

the energy change $E_1 - E_2$ and the frequency of the light ν_{12} is the familiar Einstein-Planck law as used in Bohr's early quantum theory:

$$E_1 - E_2 = h\nu_{12}.$$

(*d*) Not all transitions are allowed but selection rules operate to limit the permitted jumps. These selection rules are that while n may change arbitrarily, m_s does not change at all and l changes by ± 1 . This means that allowed transitions are:

$$\begin{aligned} s &\rightarrow p, \\ p &\rightarrow s \quad \text{or} \quad d, \\ d &\rightarrow p \quad \text{or} \quad f, \quad \text{etc.} \end{aligned}$$

All this has been completely verified experimentally, allowance being made for certain small relativistic and other effects.

2.7. The self-consistent-field model of an atom

The method of dealing with an atom containing several electrons has already been stated on p. 16. We are to write down the appropriate wave equation and then solve it. Now it is easy to write down the equation (see Chapter III) but quite impossible to solve it in the same sort of exact way that was possible for the hydrogen atom with only one electron. The fundamental difficulty is, of course, that each electron repels every other electron with an inverse-square-law force, so that the motion of any one electron is dependent on the motion of all the others. It is this non-separability of the individual electron orbits which introduces the real complexity into this problem, and at the same time suggests a way out of the difficulty. Let us suppose that when dealing with one of the electrons we disregard its instantaneous interactions with the other electrons, and imagine it to move in an effective electric field which is obtained by averaging over all possible positions of all the other electrons. In such a case each electron would be described by a wave equation which involved only its own coordinates, and not the coordinates of any other electron; the effect of all the other electrons would be shown by the existence of a potential energy function for the first electron. Such a wave equation is vastly easier to deal with than the more strictly accurate one, and can always be solved by numerical methods.

On account of the fact that the average potential due to the other electrons has spherical symmetry,† the s , p , d ,... classification still remains, so that the wave functions resemble quite closely the functions previously described for hydrogen.

Of course this does not solve our problem. For according to this scheme we can only write down the wave equation for any one electron if we already know the wave functions for all the others! But we can approach our complete solution in stages, as suggested first by Hartree,‡ to whom this model of an atom is due. Suppose that there are n electrons in our atom. Then let us first guess plausible wave functions for each of these electrons; this process is nothing like so difficult as it may at first appear, for after a little experience quite good wave functions may be guessed without much trouble. Now choose one of the electrons and find the average field provided by all the others. This average field is simply the field that would be provided if each of these electrons was a charge-cloud as in § 2. If necessary we average this field over all angles to make it spherically symmetrical. This process allows us to write down, and then to solve, the wave equation for our chosen electron. We obtain what may be called a first-improved wave function for this electron. This new function may next be used to calculate the average field for a second electron, and enables us to get a first-improved wave function for this electron also. The process is continued until we have a complete bunch of first-improved orbitals. In the same way starting with these we may improve them, one by one, and calculate second-improved a.o.'s. This technique is continued until successive iteration makes no appreciable difference to the orbitals. We may then say that the set of a.o.'s are self-consistent; this means that if we choose any one electron, its charge-cloud is precisely that which comes from solving the wave equation in which the potential field is due to the charge on the nucleus and the sum of the charge-

† This is not strictly true, but it is always assumed.

‡ D. R. Hartree, *Proc. Camb. Phil. Soc.*, 1928, **24**, 89. A list of atoms for which wave functions have been obtained up to 1943 is given in Mott and Sneddon, *Wave Mechanics*, Oxford, 1948, p. 141. Even more recent results are listed by D. R. Hartree, *Reports on Progress in Physics*, Physical Society, 1946-7, **11**, 113.

clouds of all the other electrons. This is true whichever electron we choose. For this reason it is called the method of the self-consistent field.

Naturally enough, there are certain errors in the above procedure. These arise chiefly from 'smoothing-out' the distribution of all electrons except the one being considered. However, it may be shown that these errors are not serious and, if we are prepared to spend sufficient time, the wave functions obtained in this way may be used as a very good basis for more accurate calculations in which no such 'smoothing-out' occurs. It turns out that the resulting charge distribution is only altered by a few per cent. of its maximum value, so that the simpler procedure is quite adequate for most purposes.

The 'smoothing-out' process referred to above is likely to be more satisfactory in heavy atoms than in light ones. For in atoms with a large nuclear charge the field arising from this is more important than the field from any individual electron, so that to average the latter is not so serious an approximation as when the central nuclear charge is smaller.

In view of its later applicability to molecules, it may be desirable at this stage to summarize the principles which we use for describing the electronic structure of an atom. It will be recognized at once that these principles are natural extensions of those principles listed on p. 31 for atomic hydrogen. They are:

(a) Each electron is represented by wave function ψ , called an atomic orbital; this orbital is found by solution of the appropriate Schrödinger wave equation, obtained by the Hartree procedure, or some similar technique, and is such that ψ^2 measures the density of the charge-cloud for this electron.

(b) Each a.o. is designated in terms of a set of quantum numbers. First there is the principal quantum number n , which chiefly determines the energy and also the size of the orbital. Next there is the geometrical shape, given by the quantum number l , or the label s, p, d, \dots with an appropriate suffix, e.g. p_x, p_y, p_z , to show which of the degenerate orbitals of this symmetry we are actually using. Finally there is the spin quantum number m_s which has the value $\pm\frac{1}{2}$.

(c) Each a.o. has a characteristic energy which is found from the wave equation. This energy measures very approximately the work required to remove this particular electron, i.e. to ionize the

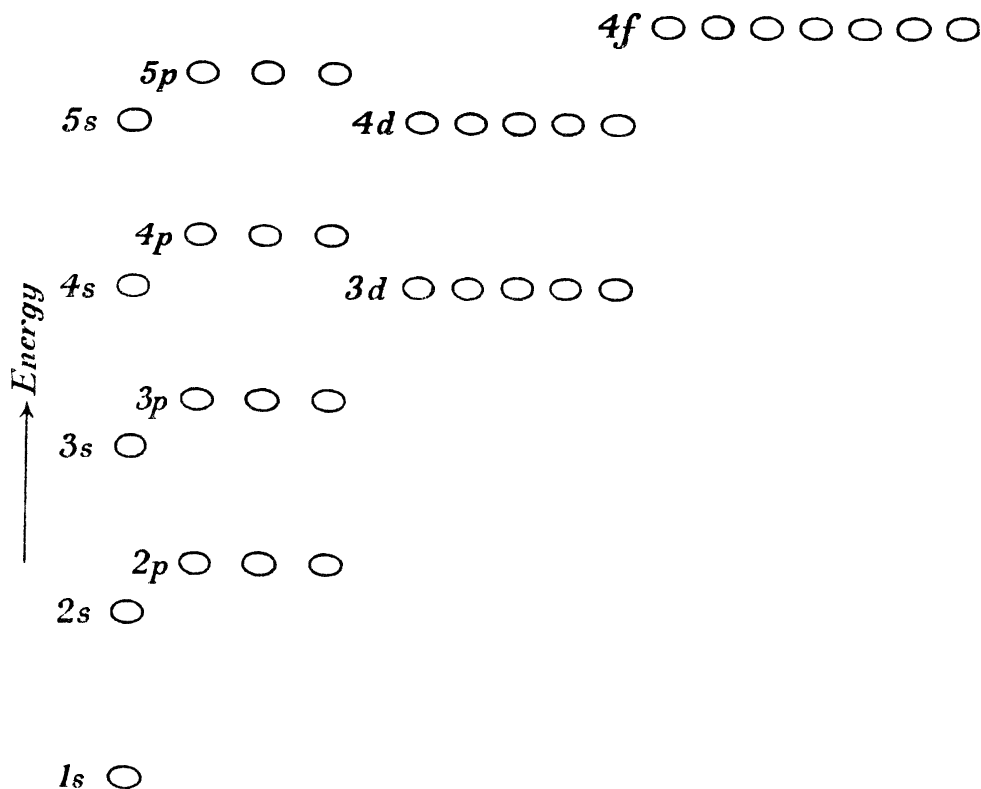


FIG. 2.6. Energy levels and cells for atoms. Each cell will hold not more than two electrons.

atom. Each type of electron has its own ionization potential. The order of energies is (see Fig. 6)

$$1s < 2s < 2p < 3s < 3p < 3d \sim 4s \dots,$$

and the order of ionization potentials is, of course, just the reverse of this. The total energy of an atom is now the sum of the energies of all the a.o.'s which are occupied by electrons, corrected for their mutual interaction. This interaction has, in fact, been counted twice over, because the Coulomb repulsion e^2/r_{ij} between electrons i and j has been included in the wave equations—and hence in the energy values—of both electrons separately.

(d) Transitions take place between one a.o. and another, accompanied by emission or absorption of light, the frequency of which is related to the difference of the two energies by the Bohr

frequency relation $E_1 - E_2 = h\nu_{12}$. Selection rules operate to allow certain transitions and forbid others.

(e) When assigning electrons to the various allowed a.o.'s, we must take account of the Pauli Exclusion Principle. This states that under no circumstances whatever may two electrons have precisely the same set of quantum numbers. Two electrons may indeed have the same space ψ , or orbital wave function, but only if their spins are opposed; i.e. $+\frac{1}{2}$ and $-\frac{1}{2}$. In this case we call them paired. Such electrons usually exert a repulsion (p. 170) upon electrons near them in addition to their electrostatic interaction.

2.8. The *aufbau* principle

The principles (a)–(e) listed at the end of § 7 lead us at once to an *aufbau*, or building-up process, when giving the electronic state of an atom. This means that we first determine the allowed orbitals and then feed the electrons one at a time into these levels, beginning with 1s which is the lowest, and satisfying the exclusion principle by allowing only two electrons to each of the orbitals just described. Thus hydrogen is represented in its ground state by (1s), helium by (1s)², lithium by (1s)²(2s), nitrogen by (1s)²(2s)²(2p)³, etc. The method is very simply portrayed on a diagram if we adopt the procedure of Fig. 6, in which each orbital is represented by a small oval, and energy is plotted upwards. Each of these 'cells' represents a possible orbital; if it is unoccupied in a given state of the atom, this cell is left empty; if it is singly-occupied, we place one arrow inside it, pointing upwards or downwards according as the spin is $\pm\frac{1}{2}$; if it is doubly-occupied we place two arrows in the cell, one up and the other down. Diagrams of this kind for the first ten atoms of the periodic table are shown in Fig. 7. In drawing these diagrams we have had to use Hund's rules† to decide, in the cases of nitrogen and oxygen, and all other atoms containing incomplete groups of electrons, just which of the equivalent orbitals (here the $2p_x$, $2p_y$, $2p_z$ orbitals) are filled. These rules are that for equivalent orbitals:

- (i) electrons tend to avoid being in the same space orbit, or cell, so far as is possible, and

† See, e.g., G. Herzberg, *Atomic Spectra and Atomic Structure*, Blackie, ch. iii.