔW, or

$$W_{J+1} - W_J = \tfrac{1}{2}B[(J + 1)(J + 2) - J(J + 1)] = B(J + 1) \tag{166}$$

This equation expresses Landé's interval rule: *The energy differences between two successive J levels are proportional, in a given LS term, to the larger of the two values of J.* The rule is of great help in determining the values of J that are to be assigned to various observed levels.

According to Eq. (165), ΔW is positive for some values of J and negative for others. The weighted average of ΔW vanishes, provided each level is weighted in proportion to the number, equal to $2J + 1$, of the M states composing it. The total energy of the weighted-average level is given by the formula

$$\overline{W}_{LS} = \frac{\sum_J (2J + 1)W_J}{\sum_J (2J + 1)} \tag{167}$$

It is to such a weighted-average level that a Rydberg formula really refers when it is written without regard to the fine structure of the terms.

As an alternative, a separate Rydberg formula is sometimes written for each component of the multiplets forming a series.

Equation (165) can be arrived at by the following semiclassical argument. Draw a vector diagram representing addition of the electronic vector orbital angular momenta G_{l1}, G_{l2}, . . . into a resultant G_L, similarly of the spin momenta G_{s1}, G_{s2}, . . . into G_S, and, finally, of G_L and G_S into G_J. A case is illustrated in Fig. 80. By Eq. (153) the total spin-orbit energy is proportional to $\Sigma(k = 1 \text{ to } N)G_{lk} \cdot G_{sk}$, where N is the number of electrons involved. Now resolve each G_{lk} into components G'_{lk} and G''_{lk} respectively parallel and perpendicular to G_L, and similarly G_{sk} into G'_{sk} and G''_{sk} parallel and perpendicular to G_S. Then

Fig. 80.

$$G_{lk} \cdot G_{sk} = G'_{lk} \cdot G'_{sk} + G'_{lk} \cdot G''_{sk} + G''_{lk} \cdot G'_{sk} + G''_{lk} \cdot G''_{sk}$$

But, according to wave-mechanical theory, the components G''_{lk} and G''_{sk} are indeterminate with equal probability for all directions. It is as if the whole G_l figure were rigid and precessing at a uniform rate about G_L, and the G_s figure precessing similarly but at a different rate about G_S. In such a motion the last three terms of the last equation would average zero; let them therefore be dropped. We can then write

$$G_{lk} \cdot G_{sk} = G'_{lk} \cdot G'_{sk} = G'_{lk}G'_{sk} \cos(G_L,G_S)$$

where $\cos(G_L,G_S)$ is the angle between the directions of G_L and G_S. Thus the spin-orbit energy is proportional to $(\Sigma G'_{lk}G'_{sk}) \cos(G_L,G_S)$ and so, for given L and S but different values of J, to $\cos(G_L,G_S)$ itself. But by geometry,

$$\cos(G_L,G_S) = \frac{1}{G_L G_S}(G_L{}^2 + G_S{}^2 - G_J{}^2)$$

$$= \frac{1}{G_L G_S}\frac{h^2}{4\pi^2}[L(L + 1) + S(S + 1) - J(J + 1)]$$

Here G_L, G_S, G_J stand for the magnitudes of the vectors, and the wave-mechanical values of $G_L{}^2$, $G_S{}^2$, and $G_J{}^2$ have been inserted. Since $G_L G_S$ is independent of J, Eq. (165) follows.

Many examples of LS coupling could be described. We have space in this book for only one or two.

126. The Arc Spectrum of Mercury. The familiar arc spectrum of mercury presents spectroscopic features of great interest. The principal levels and many of the lines are shown in the usual way in Fig. 81, wavelengths being given in angstroms. The levels that are considered to form
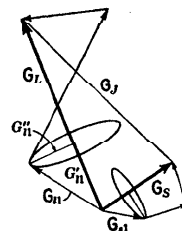
a sequence are placed under each other, with an appropriate spectroscopic designation at the top.

The levels fall into two classes: singlets, and levels that naturally group themselves into triplets, although in the case of the higher levels the sep-

FIG. 81. The most important energy levels and spectral lines for the neutral mercury atom.

aration is too small to be shown in the diagram. Thus the spectrum evidently presents a fair example of LS coupling for two electrons. A number of intercombination lines, between singlet and triplet terms, are found, however, so that the LS coupling is not perfect in mercury.

Evidence from the theory of the periodic table indicates that mercury should have two electrons outside five completed shells. It is assumed

that these electrons normally form the closed subshell $6s^2$ but that in those excited atomic states which are represented in the diagram one of these electrons is displaced into an electronic state of higher energy. Since one electronic l is thus always 0, the value of L is always equal to that of the other l. Thus each electronic configuration furnishes at most two LS terms, with $S = 0$ or 1. The configuration in the normal state of the atom, $6s6s$, gives only one term, and, in fact, only one level, with $L = S = J = 0$; thus the normal state of the mercury atom is a $^1S_0$ state. In four of the most important terms, viz., $6s6p$ ^1P, $6s6p$ ^3P, $6s6d$ ^1D, and $6s6d$ ^3D, the mere change of an electronic l with no change in n results in a comparatively large increment of atomic energy.

The intercombination line, $6s6p$ $^3P_1 \rightarrow 6s^2$ $^1S_0$, $\lambda = 2,536.52$, is one of the principal ultraviolet lines in the mercury spectrum. Its strength, however, is not necessarily an indication of a high transition probability between these levels. It is more likely that the strength of this line is due to a piling up of atoms in the $6s6p$ $^3P_1$ level. As the atoms are thrown into this state following collisions with electrons in the arc, or drop into it from higher levels, they have nowhere else to go, therefore they accumulate until through sheer numbers they are able to leave as fast as they enter. It is somewhat like water piling up in a pool until its depth becomes great enough to force a sufficiently rapid discharge through a small drain.

Atoms must accumulate also, of course, in the $^3P_2$ and $^3P_0$ levels of the $6s6p$ configuration. From these levels they cannot pass by a radiative jump to the normal state, for $^3P_2 \rightarrow$ $^1S_0$ would mean $\Delta J = 2$, and $^3P_0 \rightarrow$ $^1S_0$ would mean a jump from $J = 0$ to $J = 0$, both of which are forbidden by the selection rules for J. Levels lying above the normal state out of which radiative transitions are impossible are called "metastable" levels. An atom can stay in such a level for a long time if it is not disturbed by outside influences. It may eventually be brought back into the normal state, however, by a "collision of the second kind" (cf. Sec. 87c), and it is presumably in this manner that the atoms in the $^3P_2$ and $^3P_0$ levels are eventually returned to their normal state.

Contrary to the selection rule for S, that for L is pretty well obeyed. With values of L assigned as in the diagram, S terms combine only with P terms, P with S and D, and so on. However, a few weak lines, not shown on the diagram, have been observed corresponding to $\Delta L = 2$. All the transitions shown in Fig. 81 are in harmony with the selection rule for configurations. Only one electron changes its n and l, and always $\Delta l = +1$.

The spectral lines can be grouped into series, if desired. Thus, within the singlet system, all lines ending on the lowest $^1S_0$ level form the singlet principal series. Only these and the line $\lambda = 2,536$ A can be observed in

absorption in mercury vapor. Of the lines ending on the lowest ^1P level, those originating from ^1S terms form a sharp series, those originating from ^1D terms, a diffuse series, just as in sodium; and so on. Similar series can be picked out within the triplet system. It is really not very interesting to group the lines of such a complex spectrum into series, however, especially when the "fine structure" is as coarse as it is in the mercury spectrum. Thus the great spectral sextet of ultraviolet lines, $\lambda = 2,967$ to $\lambda = 3,663$, from the lowest ^3D to the lowest ^3P term, would constitute together the first "line" of the triplet diffuse series. The student will recognize the lines $^1D_2 \rightarrow {}^1P_1$ (λ 5,791), $^3S_1 \rightarrow {}^3P_2$ (λ 5,461), and $^3S_1 \rightarrow {}^3P_1$ (λ 4,358) as the familiar yellow, green, and blue lines emitted from the mercury arc.

It may also happen that, when the atom is excited, *both* valence electrons are displaced into higher electronic states. A few levels ascribed to the $6p^2$ configuration have been discovered.

Among other neutral atoms which have spectra similar to that of mercury may be mentioned helium; then the alkaline earths, beryllium, magnesium, calcium, strontium, and barium; and the close relatives of mercury, zinc and cadmium. Ions with similar electronic exteriors are C^{++}, Al^+, Si^{++}, Pb^{++} (the number of plus signs indicating the number of positive charges on the ion). Such atoms are called isoelectronic.

A second subclass of atoms with two optically active electrons is formed by those which, in their normal states, contain two s and two p valence electrons. In such cases the two s electrons usually (but not always) stay put, only the two p electrons being active. Examples of such atoms are neutral carbon, silicon, germanium, tin, and lead. Furthermore, certain observed spectra of the same type have been ascribed to singly (positively) ionized atoms of nitrogen, phosphorus, and bismuth.

127. Equivalent Electrons. Hitherto, it has been assumed that all the electrons in a configuration have either different n's or different l's. When two electrons have the same n and also the same l, they are called *equivalent electrons*. In configurations containing equivalent electrons, such as $5s^2$ or $5s7p^3$, certain LS terms that might otherwise occur are excluded through the operation of the exclusion principle.

Consider, for example, the simple configuration $1s^2$ in helium, or $6s^2$ in mercury. Four different combinations of the $n l \lambda \mu$ electronic states can be made for the two electrons; these may be indicated, in an obvious notation, as follows:

$$(n00\tfrac{1}{2},\ n00\tfrac{1}{2}) \qquad (n00\tfrac{1}{2},\ n00 - \tfrac{1}{2})$$
$$(n00 - \tfrac{1}{2},\ n00\tfrac{1}{2}) \qquad (n00 - \tfrac{1}{2},\ n00 - \tfrac{1}{2})$$

where $n = 1$ for helium or $n = 6$ for mercury. All these states have $l = 0$. Since the total angular momentum is the sum of the orbital and

spin momenta, the first and last of the four combinations suggest atomic states with $M = 1$ or -1, and hence, with $J = 1$; but these particular combinations, in which both electrons are in the same electronic state, are ruled out by the exclusion principle. Furthermore, the other two combinations differ only in that the two electrons exchange quantum states, and according to another aspect of the exclusion principle, as stated in Sec. 107, it makes no difference which electron is in which state; thus *each combination* of $n l \lambda \mu$'s, regardless of the order of these numbers, furnishes just one quantum state for the atom as a whole. Hence we obtain out of the configuration under discussion a single atomic state, represented in wave mechanics by a single wave function ψ. This must be a $^1S_0$ state, with $L = S = M = J = 0$. The $^3S_1$ set of three states, with $M = 1$, 0, or -1, is missing.

The same kind of reduction occurs, in particular, for any closed subshell. When so many electrons are present with given values of n and of l that, in assigning them to different electronic states, every allowed value of λ and μ must be used, only a single combination of electronic states is possible, and it can lead to only a single atomic state. This is necessarily a state with $J = 0$, since any other value of J requires the existence of several atomic states with different values of M. Thus atoms whose electronic exterior is formed of closed subshells are necessarily in a $^1S_0$ state.

In the simple example just discussed, the reduction in the number of states happens to be in accord with the predictions of the vector diagram for LS coupling. In more complicated cases, some of the LS terms that are predicted by the diagram are themselves missing. General rules can be given for determining which states are allowed for any given configuration containing equivalent electrons.[1] All the J levels belonging to a given LS term always appear or drop out together.

128. Coupling of the jj Type. The validity of LS coupling is limited to atoms that are not too heavy. As the nuclear charge increases, the spin-orbit effects become rapidly larger; as a consequence, the J levels tend less and less to group themselves into recognizable LS multiplets and the selection rules for L and S fail more and more. Finally, in very heavy atoms the spin-orbit effects may predominate over the residual electrostatic interaction to such an extent that an approximation occurs to the other type of coupling mentioned in Sec. 122, known as "jj coupling."

In the zero-order stage of perturbation theory, let the electrostatic interaction of the electrons be ignored, except in so far as allowance is made for its average effect as represented in the central field. Each electron can be assumed to occupy one of the $n l j m$ states described in Sec. 118. A quantum state for the atom is then specified by assigning

[1] H. E. White, "Introduction to Atomic Spectra," 1934.