

# QUANTUM MECHANICS

THIRD EDITION

**LEONARD I. SCHIFF**

Professor of Physics  
Stanford University

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## PERIODIC SYSTEM OF THE ELEMENTS

According to the Pauli exclusion principle (see the discussion of anti-symmetric wave functions in Sec. 40), not more than one electron in an atom can have a particular set of values of the four quantum numbers given above. As  $Z$  increases, electrons fill the one-electron states of lowest energy in succession; the ground state of an atom in the central-field approximation is that in which there are no unfilled electron states that have lower energy than any that are occupied. Because of the degeneracy with respect to  $m_l$  and  $m_s$ , there can be as many as  $2(2l + 1)$  electrons with the same energy in a shell that is specified by  $n$  and  $l$ . It is apparent, then, that the ground-state configuration of the electrons in an atom can be described by specifying the number of electrons in each shell. In the central-field approximation, all shells that contain any electrons are full except perhaps that which has the highest energy.

The chemical properties of atoms are determined for the most part by the least tightly bound, or *valence*, electrons, which are in the shell of highest energy. The most important factors are the number of occupied and unoccupied electron states in this shell, and the energy interval between this and the next higher (empty) shell. For example, an atom tends to be chemically inert if its highest shell is full and there is an appreciable energy gap to the next higher shell, since then electrons are not readily shared with other atoms to form a molecule. The quasi-periodic recurrence of similar highest-shell structures as  $Z$  increases is responsible for the *periodic system* of the chemical elements.

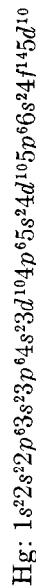
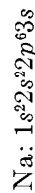
In the usual spectroscopic notation, the  $n$  value of a shell is given as a number, the  $l$  value as a letter, and the number of electrons in the shell as a numerical superscript. The letter code for  $l$  and the maximum number  $2(2l + 1)$  of electrons in a shell are as follows:

$$l = 0, 1, 2, 3, 4, 5, \dots$$

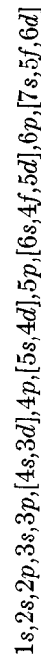
$$s, p, d, f, g, h, \dots$$

$$2(2l + 1) = 2, 6, 10, 14, 18, 22, \dots$$

For example, the ground-state configurations of sodium ( $Z = 11$ ) and of mercury ( $Z = 80$ ) are



The ground-state configurations of many of the elements can be written down simply from a knowledge of the order in which the energies of the shells increase. This order can be inferred from spectroscopic evidence and is as follows:



The brackets enclose shells that have so nearly the same energy that they are not always filled in sequence. These shell energies are close together because the increase in  $n$  and the decrease in  $l$  tend to compensate each other; thus the  $4s$  state, which has a higher energy than the  $3d$  state in hydrogen, is depressed by the penetration caused by its low angular momentum. The  $s$  shell in each bracket is always filled first, although it can lose one or both of its electrons as the other shells in the bracket fill up. Apart from the brackets, there are no deviations from the indicated order of filling.

Table 2 gives the ground-state configurations of each of the elements. An atom contains all the full shells that occur above and to the left of its position in the table. Since the number of  $s$  electrons varies as each  $d$  shell fills, the  $d$  columns are subdivided to show the number of  $s$  electrons. The two groups of atoms that have a partially full  $f$  shell in their ground-state configurations fit in at \* (rare earths) and at † (heaviest elements). The first group has the  $6s$  shell full and the second has the  $7s$  shell full; the distribution of electrons in  $d$  and  $f$  shells for each group is shown below the main table.

A few of the periodicities are worth explicit mention. The first electron to go into each  $s$  shell beyond  $1s$  gives an alkali, and the elements just before each of these (full  $1s$  shell or a full  $p$  shell) are rare gases. The elements with the same number of electrons in a  $p$  shell have similar chemical properties; this is especially striking in the case of the halogens (one electron short of a full  $p$  shell). The elements with full  $2s$  and  $3s$  shells (Be and Mg) that are followed by  $p$  shells have somewhat different properties from the alkaline earths, which have full  $s$  shells followed by  $d$  or  $f$  shells. The filling of the  $4s, 3d$  shells gives elements somewhat similar to those arising from the filling of the  $5s, 4d$  shells. The elements that correspond to full bracketed shells (Zn, Cd, and Hg) are quite similar, as are the noble metals (Cu, Ag, and Au) in which an  $s$  electron is missing from the full bracketed shells.

## THOMAS-FERMI STATISTICAL MODEL

We now turn to the first of the problems associated with the central-field approximation. Two methods have been used for the determination of the potential energy  $V(r)$ . The first of these, due to Thomas<sup>1</sup> and Fermi,<sup>2</sup> is discussed here, and the second, due to Hartree, is taken up later. The *Thomas-Fermi statistical model* assumes that  $V(r)$  varies slowly enough in an electron wavelength so that many electrons can be localized within a volume over which the potential changes by a small fraction of itself. The electrons can then be treated by statistical mechanics and obey the

<sup>1</sup> L. H. Thomas, *Proc. Cambridge Phil. Soc.* **23**, 542 (1927).

<sup>2</sup> E. Fermi, *Z. Physik* **48**, 73 (1928).

Table 2 Ground-state electron configurations of the elements<sup>1</sup>

	s	s <sup>2</sup>	p	p <sup>2</sup>	p <sup>3</sup>	p <sup>4</sup>	p <sup>5</sup>	p <sup>6</sup>	d	d <sup>2</sup>	d <sup>3</sup>	d <sup>4</sup>	d <sup>5</sup>	d <sup>6</sup>	d <sup>7</sup>	d <sup>8</sup>	d <sup>9</sup>	d <sup>10</sup>	
1s	H 1	He 2																	
2s	Li 3	Be 4																	
2p			B 5	C 6	N 7	O 8	F 9	Ne 10											
3s	Na 11	Mg 12																	
3p			Al 13	Si 14	P 15	S 16	Cl 17	A 18											
4s, 3d	K 19	Ca 20																	
4p			Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36											
5s, 4d	Rb 37	Sr 38																	
5p			In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54											
6s, 4f, 3d	Cs 55	Ba 56																	
6p			Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86											
7s, 5f, 6d	Fa 87	Ra 88																	

* 4f:	Ce 58	Pr 59							Eu 63	Gd 64									
5d																			
6d																			
† 5f:																			

<sup>1</sup> This table is taken from Condon and Shortley, *op. cit.*, p. 333, with recent assignments from G. W. C. Kaye and T. H. Laby, "Tables of Physical and Chemical Constants," pp. 108-109 (Longmans, London, 1966). The heaviest elements, not included in the table, are americium (Am, 95), curium (Cm, 96), berkelium (Bk, 97), californium (Cf, 98), einsteinium (Es, 99), fermium (Fm, 100), mendelevium (Md, 101), nobelium (No, 102), and lawrencium (Lr, 103).

Fermi-Dirac statistics mentioned in Sec. 40. At normal temperatures, the thermal energy  $kT$  is very small in comparison with  $V(r)$  everywhere except at the edge of the atom, where the chance of finding an electron is small. In this case, the Fermi-Dirac statistics requires that the electron states fill in order of increasing energy, as assumed above. The difference between the present treatment and the more general discussion given earlier in this section lies in the additional assumption that  $V(r)$  is sensibly constant over a region in which many electrons can be localized.

The number of electron states in a cube of edge length  $L$  at the walls of which the wave functions obey periodic boundary conditions was computed in Sec. 11 to be  $(L/2\pi)^3 dk_x dk_y dk_z$ . This must be multiplied by 2 to take account of the two possible spin states; then the number of states for which the magnitude of the momentum  $\mathbf{p} = \hbar\mathbf{k}$  is less than or equal to  $p_0$  is

$$2 \left( \frac{L}{2\pi} \right)^3 \int_0^{p_0/\hbar} \int_0^\pi k^2 dk \sin \theta d\theta d\phi = \frac{p_0^3 L^3}{3\pi^2 \hbar^3}$$

If all these states are occupied, the number of electrons per unit volume whose kinetic energy does not exceed  $p_0^2/2m$  is  $p_0^3/3\pi^2 \hbar^3$ . Now the maximum kinetic energy at any distance  $r$  from the nucleus is  $-V(r)$ , since otherwise electrons would escape from the atom. We thus obtain a relation between the volume density of electrons,  $n(r)$ , and the potential energy:

$$n(r) = \frac{[-2mV(r)]^{3/2}}{3\pi^2 \hbar^3} \tag{47.1}$$

The electrostatic potential  $-V(r)/e$  is also determined by Poisson's equation in terms of the charge density  $-en(r)$ :

$$-\frac{1}{e} \nabla^2 V = -\frac{1}{er^2} \frac{d}{dr} \left( r^2 \frac{dV}{dr} \right) = 4\pi en(r) \tag{47.2}$$

Equations (47.1) and (47.2) are two simultaneous equations for  $n$  and  $V$ . The boundary conditions on the solutions can be expressed in terms of  $V$  alone for a neutral atom of atomic number  $Z$ . As  $r \rightarrow 0$ , the leading term in the potential energy must be due to the nucleus, so that  $V(r) \rightarrow -Ze^2/r$ . As  $r \rightarrow \infty$ , there must be no net charge inside the sphere of radius  $r$ , so that  $V$  falls off more rapidly than  $1/r$ , and  $rV(r) \rightarrow 0$ . The boundary condition at infinity is different from that assumed earlier in this section, where  $V$  was taken to have the asymptotic form  $-e^2/r$ . The  $V$  discussed earlier is the potential experienced by one of the atomic electrons, whereas the Thomas-Fermi potential is that experienced by an infinitesimal test charge. The difference between the two potentials emphasizes the statistical nature of the approximation made by Thomas and Fermi.

The solution for  $V$  is exact in the limit in which  $m$  becomes infinite and  $e$  becomes zero in such a way that  $m^2e^4$  remains constant; then the electron wavelength becomes zero, and the density of particles becomes infinite. In this limit the potential is constant over many wavelengths, and enough particles are present so that statistical mechanics can be applied.

**EVALUATION OF THE POTENTIAL**

Elimination of  $n_i(r)$  from Eqs. (47.1) and (47.2) leads to an equation for  $-V(r)$

$$\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{d(-V)}{dr} \right] = \frac{4e^2[-2mV(r)]^{\frac{1}{2}}}{3\pi\hbar^3} \tag{47.3}$$

Equation (47.3) and the boundary conditions given above are conveniently expressed in a dimensionless form in which  $Z, E, m,$  and  $\hbar$  appear only in scale factors. We put

$$V(r) = -\frac{Ze^2}{r} \chi \quad r = b\alpha$$

$$b = \frac{1}{2} \left( \frac{3\pi}{4} \right)^{\frac{1}{3}} \frac{\hbar^2}{me^2 Z^{\frac{1}{3}}} = \frac{0.885a_0}{Z^{\frac{1}{3}}} \tag{47.4}$$

where  $a_0 = \hbar^2/me^2$ . With these substitutions, (47.3) becomes

$$\alpha^3 \frac{d^2\chi}{d\alpha^2} = \chi^{\frac{1}{2}} \quad \chi = 1 \text{ at } \alpha = 0 \quad \chi = 0 \text{ at } \alpha = \infty \tag{47.5}$$

The most accurate solution of Eq. (47.5) was computed by Bush and Caldwell<sup>1</sup> with the help of the original differential analyzer, and is expressed in the form of a numerical table.

Equations (47.4) show that the "radius" of an atom is inversely proportional to the cube root of the atomic number, if this radius is interpreted to be that of a sphere that encloses a fixed fraction of all the electrons (see Prob. 1). These equations can also be used to show that the Thomas-Fermi approximation improves with increasing  $Z$ . The potential at the atomic radius is proportional to  $Z^{\frac{1}{3}}$ , so that a typical electron wavelength is proportional to  $Z^{-\frac{1}{3}}$ . The distance over which the potential changes by a definite fraction of itself is proportional to the atomic radius, or  $Z^{-\frac{1}{3}}$ . Thus the fractional change of the potential in an electron wavelength is proportional to  $Z^{-\frac{1}{3}}$  and decreases with increasing  $Z$ . Moreover, since the number of electrons is equal to  $Z$ , the use of the statistical method is better justified as  $Z$  increases.

<sup>1</sup> V. Bush and S. H. Caldwell, *Phys. Rev.* **38**, 1898 (1931).

**HARTREE'S SELF-CONSISTENT FIELDS**

The second method for obtaining a central field is due to Hartree.<sup>1</sup> This model assumes that each electron moves in a central field that can be calculated from the nuclear potential and the wave functions of all the other electrons, by assuming that the charge density associated with an electron is  $-e$  times its position probability density. The Schrödinger equation is solved for each electron in its own central field, and the resulting wave functions made consistent with the fields from which they are calculated. Thus the  $k$ th electron is described by a normalized wave function  $u_k(\mathbf{r}_k)$  that is a solution of the equation

$$\left[ -\frac{\hbar^2}{2m} \nabla_k^2 - \frac{Ze^2}{r_k} + \sum_{j \neq k} \int |u_j(\mathbf{r}_j)|^2 \frac{e^2}{r_{jk}} \right] u_k(\mathbf{r}_k) = \epsilon_k u_k(\mathbf{r}_k) \tag{47.6}$$

where  $r_{jk} = |\mathbf{r}_j - \mathbf{r}_k|$ . If there are  $Z$  electrons in the atom, (47.6) constitutes a set of  $Z$  simultaneous nonlinear integrodifferential equations for the  $Z$  functions  $u_k(\mathbf{r}_k)$ . It is therefore not feasible to solve these equations directly, and Hartree used a method of successive approximations.

A potential energy that approximately represents the second and third terms in (47.6) is assumed, electron wave functions computed, and new potentials for each electron found from these wave functions. This process is continued until the potentials are self-consistent to a high order of accuracy. The principal approximation made is the averaging of the potential energy given as the third term in (47.6) over the angles of  $\mathbf{r}_k$  to make it spherically symmetric. The solutions of (47.6) can then be expressed as products of radial functions and spherical harmonics. A further simplification is made so that the  $2(2l + 1)$  or fewer electrons in a shell all move in the same potential and have the same radial wave function.

It is apparent that the Hartree approximation neglects correlations between the positions of the electrons, since the entire wave function for all the electrons is assumed to be a simple product of one-electron functions

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z) = u_1(\mathbf{r}_1)u_2(\mathbf{r}_2) \cdots u_Z(\mathbf{r}_Z) \tag{47.7}$$

It is also clear from (47.7) that antisymmetrized wave functions are not employed. The antisymmetry is considered only insofar as the quantum numbers of the one-electron states  $u_k$  are chosen in agreement with the exclusion principle.<sup>2</sup>

<sup>1</sup> D. R. Hartree, *Proc. Cambridge Phil. Soc.* **24**, 111 (1928).

<sup>2</sup> Antisymmetrization is taken into account in the Hartree-Fock method; see, for example, Slater, *op. cit.*, chap. 17.

## CONNECTION WITH THE VARIATION METHOD

We now show that the Hartree approximation results from an optimum variation calculation with the trial function (47.7).<sup>1</sup> The wave equation with inclusion of interelectronic interactions but neglect of spin-orbit terms (see below) is

$$H\psi = E\psi$$

$$H = \sum_k \left( -\frac{\hbar^2}{2m} \nabla_k^2 - \frac{Ze^2}{r_k} \right) + \sum_{j>k} \sum_{r_{jk}} \frac{e^2}{r_{jk}} \quad (47.8)$$

where  $j > k$  implies a double summation over all different pairs of indices  $j$  and  $k$ . We wish to minimize the expectation value of  $H$ .

From (47.7) and (47.8) we obtain

$$\int \dots \int \psi^* H \psi d^3r_1 \dots d^3r_Z$$

$$= \sum_k \int u_k^*(\mathbf{r}_k) \left( -\frac{\hbar^2}{2m} \nabla_k^2 - \frac{Ze^2}{r_k} \right) u_k(\mathbf{r}_k) d^3r_k$$

$$+ \sum_{j>k} \int \int u_j^*(\mathbf{r}_j) u_k^*(\mathbf{r}_k) \frac{e^2}{r_{jk}} u_j(\mathbf{r}_j) u_k(\mathbf{r}_k) d^3r_j d^3r_k \quad (47.9)$$

since the  $u_k$  are normalized. The optimum  $\psi$  is obtained by varying each of the  $u_k$  separately to minimize (47.9). The only dependence of (47.9) on a particular one-electron function  $u_k$  is through the terms

$$\int u_k^*(\mathbf{r}_k) \left( -\frac{\hbar^2}{2m} \nabla_k^2 - \frac{Ze^2}{r_k} \right) u_k(\mathbf{r}_k) d^3r_k$$

$$+ \sum_{j \neq k} \int \int u_j^*(\mathbf{r}_j) u_k^*(\mathbf{r}_k) \frac{e^2}{r_{jk}} u_j(\mathbf{r}_j) u_k(\mathbf{r}_k) d^3r_j d^3r_k$$

$$= \int u_k^*(\mathbf{r}_k) H_k u_k(\mathbf{r}_k) d^3r_k \quad (47.10)$$

The integral in (47.10) is the expectation value of the operator  $H_k$  for the function  $u_k$ . From the discussion of Sec. 32, it follows that this is a minimum when  $u_k$  is an eigenfunction of  $H_k$  that corresponds to its lowest eigenvalue  $\epsilon_k$ .

$$H_k u_k = \epsilon_k u_k \quad (47.11)$$

Since Eqs. (47.11) and (47.6) are identical, we see that the Hartree wave

<sup>1</sup> J. C. Slater, *Phys. Rev.* **35**, 210 (1930); V. Fock, *Z. Physik* **61**, 126 (1930).

functions are the best from the point of view of the variation method that can be written in the form (47.7).

The energy associated with this wave function is just the integral (47.9), which can be written with the help of (47.6)

$$\int \dots \int \psi^* H \psi d^3r_1 \dots d^3r_Z = \sum_k \epsilon_k$$

$$- \sum_{j>k} \int \int |u_j(\mathbf{r}_j)|^2 |u_k(\mathbf{r}_k)|^2 \frac{e^2}{r_{jk}} d^3r_j d^3r_k \quad (47.12)$$

The electrostatic interaction terms between electrons are counted twice in the summation over  $\epsilon_k$  and so have to be subtracted out to give (47.12). Thus the energy of the atom is not just the sum of the  $\epsilon_k$ , although each  $\epsilon_k$  is roughly the energy of removal of the  $k$ th electron. This last is not strictly true, since the removal of an electron alters the self-consistent fields and hence the wave functions and  $\epsilon_k$ 's for the remaining electrons. However,  $\epsilon_k$  is found to be an especially good approximation to the energy of removal in the case of an inner electron (x-ray level).

## CORRECTIONS TO THE CENTRAL-FIELD APPROXIMATION

We now turn to the second problem mentioned at the beginning of this section, the correction of the approximate results obtained from the central field. Two terms are omitted in the central-field approximation: the difference between the actual electrostatic interaction between electrons and the average interaction that is included in the central field, and the spin-orbit energy. The latter is an interaction energy between the spin and the orbital motion of each electron and has the form

$$\sum_k \xi(r_k) \mathbf{L}_k \cdot \mathbf{S}_k \quad (47.13)$$

Here,  $\mathbf{L}_k$  is the orbital angular momentum operator  $\mathbf{r}_k \times \mathbf{p}_k$  of the  $k$ th electron and has the properties of the  $\mathbf{J}$  operator introduced in Sec. 27; the eigenvalues of  $\mathbf{L}_k^2$  and  $L_{kz}$  are given in terms of the quantum numbers  $l$  and  $m_l$  for the  $k$ th electron as  $l(l+1)\hbar^2$  and  $m_l\hbar$ , respectively.  $\mathbf{S}_k$  is the spin angular momentum  $\frac{1}{2}\hbar\delta_k$  of the  $k$ th electron that was introduced in Sec. 41. The function  $\xi(r)$  is given by<sup>1</sup>

$$\xi(r) = \frac{1}{2m^2c^2} \frac{dV}{dr}$$

in terms of the central-field potential energy  $V(r)$ .

<sup>1</sup> L. H. Thomas, *Nature* **117**, 514 (1926). This energy is a consequence of relativity and is derived as such in Chap. 13. It was first obtained from the precession of the spin axis of the electron, part of which is of electromagnetic origin (Larmor precession) and part of which comes from relativistic kinematics (Thomas precession).

In considering the effects of these terms, we shall assume that the perturbed eigenfunctions, which are linear combinations of various configuration wave functions, have only negligibly small amounts of all but one configuration mixed in them. From Eq. (31.10), it is apparent that this is the case if the interconfiguration matrix elements of the perturbation are small in comparison with the energy intervals between unperturbed configuration energies.

It can be shown that the part of the summation in (47.13) that includes electrons in full shells is zero, since the function  $\xi$  is the same for all electrons in a shell and the contributions from electrons with opposite  $m_l$  and  $m_s$  cancel. Thus the electrons in full shells can be ignored and the summation extended only over the remaining electrons. The case in which there is just one electron outside full shells is of interest in connection with the ground state and low excited states of the alkali atoms; it will be discussed in some detail in the next section. For the present, we consider very briefly the more general situation, always assuming that each atomic state is based on just one configuration of the electrons.

**LS COUPLING SCHEME**

There are, in general, a number of states that belong to the same configuration and that are degenerate in the central-field approximation. These states differ in the assignment of  $m_l$  and  $m_s$ , quantum numbers to the individual electrons. The theory of complex spectra consists in determining the linear combinations of such suitably antisymmetrized wave functions that diagonalize the perturbation to first order (see Sec. 31), along with the corresponding perturbed energy levels.

The most usual situation is that in which the hitherto-neglected electrostatic terms are larger than the spin-orbit energy; this is called the *Russell-Saunders case*.<sup>1</sup> States of the same configuration can be classified as eigenfunctions of any dynamical variables that commute with the hamiltonian and hence are constants of the motion (see Sec. 24). When all perturbations are included, the only true constants of the motion are the total parity and the total angular momentum  $\mathbf{J}$  of the electrons

$$\mathbf{J} = \mathbf{L} + \mathbf{S} = \sum_k (\mathbf{L}_k + \mathbf{S}_k) \tag{47.15}$$

$\mathbf{J}$  is a constant because the angles that specify the orientation of the atom as a whole, and that are the canonically conjugate variables to the components of  $\mathbf{J}$ , do not appear in the hamiltonian of an isolated atom. When the electrostatic perturbation is included but the spin-orbit energy neglected, the same argument can be applied to show that the total orbital

<sup>1</sup> H. N. Russell and F. A. Saunders, *Astrophys. J.* **61**, 38 (1925).

angular momentum  $\mathbf{L}$  and the total spin angular momentum  $\mathbf{S}$  are separately constants of the motion. The individual  $\mathbf{S}_k$  need not be constants, even though no spin-dependent forces act in this approximation, since the use of antisymmetric wave functions couples the spins to the electrostatic energy (see the discussion of the excited states of helium in Sec. 41).

A state can be specified by the quantum numbers,  $J, L, S, M, M_L,$  and  $M_S$ , which are connected with eigenvalues of angular momentum operators through

$$\begin{aligned} J^2 &= J(J + 1)\hbar^2 & J_z &= M\hbar \\ L^2 &= L(L + 1)\hbar^2 & L_z &= M_L\hbar \\ S^2 &= S(S + 1)\hbar^2 & S_z &= M_S\hbar \end{aligned} \tag{47.16}$$

When the spin-orbit energy is neglected, the electrostatic energy separates states of different  $L$ ; in some cases, only particular  $S$  values are permitted because of the exclusion principle. Only two of the other four quantum numbers are independent, and so we can use either  $LSM_LM_S$  or  $LSJM$  to specify a state. Because of the spherical symmetry of the hamiltonian with respect to its space and spin parts separately, the energy is independent of the directional quantum numbers  $M_L$  and  $M_S$ , and there are  $(2L + 1)(2S + 1)$  degenerate states. For given  $L$  and  $S$ , the states specified by  $J$  and  $M$  are linear combinations of those specified by  $M_L$  and  $M_S$ , so that the same amount of degeneracy appears in the  $LSJM$  representation; these linear combinations can be expressed in terms of the Clebsch-Gordan coefficients discussed in Sec. 28. This is called the *LS coupling scheme*, since the individual  $L_k$  are coupled together to form the total  $L$ , and the individual  $S_k$  to form the total  $S$ .

If now the spin-orbit energy is included,  $L$  and  $S$  are no longer constants of the motion, although  $J$  and  $M$  still are. However, we assume that states of different  $L$  and  $S$  are sufficiently well separated by the electrostatic energy so that their mixing due to spin-orbit energy can be neglected. This is analogous to the earlier assumption that different configurations are sufficiently well separated by the central field so that their mixing due to the electrostatic energy can be neglected. States of different  $J$  in the  $LSJM$  representation are now split apart by the spin-orbit energy; the energy is still independent of  $M$ , so that there are  $2J + 1$  degenerate states. A Russell-Saunders state is usually written in the form  ${}^4D_{3/2}$ , where the superscript is the *multiplicity*  $2S + 1$ , the letter (now capitalized) is the  $L$  value according to the code given earlier in this section, and the subscript is the  $J$  value; in this case  $S = \frac{3}{2}, L = 2$ , and  $J = \frac{3}{2}$ . Since  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ , the triangle rule discussed at the beginning of Sec. 28 shows that  $J$  can only be one of the numbers  $L + S, L + S - 1, \dots, |L - S|$ .

## SELECTION RULES

The selection rules in the Russell-Saunders case can be obtained from the discussion of Sec. 46. Only one electron is involved in a transition, so that in an allowed transition the configuration changes through a change in one of the  $l$ 's by one unit; this also changes the parity. Since the electric dipole moment does not involve the spins, and the spin functions for different  $S$  are orthogonal (see Prob. 4),  $S$  does not change in an allowed transition. The conservation of angular momentum between atom and radiation field further requires that  $J$  and  $L$  each change by 1 or 0. Transitions between states both of which have  $J = 0$  are strictly forbidden.

Intersystem lines that join states of different multiplicity (change in  $S$ ) sometimes occur and indicate a partial breakdown of  $LS$  coupling. The very intense mercury resonance line at 2537 Å is an intersystem line:  $^3P_1 \rightarrow ^1S_0$ . This transition is allowed so far as the changes in  $J$ ,  $L$ , configuration, and parity are concerned but not as regards the change in  $S$ . The  $^3P_1$  state is partially mixed by the spin-orbit energy with a higher singlet ( $S = 0$ ) state of the same  $J$  and parity, and this makes an electric dipole transition possible.

 $jj$  COUPLING SCHEME

The opposite approximation to that involved in  $LS$  coupling assumes that the spin-orbit energy is large in comparison with the electrostatic energy. If the latter is neglected, each electron can be characterized by the quantum numbers  $n, l, j, m$  rather than  $n, l, m, m_s$ , where  $(\mathbf{L}_k + \mathbf{S}_k)^2 = j(j+1)\hbar^2$  and  $L_{kz} + S_{kz} = m\hbar$ . The electrostatic energy then splits apart states of different  $J$ .

This is called the  $jj$  coupling scheme, since the orbital and spin angular momenta of the individual electrons are coupled together to form  $j$ 's, from which the states are built up. It is mainly of interest in heavy atoms, where the large  $V(r)$  makes the spin-orbit energy (47.13) the dominant perturbation.

## 48 □ THE ALKALI ATOMS

The ground-state configuration of an alkali atom consists of a series of full shells followed by a single  $s$  electron and so is  $^2S_1/2$ . The inner rare-gas configuration is so stable that all but quite high excited states of the atom involve only the valence electron. Thus the alkalis can be treated to quite good approximation in terms of a model in which a single electron moves in a spherically symmetric noncoulomb potential energy  $V(r)$ . In this section we calculate the energy levels and the intensities of allowed transitions in the absence and presence of an external magnetic field.

## DOUBLET SEPARATION

The configuration of an alkali atom can be specified by a single pair of quantum numbers  $nl$ . Since there is only one electron, the perturbing electrostatic term mentioned in the preceding section does not appear. In the absence of external fields the hamiltonian, including the spin-orbit energy (47.13), is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r) + \xi(r)\mathbf{L} \cdot \mathbf{S} \quad (48.1)$$

where  $\xi(r)$  is given by (47.14). As in Sec. 47, we neglect the mixing of different configurations produced by the spin-orbit energy and regard this term as a perturbation that removes the  $m, m_s$  degeneracy within each configuration. The total angular momentum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  of the valence electron is a constant of the motion (see Prob. 5), so that states can be designated by  $j, m$  instead of  $m, m_s$ , where  $\mathbf{J}^2 = j(j+1)\hbar^2$  and  $J_z = m\hbar$ . The states of different  $j$  have different energies, but there is still a  $(2j+1)$ -fold degeneracy due to  $m$ . The removal of the  $m$  degeneracy by a magnetic field is discussed later in this section.

The difference in energy between states of different  $j$  is due to the  $\mathbf{L} \cdot \mathbf{S}$  term in (48.1) and can be found from its expectation value or diagonal matrix element [see Eq. (31.8)]. We have the operator relation

$$\mathbf{J}^2 = (\mathbf{L} + \mathbf{S})^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L} \cdot \mathbf{S} \quad (48.2)$$

Since  $l, j$ , and  $s$  are all good quantum numbers ( $s = \frac{1}{2}$  for one electron), Eq. (48.2) can be solved for the diagonal matrix element of  $\mathbf{L} \cdot \mathbf{S}$ :

$$\langle j|\mathbf{L} \cdot \mathbf{S}|j\rangle = \frac{1}{2}[j(j+1) - l(l+1) - \frac{3}{4}]\hbar^2 \quad (48.3)$$

Now if  $l$  is different from 0,  $j$  can be either  $l + \frac{1}{2}$  or  $l - \frac{1}{2}$ . Thus the first-order perturbation arising from  $\xi(r)\mathbf{L} \cdot \mathbf{S}$  is

$$\begin{aligned} \frac{1}{2}\xi_{nl} & \text{if } j = l + \frac{1}{2} \\ -\frac{1}{2}(l+1)\xi_{nl} & \text{if } j = l - \frac{1}{2} \end{aligned} \quad (48.4)$$

$$\xi_{nl} \equiv \hbar^2 \int_0^\infty |R_{nl}(r)|^2 \xi(r) r^2 dr \quad l > 0$$

where  $R_{nl}(r)$  is the normalized radial part of the unperturbed eigenfunction associated with the  $nl$  configuration. Since  $V(r)$  represents an attractive potential energy,  $\xi(r)$  given by (47.14) is positive and  $\xi_{nl}$  is positive. Thus (48.4) shows that the state with higher  $j$  has the higher energy. The pair of states is called a *doublet*; the doublet structure characterizes all the moderately excited levels of the alkali atoms except those for which  $l = 0$ , in which case  $j$  can only be  $\frac{1}{2}$ .

The doublet separations can be calculated from (48.4) if the radial function is known. We can get a rough estimate of their dependence on  $n$  by using the hydrogenic wave functions given in Eq. (16.24) and assum-

ing that  $V(r)$  has the coulomb form  $-Ze^2/r$ . Substitution into (47.14) and (48.4) gives, with the help of the generating function (16.21) for the associated Laguerre polynomials,

$$\begin{aligned} \zeta_{nl} &= \frac{\hbar^2 Z e^2}{2m^2 c^2} \int_0^\infty \frac{1}{r} R_{nl}^2(r) dr \\ &= \frac{2m^2 c^2 a_0^3 n^3 l(l + \frac{1}{2})(l + 1)}{e^2 \hbar^3 Z^4} \end{aligned} \quad (48.5)$$

This is valid only for  $l > 0$ ; the singularity in  $\xi(r)$  at  $r = 0$  makes the integral for  $\zeta_{n0}$  diverge there, so that the perturbation approximation is not valid. It follows from (48.4) and (48.5) that the doublet separation is proportional to  $n^{-3}$ , and this is in fair agreement with observation. The absolute value of the doublet separation and its dependence on  $l$  are not given at all by this simple theory, since the effective  $Z$  is difficult to estimate and depends markedly on  $l$  because of penetration.<sup>1</sup>

#### DOUBLET INTENSITY

We now calculate the relative intensities of the two lines of the allowed doublet  ${}^2P_{\frac{3}{2}} \rightarrow {}^2S_{\frac{1}{2}}$  and  ${}^2P_{\frac{1}{2}} \rightarrow {}^2S_{\frac{1}{2}}$ , under the assumption that the radial wave functions are the same for the two excited  ${}^2P$  states. Transitions of this type give rise to the principal series in the alkali spectra. From Eq. (45.22), the spontaneous transition probabilities, and hence the observed intensities if the two  $P$  states are equally likely to be occupied, are proportional to the squares of the dipole matrix elements.<sup>2</sup>

The dependence of the two excited  ${}^2P$  states and the ground  ${}^2S$  state on the angular and spin coordinates of the electron is obtained by finding linear combinations of products of the four spherical harmonics  $Y_{1,1}(\theta, \phi)$ ,  $Y_{1,0}(\theta, \phi)$ ,  $Y_{1,-1}(\theta, \phi)$ , and  $Y_{0,0}(\theta, \phi)$ , and the two spin wave functions  $(+)$  and  $(-)$ , that are eigenfunctions of  $J^2$  and  $J_z$  (see Secs. 14 and 41 for discussion of the angle and spin functions). These combinations can be obtained from the Clebsch-Gordan coefficients given in Eq. (28.13):

$$\begin{aligned} {}^2P_{\frac{3}{2}} \begin{cases} m = \frac{3}{2} & (+)Y_{1,1} \\ \frac{1}{2} & 3^{-\frac{1}{2}}[2^{\frac{1}{2}}(+ )Y_{1,0} + (-)Y_{1,1}] \\ -\frac{1}{2} & 3^{-\frac{1}{2}}[2^{\frac{1}{2}}(-)Y_{1,0} + (+)Y_{1,-1}] \\ -\frac{3}{2} & (-)Y_{1,-1} \end{cases} \\ {}^2P_{\frac{1}{2}} \begin{cases} m = \frac{1}{2} & 3^{-\frac{1}{2}}[-(+ )Y_{1,0} + 2^{\frac{1}{2}}(-)Y_{1,1}] \\ -\frac{1}{2} & 3^{-\frac{1}{2}}[(-)Y_{1,0} - 2^{\frac{1}{2}}(+ )Y_{1,-1}] \end{cases} \\ {}^2S_{\frac{1}{2}} \begin{cases} m = \frac{1}{2} & (+)Y_{0,0} \\ -\frac{1}{2} & (-)Y_{0,0} \end{cases} \end{aligned} \quad (48.6)$$

<sup>1</sup> The effect of the spin-orbit interaction on the energy levels of hydrogen is found in the next chapter as part of an exact relativistic calculation.

<sup>2</sup> The energy difference between the two upper states is so small that the  $\omega^3$  factor in (45.22) does not affect the intensity ratio appreciably.

The wave functions (48.6) can be used to calculate the matrix elements of  $x = r \sin \theta \cos \phi$ ,  $y = r \sin \theta \sin \phi$ , and  $z = r \cos \theta$ . We assume that the radial functions associated with (48.6) are all the same, so that the radial part of the matrix-element integral is a common factor throughout. The angle parts of the integrals are easily evaluated by making use of the explicit expressions for the  $Y$ 's in terms of  $\theta$  and  $\phi$  given in (14.16).<sup>1</sup> The products of spin functions follow the simple rules  $(+)^{\dagger}(+) = 1$ ,  $(-)^{\dagger}(+) = 0$ , etc. In this way we obtain the following values for the squares of the magnitudes of the indicated matrix elements, expressed in units of  $\frac{1}{18}$  of the common radial factor:

$$\begin{aligned} {}^2P_{\frac{3}{2}} \rightarrow {}^2S_{\frac{1}{2}} \begin{cases} m = \frac{3}{2} \text{ to } m = \frac{1}{2} & |x|^2 = |y|^2 = 3 & |z|^2 = 0 \\ \frac{3}{2} \text{ to } -\frac{1}{2} & |x|^2 = |y|^2 = |z|^2 = 0 \\ \frac{1}{2} \text{ to } \frac{1}{2} & |x|^2 = |y|^2 = 0 & |z|^2 = 4 \\ \frac{1}{2} \text{ to } -\frac{1}{2} & |x|^2 = |y|^2 = 1 & |z|^2 = 0 \\ \frac{1}{2} \text{ to } -\frac{3}{2} & |x|^2 = |y|^2 = 0 & |z|^2 = 2 \end{cases} \\ {}^2P_{\frac{1}{2}} \rightarrow {}^2S_{\frac{1}{2}} \begin{cases} m = \frac{1}{2} \text{ to } m = \frac{1}{2} & |x|^2 = |y|^2 = 0 \\ \frac{1}{2} \text{ to } -\frac{1}{2} & |x|^2 = |y|^2 = 2 \end{cases} \end{aligned} \quad (48.7)$$

Similar results are obtained for the transitions that start from  $m = -\frac{1}{2}$  and  $-\frac{3}{2}$ ; altogether, they confirm the  $m$  selection rules of Sec. 46.

It follows from (48.7) that the sum of the intensities of all the lines that originate on each of the four  ${}^2P_{\frac{3}{2}}$  states is equal to 6, in the above units. It is to be expected that these sums are equal since the four values of  $m$  differ only in the orientation of the angular momentum, and this should not affect the intensity. However, the total intensity from each of the two  ${}^2P_{\frac{3}{2}}$  states is also equal to 6. The equality of total intensities from each state formed from a given  $L$  and  $S$  is a general property of  $L$ - $S$  coupling; this makes the observed intensity, which is that from all the states that are degenerate with respect to  $m$ , proportional to  $2J + 1$ . In the example considered here, the two lines of the doublet have intensities in the ratio 2:1. This is observed for the lowest doublets of the alkalis, although for the higher doublets the intensity ratio exceeds 2. This is because the spin-orbit energy actually mixes different configurations ( ${}^2P$  states with the same  $j$  but different  $n$ ); the amount of mixing different for the two  $j$  values, so that the two radial functions are not the same. A small admixture of the low-intensity upper states in the high-intensity lowest  ${}^2P$  states has little effect, whereas in the opposite case there is a large effect on the doublet intensity ratio.<sup>3</sup>

<sup>1</sup> In the general case in which  $Y_{lm}$ 's with  $l > 1$  are involved, it is often easier to use a formula for the integral of the product of three spherical harmonics given by J. Gaunt; see Condon and Shortley, *op. cit.*, p. 176. Gaunt's formula can be derived making use of the Clebsch-Gordan coefficients.

<sup>2</sup> Condon and Shortley, *op. cit.*, p. 238.

<sup>3</sup> E. Fermi, *Z. Physik* **59**, 680 (1929).



## EFFECT OF A MAGNETIC FIELD:

We now consider the effect of a magnetic field on the energy levels and transition intensities of an alkali atom. As discussed in Sec. 31, a constant magnetic field can be represented by the vector potential

$$\mathbf{A} = \frac{1}{2} \mathbf{H} \times \mathbf{r} \quad (48.8)$$

and the extra energy associated with the orbital motion of an electron of charge  $-e$  is

$$\frac{e}{2mc} \mathbf{H} \cdot \mathbf{L} + \frac{e^2}{8mc^2} \hbar^2 r^2 \sin^2 \theta \quad (48.9)$$

where  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$  and  $\theta$  is the angle between  $\mathbf{r}$  and  $\mathbf{H}$ .

The electron also has an intrinsic magnetic moment in the direction of its spin axis. The magnitude of this moment can be determined from comparison between experiment and the theory of the Zeeman effect presented below and is in agreement with the value deduced from Dirac's relativistic theory of the electron (see Chap. 13); it is  $-e\hbar/2mc$ , or  $-e/mc$  times the spin angular momentum of the electron.<sup>2</sup> This is twice the ratio of magnetic moment to angular momentum of a classical charge distribution for which the ratio of charge to mass density is constant. The magnetic moment operator is  $-(e/mc)\mathbf{S}$ , and the extra energy in a magnetic field is

$$-\frac{e}{mc} \mathbf{H} \cdot \mathbf{S} \quad (48.10)$$

The ratio of (48.9) to the kinetic energy is quite small for magnetic field strengths commonly attainable in the laboratory (see Prob. 6). It is therefore permissible to use perturbation theory to find the effect of the  $\mathbf{H}$  terms on the wave functions and energy levels. In most cases, only the linear terms need be considered. However, for very strong fields and large orbits, the quadratic terms can become of interest (see the discussion of the quadratic Zeeman effect below). Also, the diamagnetic susceptibility can be obtained from the terms in the energy that are proportional to  $\mathbf{H}^2$ .

## WEAK-FIELD CASE

For the present, we consider only the first-order effects of  $\mathbf{H}$ . The hamiltonian (48.1) then becomes, with (48.9) and (48.10),

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(r) + \xi(r) \mathbf{L} \cdot \mathbf{S} + \epsilon(L_z + 2S_z), \epsilon \equiv \frac{e\hbar}{2mc} \quad (48.11)$$

<sup>1</sup> W. Heisenberg and P. Jordan, *Z. Physik* **37**, 263 (1926).

<sup>2</sup> The quantity  $e\hbar/2mc$  is called the *Bohr magneton*, and is equal to  $0.927 \times 10^{-20}$  erg/oersted.

where the field is along the  $z$  axis. The magnetic field can now be classified as weak or strong according as the last term in (48.11) is small or large in comparison with the spin-orbit energy. The *Zeeman effect* usually refers to the weak-field case, and the *Paschen-Back effect* to the strong-field case, although the term Zeeman effect is sometimes used to include all magnetic effects.

In the weak-field case, we can make use of the wave functions (48.6), which are eigenfunctions of  $\mathbf{J}^2$  and  $J_z$ . It is easily verified that the magnetic energy  $\epsilon(L_z + 2S_z) = \epsilon(J_z + S_z)$  has matrix elements between states of different  $j$  but not between states of the same  $j$  and different  $m$ . We neglect the former, because of the relatively large energy separation between states of different  $j$ . Thus the magnetic energy is diagonal with respect to  $m$  for each  $j$  and shifts the energy of each of the states (48.6) by its expectation value for that state. In each case,  $J_z$  is diagonal, and so its expectation value is  $m\hbar$ . The expectation value of  $S_z$  for the  ${}^2P_{\frac{3}{2}}$  state with  $m = \frac{1}{2}$ , for example, is

$$\begin{aligned} & \int \int 3^{-1} [2^{\frac{1}{2}}(+)^{\dagger} Y_{1,0}^* + (-)^{\dagger} Y_{1,1}^*] \frac{1}{2} \hbar \sigma_z 3^{-1} [2^{\frac{1}{2}}(+)^{\dagger} Y_{1,0} \\ & \quad + (-)^{\dagger} Y_{1,1}] \sin \theta \, d\theta \, d\phi \\ & = \frac{\hbar}{6} \iint [2^{\frac{1}{2}}(+)^{\dagger} Y_{1,0}^* + (-)^{\dagger} Y_{1,1}^*] [2^{\frac{1}{2}}(+)^{\dagger} Y_{1,0} \\ & \quad - (-)^{\dagger} Y_{1,1}] \sin \theta \, d\theta \, d\phi \\ & = \frac{\hbar}{6} (2 - 1) = \frac{\hbar}{6} \end{aligned}$$

with the help of (41.5) and the orthonormality of the spin functions and the  $Y$ 's. Thus the magnetic energy of this state is  $e\hbar(\frac{1}{2} + \frac{1}{6}) = \frac{2}{3}e\hbar$ . This and the similar results for the other states (48.6) can be expressed in terms of the *Landé  $g$  factor*; the magnetic energy is

$$\epsilon m \hbar g \quad g = \frac{2}{3} \text{ for } {}^2P_{\frac{3}{2}} \quad g = \frac{2}{3} \text{ for } {}^2P_{\frac{1}{2}} \quad g = 2 \text{ for } {}^2S_{\frac{1}{2}} \quad (48.12)$$

The weak-field transition intensities are given directly by (48.7). According to the discussion of Sec. 46, the radiation from the transitions in which  $m$  changes by unity is circularly polarized when viewed along the field and linearly polarized perpendicular to the field when viewed in the  $xy$  plane; these are called the  $\sigma$  components (from the German *senkrecht*). When  $m$  does not change in a transition, the radiation does not appear along the field and is polarized parallel to the field ( $\pi$  components) when viewed in the  $xy$  plane. For observation in the  $xy$  plane, the  $\pi$  intensity is proportional to  $|x|^2$  in (48.7) and the  $\sigma$  intensity is proportional to either  $|x|^2$  or  $|y|^2$  (but not to their sum).