

Fig. 55. Energy Level Diagram for C I. The unobserved  $3p\ ^1S$  term is indicated with a dotted line.

**Selection Rules** In the case of *LS* coupling, the selection rules that govern allowed transition for dipole radiation are the following:

$$\Delta L = 0, \pm 1$$

$$\Delta S = 0$$

$$\Delta J = 0, \pm 1, (J = 0 \rightarrow J = 0 \text{ forbidden})$$

In all cases, the symbol  $\Delta$  means the difference between the corresponding quantum numbers of the initial and final states of the transition.

**Parity** In addition to the above selection rules, there is another important rule involving a concept known as *parity*. The parity of an atomic state can be even or odd. This is determined by the sum of the *l*-values of the individual electrons. If the sum is even (odd), the parity is even (odd). For example, consider the states of a two-electron atom. If one electron is an *s* electron ( $l_1 = 0$ ) and the other is a *p* electron ( $l_2 = 1$ ), then  $l_1 + l_2 = 1$ , hence all *sp* states are of odd parity. Similarly, all *sd* states are of even parity, and so forth. The following selection rule holds for electric dipole radiation from transitions between two states:

$$\left. \begin{array}{l} \text{even} \leftrightarrow \text{odd (allowed)} \\ \text{odd} \rightarrow \text{odd} \\ \text{even} \rightarrow \text{even} \end{array} \right\} \text{(forbidden)}$$

In other words the parity of the final state must be different from the parity of the initial state.

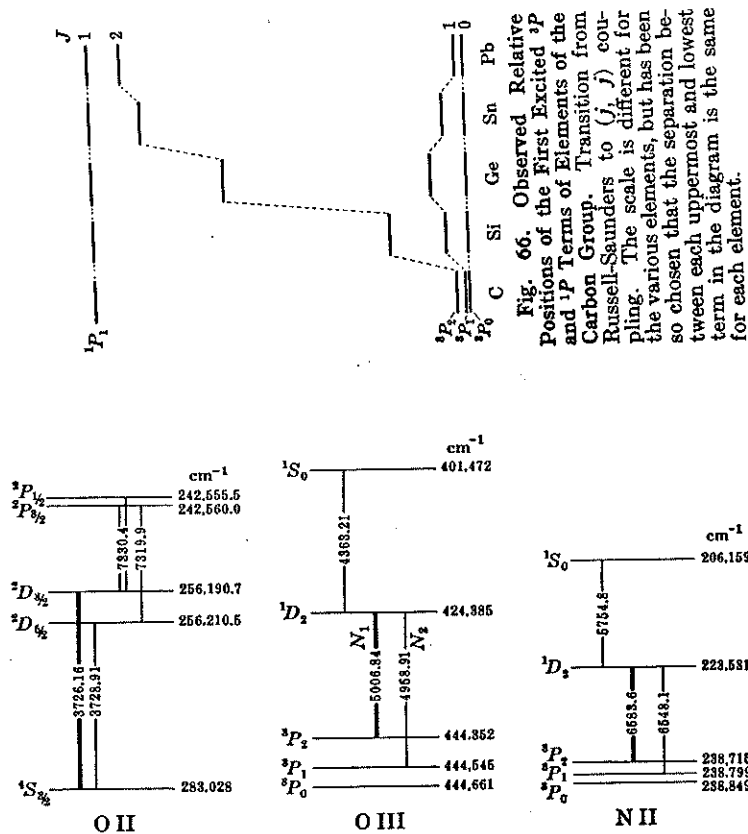


Fig. 58. Origin of the Most Important Nebular Lines (Transitions Between the Low Terms of O II, O III, and N II). The triplet and doublet splitting is drawn to a much larger scale than the rest of the figure. Term values are written to the right. The O III lines, 5006.8 Å and 4958.9 Å, are the most intense nebular lines and are sometimes designated  $N_1$  and  $N_2$ .

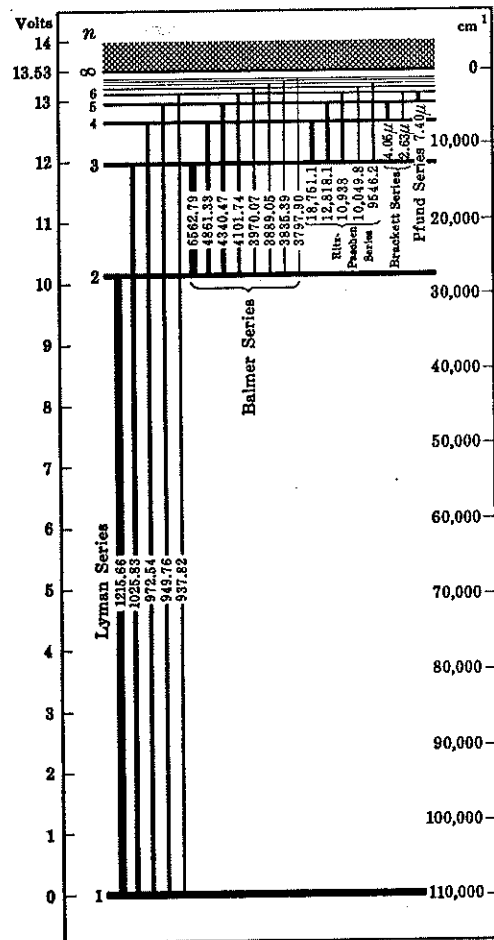


Fig. 12. Energy Level Diagram of the H Atom [Grotrian (8)].

Fig. 66. Observed Relative Positions of the First Excited  $^3P$  and  $^1P$  Terms of Elements of the Carbon Group. Transition from Russell-Saunders to ( $J, J$ ) coupling. The scale is different for the various elements, but has been chosen so that the separation between each uppermost and lowest term in the diagram is the same for each element.

TABLE 10  
TERMS OF NON-EQUIVALENT ELECTRONS

Electron Configuration	Terms
<i>s s</i>	<sup>1</sup> S, <sup>3</sup> S
<i>s p</i>	<sup>1</sup> P, <sup>3</sup> P
<i>s d</i>	<sup>1</sup> D, <sup>3</sup> D
<i>p p</i>	<sup>1</sup> S, <sup>1</sup> P, <sup>1</sup> D, <sup>3</sup> S, <sup>3</sup> P, <sup>3</sup> D
<i>p d</i>	<sup>1</sup> P, <sup>1</sup> D, <sup>1</sup> F, <sup>3</sup> P, <sup>3</sup> D, <sup>3</sup> F
<i>d d</i>	<sup>1</sup> S, <sup>1</sup> P, <sup>1</sup> D, <sup>1</sup> F, <sup>1</sup> G, <sup>3</sup> S, <sup>3</sup> P, <sup>3</sup> D, <sup>3</sup> F, <sup>3</sup> G
<i>s s s</i>	<sup>2</sup> S, <sup>2</sup> S, <sup>4</sup> S
<i>s s p</i>	<sup>2</sup> P, <sup>2</sup> P, <sup>4</sup> P
<i>s s d</i>	<sup>2</sup> D, <sup>2</sup> D, <sup>4</sup> D
<i>s p p</i>	<sup>2</sup> S, <sup>2</sup> P, <sup>2</sup> D, <sup>2</sup> S, <sup>2</sup> P, <sup>2</sup> D, <sup>4</sup> S, <sup>4</sup> P, <sup>4</sup> D
<i>s p d</i>	<sup>2</sup> P, <sup>2</sup> D, <sup>2</sup> F, <sup>2</sup> P, <sup>2</sup> D, <sup>2</sup> F, <sup>4</sup> P, <sup>4</sup> D, <sup>4</sup> F
<i>p p p</i>	<sup>2</sup> S(2), <sup>2</sup> P(6), <sup>2</sup> D(4), <sup>2</sup> F(2), <sup>4</sup> S(1), <sup>4</sup> P(3), <sup>4</sup> D(2), <sup>4</sup> F(1)
<i>p p d</i>	<sup>2</sup> S(2), <sup>2</sup> P(4), <sup>2</sup> D(6), <sup>2</sup> F(4), <sup>2</sup> G(2), <sup>4</sup> S(1), <sup>4</sup> P(2), <sup>4</sup> D(3), <sup>4</sup> F(2), <sup>4</sup> G(1)
<i>p d f</i>	<sup>2</sup> S(2), <sup>2</sup> P(4), <sup>2</sup> D(6), <sup>2</sup> F(6), <sup>2</sup> G(6), <sup>2</sup> H(4), <sup>2</sup> I(2) <sup>4</sup> S(1), <sup>4</sup> P(2), <sup>4</sup> D(3), <sup>4</sup> F(3), <sup>4</sup> G(3), <sup>4</sup> H(2), <sup>4</sup> I(1)

TABLE 11  
TERMS OF EQUIVALENT ELECTRONS

Electron Configuration	Terms
<i>s<sup>2</sup></i>	<sup>1</sup> S
<i>p<sup>2</sup></i>	<sup>1</sup> S, <sup>1</sup> D, <sup>3</sup> P
<i>p<sup>3</sup></i>	<sup>2</sup> P, <sup>2</sup> D, <sup>4</sup> S
<i>p<sup>4</sup></i>	<sup>1</sup> S, <sup>1</sup> D, <sup>3</sup> P
<i>p<sup>5</sup></i>	<sup>2</sup> P
<i>s<sup>3</sup></i>	<sup>1</sup> S
<i>d<sup>2</sup></i>	<sup>1</sup> S, <sup>1</sup> D, <sup>1</sup> G, <sup>3</sup> P, <sup>3</sup> F
<i>d<sup>3</sup></i>	<sup>2</sup> P, <sup>2</sup> D(2), <sup>2</sup> F, <sup>2</sup> G, <sup>2</sup> H, <sup>4</sup> P, <sup>4</sup> F
<i>d<sup>4</sup></i>	<sup>1</sup> S(2), <sup>1</sup> D(2), <sup>1</sup> F, <sup>1</sup> G(2), <sup>1</sup> I, <sup>3</sup> P(2), <sup>3</sup> D, <sup>3</sup> F(2), <sup>3</sup> G, <sup>3</sup> H, <sup>5</sup> D
<i>d<sup>5</sup></i>	<sup>2</sup> S, <sup>2</sup> P, <sup>2</sup> D(3), <sup>2</sup> F(2), <sup>2</sup> G(2), <sup>2</sup> H, <sup>2</sup> I, <sup>4</sup> P, <sup>4</sup> D, <sup>4</sup> F, <sup>4</sup> G, <sup>4</sup> S

Table 7.4. DESIGNATION OF STATES ACCORDING TO ORBITAL ANGULAR MOMENTUM

L:	0	1	2	3	4	5	6	7	8	· · ·
Designation	S	P	D	F	G	H	I	K	M	· · ·

Table 7.3. MULTIPLICITIES OF STATES

S	MULTIPLICITY (2S + 1)	NAME
0	1	Singlet
1/2	2	Doublet
1	3	Triplet
3/2	4	Quartet
2	5	Quintet
5/2	6	Sextet

SINGLET	TRIPLET
<sup>1</sup> P <sub>1</sub>	<sup>3</sup> P <sub>0</sub> <sup>3</sup> P <sub>1</sub> <sup>3</sup> P <sub>2</sub>
<sup>1</sup> D <sub>2</sub>	<sup>3</sup> D <sub>1</sub> <sup>3</sup> D <sub>2</sub> <sup>3</sup> D <sub>3</sub>
<sup>1</sup> F <sub>3</sub>	<sup>3</sup> F <sub>2</sub> <sup>3</sup> F <sub>3</sub> <sup>3</sup> F <sub>4</sub>

BOX 3.4  
Atomic Spectroscopy and LS Coupling

- Electrons in the inner filled subshells have, in net, a spherically symmetric distribution. The valence electrons do not; consequently, their vector angular momenta, *l* and *s*, are not individually conserved. In LS coupling, the vector sums, *L* and *S*, of the orbital and spin angular momenta of all the valence electrons are assumed to be separately conserved.
- Quantum states with aligned spin angular momenta (large values of *S*) tend to have electrons which avoid each other (like Pauli's exclusion principle). This reduces the positive potential energy associated with the mutual repulsion of electrons. Thus, states with large values of *S* tend to have lower energies than states with small values of *S*.
- Quantum states with aligned orbital angular momenta (large values of *L*) correspond classically to electrons which revolve in the same sense about the nucleus. This again reduces the interaction between the electrons. Thus, states with large values of *L* tend to have lower energies than states with small values of *L*.
- The orientation of the spins of the electrons relative to their orbital angular momenta (characterized by the magnitude *J* of the total angular momentum *J* = *L* + *S*) leads to "fine structure." A spinning electron acts like a bar magnet, and can interact with the magnetic field associated with the motion of the orbiting electrons. The result is that spin-orbit states which are aligned (large values of *J*) tend to have higher energies than misaligned spin-orbit states (small values of *J*). A similar phenomenon involving the interaction of the spin of the electron with the spin of the nucleus is responsible for the "hyperfine structure" that gives rise to the 21-cm line of atomic hydrogen (Chapter 11).

Fig. 28. Energy Level Diagram for Potassium [Grotrian (8)]. Here *m* is the empirical order number of the terms (see p. 55). For S terms, the true principal quantum number of the emission electron (p. 62) is 3 greater than *m*; for P terms, it is 2 greater; for D and F terms, it is equal to *m*.

