Contents

I. Well-defined Electron Configurations

The fundamental idea most useful for the description of many-electron systems, i.e. atoms, molecules, and solids, is the *electron configuration*. As we shall elaborate, the assumption of one-electron wavefunctions, *orbitals* ψ, occupied by zero, one or at most two electrons (in the latter case with opposite spin direction) is only an approximation to the total wavefunction Ψ of the many-electron systems. In most cases, it is a fairly good approximation, but our main reason for accepting it is that, at present, any other, more sophisticated representation is much too complicated to be handled for more than some four or six electrons, restricting our field to isolated atoms such as carbon or molecules such as BeH_2. Actually, quantum mechanics in its most strict sense has only been applied to two-electron systems such as He and H_2, and, with some approximation, to Li, Be, and LiH. This is not as surprising when compared to classical mechanics, where a general solution was not found of the motion of three particles under their mutual gravitational attraction, whereas the solution (of great astronomical interest) of two particles is completely known. Both in quantum and classical mechanics, the difficulty is the same: the appropriate equations are very clear-cut, but they cannot be explicitly solved at present.

However, there are many reasons to be much more optimistic regarding electron systems of importance to atomic spectroscopy and chemistry, rather than regarding nuclei. Though the nuclei most definitely show evidence of shell structure in the same way as atomic electron systems, the interactions between the neutrons and protons are not known at present with any degree of accuracy. On the other hand, the *only potentials of importance in electron systems are electromagnetic*. Running the usual risk of conservative minds, we may even affirm that there is good evidence that, if any other interaction was of importance in electron systems, it would already have been discovered. (We may recall that the gravitational potential is 10^{40} times weaker than the electromagnetic interaction between charged elementary particles.) In addition by far the greater part of the interaction in electron systems is *purely electrostatic*. The rest are called electrodynamic or relativistic effects and they are only important for electrons coming close to nuclei with high atomic number Z.

In this chapter, we shall restrict ourselves to the electrostatic effects. Following Mulliken, we use capital letters for quantities related to total systems and small letters for one-electron quantities. The virial theorem for

an isolated atom relates the total energy $-T$, the sum of the electrostatic potential energy E_{pot} and the kinetic energy of the electrons E_{kin} by the equations

$$E_{pot} = -2T \text{ and } E_{kin} = T. \tag{1.1}$$

In systems with more than one nucleus, i.e. molecules, eq. (1.1) is only valid when the nuclei are at their equilibrium distances (or at very large mutual distances).

In the following, we write equations in atomic units, with the length unit 1 bohr $= a_0 = 0.528$ Å (1 Å $= 10^{-8}$ cm) and the energy unit 1 rydberg $= 109.7$ kK, representing the ionization energy T of a hydrogen atom with a very heavy nucleus. Many authors prefer the atomic unit 2 rydbergs ($= e^2/a_0$, where the electronic charge is $-e$). When indicating numerical results, we usually apply the rather convenient *kilokayser* kK, which is a unit of wavenumber of radiation, but also an energy unit when combined with Bohr's equation from 1913

$$E = h\sigma c, \tag{1.2}$$

the frequency ν of the radiation in sec^{-1} being the product of the wavenumber σ and the velocity of light *in vacuo* c, and h being Planck's constant. The relations between kK and some other energy units are:

$$
\begin{aligned}
&1 \text{ kK} = 1000 \text{ K} = 1000 \text{ cm}^{-1} \\
&1 \text{ eV} = 8.06 \text{ kK} \\
&1 \text{ kcal/mole} = 0.351 \text{ kK/molecule} \\
&1 \text{ joule/mole} = 8.4 \times 10^{-5} \text{ kK/molecule}.
\end{aligned}
\tag{1.3}
$$

For our purposes, we need only to consider real (and not complex) one-electron wavefunctions ψ. This restriction is essentially refraining from considering the effect of external magnetic fields on our system. The electron density in the usual three-dimensional space is then given simply by ψ^2.

One of the rather queer things about quantum mechanics is the relation between the kinetic energy e_{kin} and ψ^2, being dependent on the Laplace operator involving the second differential coefficient of ψ with respect to the Cartesian co-ordinates

$$e_{kin} = \int \frac{h^2}{4\pi^2 m} \left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right] \psi \, d\tau. \tag{1.4}$$

The constant of nature $h^2/(4\pi^2 m)$ is adapted to be 1 in atomic units, and the integration with the differential $d\tau$ in the end symbolizes all ranges of the appropriate co-ordinates, here x, y, z between limits entirely including the region where ψ is different from zero. The wavefunction ψ is normalized when

$$\int \psi^2 d\tau = 1. \tag{1.5}$$

Two normalized wavefunctions ψ_1 and ψ_2 have an overlap integral

$$S_{12} = \int \psi_1 \psi_2 d\tau. \tag{1.6}$$

If the overlap integral is zero, ψ_1 and ψ_2 are said to be *orthogonal*.

The potential energy, expressing the attraction of the electron in ψ by the nuclei with charges $+Z_1 e, +Z_2 e, \ldots, +Z_q e$, has a much simpler formulation than eq. (1.4), *viz.*

$$e_{nuc} = -\sum_k \int \frac{Z_k}{r_k} \psi^2 d\tau \tag{1.7}$$

where r_k is the distance of the electron from the nucleus Z_k. Equation (1.7) is the same expression as in classical electrostatic theory for the potential energy of a charge distribution ψ^2 in the potential $U(x, y, z) = \Sigma_k (Z_k/r_k)$. In many cases, quantum-mechanical quantities Q are obtained by the integration of $Q\psi^2$ over $d\tau$, and it is therefore practical to introduce the bracket $<Q>$ as notation for the result, and to consider this bracket as the "average value" of Q for ψ^2. For instance, in an atom or gaseous ion with only one nucleus, it is reasonable to put the origin of the co-ordinate system at the nucleus and to define the unique distance r between the nucleus and the electron by

$$r^2 = x^2 + y^2 + z^2 \tag{1.8}$$

in which case one can define average values of r^n for a given ψ^2

$$<r^n> = \int r^n \psi^2 d\tau. \tag{1.9}$$

It is seen that eq. (1.7) reduces to $-Z<r^{-1}>$ for the nuclear charge Z. However, eqs. (1.7), (1.10), (1.11), (2.27), (2.29) and (2.45) have the energy unit 2 rydbergs.

The electrostatic energy of the total system is not a simple addition of the nuclear-electronic interaction e_{nuc} from eq. (1.7), but contains also a positive *interelectronic repulsion energy*, and if the system is a molecule, the internuclear repulsion energy which has a fairly simple expression:

$$E_{nuc} = \sum_{a \neq b} \frac{Z_a Z_b}{r_{ab}}, \tag{1.10}$$

each pair of nuclei taken once, involving only their distance r_{ab} and not the electronic wavefunctions. Unfortunately, nobody can maintain that the effects of interelectronic repulsion are simple, and we only begin to foresee the difficulties when regarding the approximation on which this book is based, the well-defined electron configuration of orthogonal ψ.

The total kinetic energy E_{kin} is here the summation of the one-electron energies e_{kin} of eq. (1.4), the nuclear-nuclear and nuclear-electronic contributions to the potential energy are given by eqs. (1.10) and (1.7) respectively, and the interelectronic repulsion energy can (in this simplified case) be written as sums of Coulomb integrals J(a, b) [in special cases J(a, a)] and

"exchange" integrals $K(a, b)$ defined by integrations over two electrons (in the orbitals ψ_a and ψ_b) at the time, with the mutual distance r_{12}:

$$J(a, b) = \int \int \frac{1}{r_{12}} \psi_a^2 d\tau_1 \psi_b^2 d\tau_2$$

$$K(a, b) = \int \int \frac{1}{r_{12}} \psi_a \psi_b d\tau_1 \psi_a \psi_b d\tau_2 \qquad (1.11)$$

where $J(a, b)$ represent the classical interaction between two extended charge distributions ψ_a^2 and ψ_b^2. This quantity would also occur in the classical theory, whereas $K(a, b)$ would have no place there. The latter quantity is the electrostatic interaction between the charge distribution $\psi_a \psi_b$ and itself, and still calculated according to classical formulae.

The interelectronic repulsion energy of the system is calculated by taking each pair of electrons, in their orbitals ψ_a and ψ_b (which must be identical or orthogonal), and reckon $J(a, b) - K(a, b)$ if their spins are parallel [i.e. $m_s(a) = m_s(b)$ where m_s can assume the values $+\frac{1}{2}$ or $-\frac{1}{2}$) and $J(a, b)$ if their spins are opposite $(m_s(a) = -m_s(b))$].

A common example is a configuration with a series of orbitals ψ_a, ψ_b, . . . ψ_q all filled, i.e. occupied each by two electrons. We will denote such a configuration by the spectroscopic symbol a^2b^2 . . . q^2 writing the number of electrons in each orbital as an exponent to the name of the orbital.

We saw above that the total electronic energy of this system can be written

$$E_{kin} = T = 2 \sum_{k=a}^{q} e_{kin}(k)$$

$$E_{pot} = -2T = -2 \sum_{k=a}^{q} e_{nuc}(k) + \sum_{k=a}^{q} J(k, k) + 4 \sum_{a \neq b} J(a, b) - 2 \sum_{a \neq b} K(a, b). \qquad (1.12)$$

The ionization energy of removing one electron from the orbital ψ_m can be calculated *assuming no rearrangement of the orbitals in the new configuration* a^2b^2 . . . m^1 . . . q^2, being

$$I_m = e_{nuc}(m) - e_{kin}(m) - J(m, m) - 2 \sum_{a \neq m} J(a, m) + \sum_{a \neq m} K(a, m). \qquad (1.13)$$

The assumption of no rearrangement of the orbitals has a close connection with Koopman's theorem that the ionization and excitation energies of a given configuration are very nearly the same, either making two different calculations of the total energy of the excited state and the ground state, or using eq. (1.13).

There is a certain appeal in the idea of expressing the total energy of a system as a sum of one-electron energies, but it is not easy to define these quantities in a consistent way. In a many-electron system, the genuine one-electron operator quantities $e_{nuc}(m) - e_{kin}(m)$ are usually much larger,

frequently by a factor of ten for the loosest bound electrons, than I_m, the two-electron quantities (J and K integrals) cancelling most of the contribution from the two first terms. On the other hand, the sum of the ionization energies I_m (one electron taken at the time from the undamaged original system) is not equal to -1 times the total energy either, but is $-\Sigma J(k, k)$ too small. It might therefore seem proper to define one-electron energies as

$$i_m = I_m + \tfrac{1}{2}J(m, m) + \underset{a \neq m}{\Sigma J(a, m)} - \tfrac{1}{2}\underset{a \neq m}{\Sigma K(a, m)} \qquad (1.14)$$

which would make $T = \Sigma i_m$ and actually make the virial theorem for the system, eq. (1.1) valid for the individual one-electron energies:

$$-e_{kin}(m) = \tfrac{1}{2}[e_{nuc} - \tfrac{1}{2}J(m, m) - \underset{a \neq m}{\Sigma J(a, m)} + \tfrac{1}{2}\underset{a \neq m}{\Sigma K(a, m)}]. \qquad (1.15)$$

From the virial theorem for the system, it can be demonstrated that

$$T = \Sigma i_m = -\Sigma f_1 - \Sigma g_{12} = \Sigma I_m + \Sigma g_{12} \qquad (1.16)$$

the two-electron quantities g_{12} being taken twice in the summation of I_m, while the one-electron quantities f_1 are correctly taken into account. Of course, the sum of the *consecutive* ionization energies, gradually leading to the removal of all electrons from the nuclei, equals T.

There is no doubt, however, that the quantities i_m defined in eq. (1.14) have very little practical interest to chemists, the arithmetic mean i_m of I_m and the frequently much larger $f_1 = e_{nuc}(m) - e_{kin}(m)$ being much larger than I_m in many cases. These considerations mainly serve to demonstrate how difficult it is to define one-electron energies in both a consistent and satisfactory way.

We admit an expansion of our definition of "well-defined electron configuration" in the case of *degenerate sets of orbitals*. These sets of orbitals, having the same energy (in the sense of identical f_1 and certain conditions on the g_{12}), are extremely important in high symmetries, as we shall see, and are called *shells* in monatomic entities and *subshells* in molecules. If a number e of orbitals are degenerate, each subshell or shell in a well-defined configuration contains 0, 1, 2, 3, 4, . . . or $2e$ electrons, though it may not always be possible to assign an integral number of electrons to each definite orbital in the degenerate set.

Very frequently, the e orbitals ψ can be written in such a way that only three different parameters of interelectronic repulsion occur, *viz.* J(a, a), J(a, b), and K(a, b) where a and b are two different cases of the degenerate orbitals. Usually J(a, b) is much larger than K(a, b). This can be understood from eq. (1.11), since the charge density $\psi_a \psi_b$, being a product of two orthogonal wavefunctions, firstly has alternant positive or negative sign in various points of the space; secondly, K(a, b) has only positive contributions from places where the "squared overlap" $\psi_a{}^2 \psi_b{}^2$ is positive. For these two reasons

K(a, b) may be rather small, while J(a, b) would not vanish even if ψ_a and ψ_b were separated at some distance. The difference between J(a, a) and I(a, b) has the same order of magnitude as K(a, b).

We may consider a very simplified example for showing two important differences between interelectronic repulsion in classical and quantum mechanics. If q electrons occur in a set of degenerate orbitals, and if we make the approximation that all J integrals are identical, the classical value would be $\frac{1}{2}q^2J$, while eq. (1.12) indicates $\frac{1}{2}q(q-1)J$, that is $-\frac{1}{2}J$ less for each electron. In other words, the electron is a self-coherent particle, though for all practical purposes it functions as a charged cloud ψ^2 in a stationary state. Therefore, there is no repulsion between the electron and itself, or rather, this repulsion is taken care of in its rest mass energy. A "classical" hydrogen atom with a cloudy electron would have the ionization energy decreased $\frac{1}{2}J = \frac{5}{8}$ rydberg for this reason.

Secondly, eq. (1.12) suggests a decreased interelectronic repulsion energy for electrons having parallel spin, as expressed by the K integrals with negative coefficients. This entirely nonclassical phenomenon is caused by the action of Pauli's principle on the total wavefunction Ψ, which for a well-defined configuration can be written as an antisymmetrized Slater determinant according to rules given in Condon and Shortley's book.

These sentences have some chance of soon becoming obsolete for the following reasons. Ψ for a system with q electrons has 4q variables, that is 3q continous space variables and q spin variables, each assuming only one of two possible values. It is very difficult to have an intuitive idea of the wavefunction of a bismuth atom or the complex FeF_6^{---} containing 83 electrons being represented in a space with 249 ordinary dimensions. Actually, there are good reasons for believing that the 249 dimensions are superfluous to the physical description, and that six (or possibly rather five) continuous and two spin variables would suffice. As we saw above, in electron systems there is no trace observed of three- or more-particle interactions; one- and two-electron operators are all that is needed. As pointed out by Löwdin, this would make second-order density matrices having as variables the co-ordinates of only two electrons $(x_1, y_1, z_1, m_{s1}, x_2, y_2, z_2, m_{s2})$ a valid substitute for the much more complicated Ψ. Actually, Ψ would already now have been rejected for the same reason as the special relativistic theory abandoned the classical Galilei-space-time; that is, the description contains more information than can be obtained from experiments, if it were not for an annoying fact: there exists a definite rule, the variation principle, that the application of the Hamiltonian operator (expressing the various contributions of kinetic and potential energy discussed above) on an arbitrary trial wavefunction Ψ never gives an energy lower than the actual, observed energy. Unfortunately, one can construct seemingly decent second-order density matrices which give a more negative energy than the actual value. We have not yet found a criterion

for "permissible" second-order density matrices corresponding to possible Ψ and obeying the variation principle.

It is reasonable to hope for such a criterion to be found, and there is little doubt that Ψ has only received a provisional acquittal. Especially, we know now that the interelectronic repulsion energy is only a question of $\left< \dfrac{1}{r_{12}} \right>$ of such a second-order density matrix.

[The allusion to five rather than six independent space variables of the second-order density matrix was made because, generally, a nondegenerate state has a Ψ which has no lower symmetry than the Hamiltonian operator. Therefore, it is expected that second-order density matrices can be written as functions of $(x_1, y_1, z_1, r_2, r_{12}, m_s1, m_s2)$, since the interelectronic repulsion is spherically symmetric and dependent on r_{12} only.]

REFERENCES

Many books treat the analogies and differences between classical and quantum mechanics much more profoundly than is possible here. Thus,

Kauzmann, W., "Quantum Chemistry", Academic Press, New York, 1957;

Margenau, H., and Murphy, G. M., "The Mathematics of Physics and Chemistry", 2 ed., D. Van Nostrand, Princeton, N.J., 1956.

It must be realized that the study of quantum mechanics for its own purpose can be pursued much longer than needed for the chemical applications. A useful "chemical" book is

Eyring, H., Walter, J., and Kimball, G. E., "Quantum Chemistry", John Wiley, New York, 1944.

2. Degenerate Orbitals in High Symmetry

The highest possible symmetry in Euclidean three-dimensional space is the spherical symmetry with centre of inversion, where the physical quantities depend only on one space variable, the distance r [eq. (1.8)] from the origin of the co-ordinate system. Arguments from spherical symmetry can be used for isolated atoms and monatomic ions, while all conceivable molecules have lower symmetry, as we see in Chapter 4.

In spherical symmetry, the individual orbitals ψ have the exceptional property of being separable in a product of an angular function A_l and a radial function R/r:

$$\psi = A_l(x, y, z) \cdot R(r)/r. \tag{2.1}$$

We divide here by r to make R^2 express the charge density of ψ^2 per spherical shell ("between r and $r+dr$"), but many authors prefer to use R/r for the radial function.

In eq. (2.1) we meet for the first time a group-theoretical quantum number, the non-negative integer l characterizing the angular function A_l. For historical reasons, spectroscopists introduced trivial names for the various values of l, viz.

$$\begin{array}{cccccccccccc} l = & 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & \ldots \\ & s & p & d & f & g & h & i & k & l & m & n & \ldots \end{array} \tag{2.2}$$

and, after the development of quantum mechanics, it was discovered that l had something to do with the orbital angular momentum of the electron being equal to $\sqrt{l(l+1)}h/2\pi$.

The angular function A_l can be written as a linear combination of homogeneous polynomials A_p in Cartesian co-ordinates:

$$A_p = x^a y^b z^c / r^l \quad a+b+c = l. \tag{2.3}$$

Many authors prefer to write A_p in a polar co-ordinate system with trigonometric functions of angles substituting x, y, and z. This is a little confusing and not suitable for our purpose, because our favourite example of a molecular symmetry will be the octahedral, to which the Cartesian co-ordinates are particularly adapted.

It is seen that only one A_p exists for $l=0$. Since we neglect the normalization factors [satisfying eq. (1.5) on a spherical surface], we can write this s-electron angular function as the constant 1.

It is also obvious that three A_p exist for $l=1$; we may write them as x/r, y/r, and z/r, respectively.

One might expect that six A_l would subsist for $l=2$. Among the six A_p possible

$$xy/r^2 \quad xz/r^2 \quad yz/r^2 \quad x^2/r^2 \quad y^2/r^2 \quad z^2/r^2 \qquad (2.4)$$

something is wrong with the three last ones. They are not linearly independent, as can be seen from the fact that the sum of the last three A_p $(x^2+y^2+z^2)/r^2$ is another way of writing 1 according to eq. (1.8). In other words, the six A_p of eq. (2.4) correspond to five d orbitals A_2 and one s orbital A_0. One way of making A_2 orthogonal is to write the last two

$$(x^2-y^2)/r^2 \quad (2z^2-x^2-y^2)/r^2. \qquad (2.5)$$

In the same way, ten A_p exist for $l=3$, but three A_l are to be separated out because they represent p orbitals A_1 and not f orbitals A_3. This is a general mechanism for orthogonalization of ψ in spherical symmetry. Two orthogonal ψ_1 and ψ_2 are orthogonal either because they have different A_l values (and they would be orthogonal even if they had identical radial functions R) or because they have the same l value but orthogonal radial functions.

Among the valid forms of A_3 is evidently $(xyz)/r^3$, but the other six f orbitals have quite complicated forms, due to the singling out of the three p characteristics. Bethe and Von der Lage studied these A_l under the name of "Cubic Harmonics" and indicated as a possible choice of the residual six A_3:

$$\begin{aligned}
(x^3-\tfrac{3}{5}xr^2)/r^3 \quad & x(z^2-y^2)/r^3 \\
(y^3-\tfrac{3}{5}yr^2)/r^3 \quad & y(x^2-z^2)/r^3 \\
(z^3-\tfrac{3}{5}zr^2)/r^3 \quad & z(x^2-y^2)/r^3.
\end{aligned} \qquad (2.6)$$

Among the A_4, one is relatively simple, $(x^4+y^4+z^4-\tfrac{3}{5}r^4)/r^4$. In general, from the $(l+1)(l+2)/2$ possible A_p for a given value of l, only $(2l+1)$ genuine A_l appear, the rest corresponding to all previous l values smaller than the l value considered, and of the same parity. We introduce here the word *parity* in a very straightforward fashion, l being even for 0, 2, 4, 6 . . . and odd for 1, 3, 5, 7. . . . . Actually, parity is a much more fundamental concept. The orbitals ψ and total wavefunctions Ψ in spherical symmetry and in any other symmetry having a *centre of inversion* can be classified according to odd or even parity by substitution of the "inverted" co-ordinates $(-x, -y, -z)$:

$$\begin{aligned}
\psi_{odd} (-x, -y, -z) &= -\psi_{odd} (x, y, z) \\
\psi_{even} (-x, -y, -z) &= \psi_{even} (x, y, z).
\end{aligned} \qquad (2.7)$$

It is customary to use the German abbreviations u ($=$ ungerade) for odd and g ($=$ gerade) for even functions. An odd and an even function are necessarily orthogonal, because the contributions to the integration eq. (1.5) always cancel from opposite sides of the co-ordinate system. It is obvious that an

arbitrary function ψ^* cannot necessarily be ascribed even or odd parity. However, it can always be written as the sum of two (non-normalized) functions ψ_{even} and ψ_{odd} defined by

$$\begin{aligned}\psi_{even} &= (\psi^*(x, y, z) + \psi^*(-x, -y, -z))/2\\ \psi_{odd} &= (\psi^*(x, y, z) - \psi^*(-x, -y, -z))/2\end{aligned} \tag{2.8}$$

Whereas the angular functions of eq. (2.1) can be expressed in a definite form, the radial functions depend heavily on the *central field* U(r), the electrostatic potential to be put into Schrödinger's equation. In spherical symmetry, the kinetic energy of an orbital ψ can be divided into two parts, *radial kinetic energy*, similar to eq. (1.4) being an integration of

$$e_{rad\ kin} = \int \frac{h^2}{4\pi^2 m} \frac{d^2 R}{dr^2} \cdot R\ dr \tag{2.9}$$

while the *angular kinetic energy* has the fixed form (in atomic units, the energy unit $1\,ry = e^2/2a_0$):

$$e_{ang\ kin} = \int \frac{l(l+1)}{r^2} \psi^2 dr = l(l+1) <r^{-2}> \tag{2.10}$$

$d\tau$ being dr between the limits $r=0$ and $r=\infty$ (or larger than such r that ψ^2 has become negligible). In eq. (2.10) we can talk about a pseudo-potential of "centrifugal forces", vanishing for $l=0$.

Schrödinger's equation for R then becomes

$$\frac{h^2}{4\pi^2 m} \frac{d^2 R}{dr^2} + \left[w - U(r) - \frac{h^2}{4\pi^2 m} \frac{l(l+1)}{r^2} \right] R = 0 \tag{2.11}$$

and the solutions for negative energy w are sought. For a positive w there exists a continuous infinity of solutions, called the *continuum*, corresponding to ionized states of the system (because the zero point of w is the energy of an electron very far away from the nucleus and the other electrons, if present) and not fulfilling the virial theorem eq. (1.1), since both e_{kin} and e_{pot} are positive. For negative w there exist only a discrete set of *stationary* states, fulfilling the virial theorem and having radial functions R which vanish exponentially at large r (expressing the fact that the electron is bound to the rest of the atom). However, for all values of l, and for all monatomic entities being either neutral or positively charged, there exist an infinite number of these stationary states, queueing very densely up for w being just below zero.

We shall concentrate our attention on the lowest stationary ψ of a given *symmetry type l*. Neglecting the behaviour of R at $r=0$ and $r \to \infty$, we can talk about the number of nodes of R, values of r where $R=0$. The lowest energy is found by an orbital having no nodes [this is mainly a question of d^2R/dr^2 of eq. (2.9) necessarily being much larger when nodes occur]. The following orbital with the same l can only be made orthogonal to the first one

by having one node (because $R_1 R_2$ must be positive for some r and negative for some other interval of r values). The third orbital must have two nodes for being orthogonal on both R_1 and R_2, and so on. We define a *principal quantum number* n such that the number of nodes of R is $n - l - 1$. This has not the same direct physical significance as l, but is essentially a file number.

In a one-electron system with spherical symmetry, as represented by H, He+, Li++, ... with a nucleus of the atomic number Z, eq. (2.11) can be solved completely with $U = -2Z/r$ (the factor 2 arising from the choice of one rydberg as unit of energy).

The lowest solution for each l can be demonstrated by substitution in eq. (2.11) to be

$$R = r^{l+1} \exp(-Zr/(l+1)) \tag{2.12}$$

again neglecting normalization constants, and the corresponding energy is

$$w = -Z^2/(l+1)^2 = -Z^2/n^2. \tag{2.13}$$

A very special property of $U = -2Z/r$ occurring in one-electron systems is that the higher solutions with nodes in R, though having widely different radial functions, have the same energy as the last term in eq. (2.13), i.e. $-Z^2/n^2$ independent of l. It is interesting to note various values of $<r^q>$ [cf. eq. (1.9)] calculated for the "hydrogenic" radial functions:

$$
\begin{aligned}
<r^{-3}> &= Z^3/(n^3(l+1)(l+\tfrac{1}{2})l) \\
<r^{-1}> &= Z/n^2 \\
<r> &= (3n^2 - l(l+1))/2Z \\
<r^2> &= n^2(5n^2 + 1 - 3l(l+1))/2Z^2.
\end{aligned} \tag{2.14}
$$

The potential energy $-2T$ of a hydrogenic system being proportional to $<r^{-1}>$, eq. (2.13) corresponds to a l-independent value of the latter quantity.

In many-electron systems, the radial function R is *not hydrogenic*. The central field $U(r)$ can take care of nearly all, but not all, the effects of interelectronic repulsion, because the latter turns out to have spherical symmetry to a great extent in the actual atom. The Hartree-Fock self-consistent functions (HFSCF) R of the various shells of a definite atom minimizes the energy given in eq. (1.12) and adapts therefore the behaviour of the individual n, l shells mutually, as described in Hartree's book. This is a fairly complicated calculation, done by repeated iteration and usually by analytical approximations to R, but it is not impossible with modern computing machines and has been done for a variety of atoms. Recently, Watson (1959, 1960) has performed such calculations for iron group atoms and ions with $Z = 21$ to 30, and Watson and Freeman (1961) for the group $Z = 13$ to 18 and $Z = 31$ to 36.

A fairly good approximation to the HFSCF radial functions without nodes can be written

$$R = r^{l^* + 1} \exp(-\alpha r) \tag{2.15}$$

where l_* and α are two fractional constants. In literature, reference is frequently made to Slater's hydrogenic radial functions, having α equal to the ratio Z_*/n_* between an effective charge Z_* and an "effective principal quantum number" n_*. In nearly all cases, l_* is assumed to be equal to l of the n, l shell. However, for many purposes this is a quite unsatisfactory approximation. There are good reasons for believing that a much smaller value of l_*, say 0.5 or 0.7, is a much better approximation, and eqs. (2.16) and (2.17) show some justification for eq. (2.15) directly from Schrödinger's radial equation (2.11).

The central field $U(r)$ in a many-electron system with the ionic charge $+(Z_0-1)e$ is $-2Z_0/r$ for large r, while it is approximately $-2Z/r$ for small values of r, close to the nucleus. Since the central field increases from Coulomb behaviour with Z_0 at large r to Coulomb behaviour with Z at small r (neglecting the small effects of external screening), it is possible to expand U in a Taylor series of r^{-1}, starting with the central field outside the atom at large r.

$$U = -\frac{2Z_0}{r} - \frac{Z_2}{r^2} - \ldots \qquad (2.16)$$

Correspondingly, the energies w are situated somewhere in the interval $-Z^2/n^2$ and $-Z_0^2/n^2$, the internal shells with small $<r>$ being close to the former, more negative limit, and very external orbitals with large $<r>$ being close to hydrogenic behaviour with Z_0.

If we restrict our Taylor expansion eq. (2.16) to the two first terms, we can directly give the solution in the Schrödinger equation (2.11), because Z_2 cancels a part of the pseudo-potential $l(l+1)/r^2$ of angular kinetic energy, eq. (2.10), and the resulting solution R has the form eq. (2.15) with the constants given by

$$\begin{aligned}
\alpha &= Z_0/(l_*+1) \\
Z_2 &= l(l+1) - l_*(l_*+1) \\
w &= -\alpha^2 = -Z_0^2/(l_*+1)^2.
\end{aligned} \qquad (2.17)$$

It is seen how, for a definite Z_2, the higher values of l correspond to larger l_* and therefore less negative values of the energy w. This argument is generally valid without the specific approximation expressed in eq. (2.16) for any central field becoming more negative for small r than $-2Z_0/r$, and gives the definite order of n, l shell energies w:

$$\begin{aligned}
1s &\ll 2s < 2p \\
&\quad 3s < 3p < 3d \\
&\quad 4s < 4p < 4d < 4f \\
&\quad 5s < 5p < 5d < 5f < 5g \\
&\quad \ldots .
\end{aligned} \qquad (2.18)$$

Rydberg was the first (in 1906–13) to relate facts of atomic spectroscopy to the structure of the periodic table of elements; and N. Bohr further connected

Moseley's determination of the atomic numbers Z with the evidence from the alkali metal spectra [indicating empirically eq. (2.18)] demonstrating the composition of the closed-shell configurations corresponding to inert gases in the periodic table:

$$He(Z=2): \quad 1s^2$$
$$Ne(Z=10): \quad 1s^2 2s^2 2p^6$$
$$Ar(Z=18): \quad 1s^2 2s^2 2p^6 3s^2 3p^6$$
$$Kr(Z=36): \quad 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 = [Ar]3d^{10}4s^2 4p^6 \quad (2.19)$$
$$Xe(Z=54): \quad [Kr]4d^{10}5s^2 5p^6$$
$$Em(Z=86): \quad [Xe]4f^{14}5d^{10}6s^2 6p^6$$
$$(Z=118): [Em]5f^{14}6d^{10}7s^2 7p^6$$

where we denote the previous closed-shell configurations [Ar], etc., for saving space. It is worth noting the absence of inequality signs in eq. (2.18) between (given n, high l) and ($n+1$, low l). The relative order of such two orbitals depends on the detailed nature of $U(r)$ and in particular on the ionic charge $Z_0 - 1$. Thus, in practice, there is never any doubt that 2p has lower energy than 3s, though it was not proved from eq. (2.17). On the other hand, for neutral atoms with $Z_0 = 1$, 4s has *lower* energy than 3d at the point, $Z = 19$ (potassium), where these orbitals become important for the electron configuration of the ground state. Actually, 4s<3d only in an interval starting around carbon ($Z=6$) and finishing at copper ($Z=29$), while 3d<4s for smaller Z (approaching the behaviour in hydrogen) and for Z larger than 30 (where both 3d and 4s are internal shells). If one considers ionic charges $+e$, the interval for 3d<4s is much more narrow, and for $Z_0 = 3$, it is reduced to near coincidence in silicon ($Z=14$) and phosphorus ($Z=15$). For ionic charges higher than $+2e$, the orbital 3d is always more stable than 4s. Hence, we have seen that the question whether 3d has lower energy than 4s does not have a clear-cut answer, if we do not specify the ionic charge and the atomic number.

Similar difficulties arise with the sets of orbitals 5f, 6d, and 7s for more than 86 electrons, which tend to arrange in the hydrogenic order 5f<6d<7s for high ionic charges (say Th^{+++} or U^{+4}) and in the opposite order 7s<6d<5f in neutral Ra, Ac, and Th.

We may use eq. (1.12) to construct a model of this behaviour at the beginning of each transition group. We say a model, because we neglect the effects of rearrangement of orbitals with consequent changes of the pertinent parameters (see page 4) and we make the approximation that the inter-electronic repulsion energy in the configuration $[Ar]3d^a 4s^b$ can be written

$$a(a-1)J(3d, 3d)/2 + ab \, J(3d, 4s) + b(b-1)J(4s, 4s)/2 \quad (2.20)$$

and we avoid thinking too much about the problem of one-electron energies [see eq. (1.14)] and define energies $-\varepsilon_{3d}$ and $-\varepsilon_{4s}$ of a single electron

moving in the central field of the closed-shell configuration [Ar]. If we consider the element vanadium ($Z=23$), appropriate numerical values of the parameters are $\varepsilon_{3d}=500$ kK, $\varepsilon_{4s}=350$ kK, $J(3d, 3d)=120$ kK, $J(3d, 4s) =J(4s, 4s)=70$ kK, and we obtain the following energies in kK compared to the closed-shell ion V^{+5}:

q =	$3d^q$	$3d^{q-1}4s$	$3d^{q-2}4s^2$	
1	-500	-350	—	
2	-880	-780	-630	(2.21)
3	-1140	-1090	-990	
4	-1280	-1280	-1230	
5	-1300	-1350	$-1350.$	

There is no doubt that the radial functions in V^{+5} and V^0 are so different that the assumption of invariant ε and J parameters is not entirely fulfilled. However, eq. (2.21) shows something very important for the understanding of the energy levels in the beginning of a transition group: though the 3d orbital in the whole series of ionic charges considered is attracted 150 kK by the [Ar] core than the 4s orbital, the ground configuration of V^0 is $3d^34s^2$ and of V^+ $3d^4$ but very nearly coincident with the lowest terms of $3d^34s$, whereas it is $3d^3$ of V^{++} and $3d^2$ of V^{+++}. In other words, the relative size of the interelectronic repulsion parameters $J(3d, 3d)$ compared to $J(3d, 4s)$ and $J(4s, 4s)$ may have as a consequence that the 4s electrons are needed for the stability of the ionic charges 0 and $+1$, but *removed at first by ionization*, leaving [Ar]$3d^q$ as the lowest configuration for ionic charges at least $+2$.

This also shows how difficult it is to give a sensible definition of *experimentally determined orbital energies*. Slater has proposed considering the baricentres of the configurations which are split into more energy levels. This is very reasonable, but leads to some rather peculiar but unavoidable consequences. Before considering this problem, we must explain several features of the *multiplet term structure* of configurations involving *partly filled shells*.

The number of states of a configuration is the number of orthogonal wavefunctions Ψ it is possible to write. This number is one, if all the shells or subshells (i.e. the sets of degenerate orbitals) are fully occupied. If one shell or subshell with the degeneracy number e contains only one electron, the number of states is $2e$, but they are degenerate, forming one *energy level*, if we continue to neglect electrodynamic and relativistic effects. The same is true for $(2e-1)$ electrons in a single partly filled shell, that is one electron less than the maximum number possible. If q electrons occur in a single partly filled shell or subshell, the number of states is

$$\binom{q}{2e} = \frac{(2e)!}{q!(2e-q)!}.$$ (2.22)

This binomial expression is symmetric with respect to q and $(2-q)$. It is a much more fundamental rule, Pauli's hole equivalence, that not only the

number of states but also the symmetry types occurring of the energy levels, and their number, are identical for q electrons and q "holes" in a set of degenerate orbitals.

As long as we only consider electrostatic, and not electrodynamic effects we have the approximation of Russell-Saunders coupling, and the symmetry types of the total Ψ are of two types: the total spin S and the symmetry type L in spherical symmetry or Γ_n in lower symmetries. In analogy to eq. (2.2), the values of L have trivial names, *viz.*

$$L = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \quad 9 \quad 10 \ldots$$
$$ S \quad P \quad D \quad F \quad G \quad H \quad I \quad K \quad L \quad M \quad N \ldots \qquad (2.23)$$

and it has become customary to write $2S+1$ as left-hand superscript to the name of L or Γ_n. Thus, ^3F means a term with $L=3$ and $S=1$. S assumes integral non-negative values in systems with an even number of electrons and has then trivial names related to $2S+1$ and pronounced singlet $(S=0)$, triplet (1), quintet (2), septet (3), . . ., whereas systems with an odd number of electrons have S equal to a positive number being the sum of an integer and a half. The trivial names are doublet $(S=1/2)$, quartet (3/2), sextet (5/2), octet (7/2), ... The number of states participating in a multiplet term is $(2S+1)(2L+1)$. The term consists of one or more energy levels, which, in the latter case, can be separated by electrodynamic effects in the atom. An energy level is a number of absolutely degenerate states that can only be separated by interaction with an external electric or magnetic field decreasing the symmetry of the system, or by similar fields arising from the properties of the nucleus (hyperfine structure).

It is worth remarking that even or odd parity is also a symmetry type, and may be combined with both even or odd values of L. Many spectroscopists mark the terms of odd parity with a small circle, e.g. $^4S^\circ$ and $^2P^\circ$ of the configuration p^3 to be discussed below. For well-defined configurations, it is simply the parity of the sum of the l values which count.

One electron or one hole, i.e. $4l+1$ electrons, in the n, l shell produce the unique term $^2(l)$ as mentioned above. Two electrons or two holes produce $2l+1$ different terms, *viz.*:

$$^1S, \, ^3P, \, ^1D, \, ^3F, \, ^1G, \, ^3H, \, \ldots ., \, ^3(2l-1), \, ^1(2l). \qquad (2.24)$$

Three electrons or three holes are somewhat more complicated:

$$p^3: \quad ^4S, \, ^2D, \, ^2P$$
$$d^3, d^7: \, ^4F, \, ^4P, \, ^2G, \, ^2P, \, ^2H, \, ^2D, \, ^2F, \, ^2D' \qquad (2.25)$$
$$f^3, f^{11}: \, ^4I, \, ^4F, \, ^4S, \, ^4G, \, ^4D, \, ^2H, \, ^2G, \, ^2K, \, ^2D, \, ^2P, \, ^2I, \, ^2L, \, ^2H', \, ^2D', \, ^2F, \, ^2G', \, ^2F'$$

and it is noted that they frequently produce more than one term of the same symmetry type L, S. Hund's rule indicates that the lowest term has the maximum value of S combined with the highest value of L compatible with this

condition. Hund's rule does not indicate the order of the other terms, which at first sight seems somewhat irregular. Equation (2.25) attempts to arrange the L values of a given S according to increasing energy.

This is not the place to outline exactly how eq. (2.25) has been found, or how the similar results are obtained in general for a partly filled shell. We shall restrict ourselves to a list of the one or two lowest S values and the highest L among the following S values:

$$
\begin{aligned}
&d^4, d^6: && {}^5D, {}^3P, {}^3F, {}^3H, {}^1I, \ldots \\
&d^5: && {}^6S, {}^4G, {}^4P, {}^4D, {}^4F, {}^2I, \ldots \\
&f^4, f^{10}: && {}^5I, {}^5F, {}^5S, {}^5G, {}^5D, {}^3M, \ldots \\
&f^5, f^9: && {}^6H, {}^6F, {}^6P, {}^4M, {}^4I, {}^4K, {}^4L, {}^4F, {}^4G, {}^4H, {}^4P, {}^4D, \ldots \\
&f^6, f^8: && {}^7F, {}^5D, {}^5L, {}^5G, {}^5H, {}^5I, {}^5F, {}^5K, {}^5H', {}^5G', {}^5D', {}^5P, \ldots \\
&f^7: && {}^8S, {}^6P, {}^6I, {}^6D, {}^6G, {}^6F, {}^6H, {}^4N, \ldots
\end{aligned} \tag{2.26}
$$

Before returning to the actual calculation of interelectronic repulsion energy in simpler cases, such as p^q, we need not only the diagonal element of this energy, eq. (1.11) et seq., but also the rules for some simple non-diagonal elements. We do not treat here the general principles of perturbation theory and secular determinants, which can be seen in many books, even in "Absorption Spectra . . ." by the present writer.

If we have two different configurations which differ in more than two electrons, say Cabc and Cdef, where C is the common part of the two configurations, the nondiagonal element of the two-electron operator $1/r_{12}$ vanishes identically. If two configurations Cab and Ccd differ in two *spin orbitals* (i.e. orbital *and* spin characteristics), the nondiagonal element is

$$
\pm \left[\int \int \frac{1}{r_{12}} \psi_a \psi_c d\tau_1 \psi_b \psi_d d\tau_2 - \int \int \frac{1}{r_{12}} \psi_a \psi_d d\tau_1 \psi_b \psi_c d\tau_2 \right] \tag{2.27}
$$

where the sign of the nondiagonal element depends on the choice of the phase of the wavefunctions. The integration of each of the two terms vanishes very frequently, one necessary condition for

$$
\int \int \frac{1}{r_{12}} \psi_w \psi_x d\tau_1 \psi_y \psi_z d\tau_2 \neq 0 \text{ is } m_s(w) = m_s(x) \text{ and } m_s(y) = m_s(z). \tag{2.28}
$$

Another necessary condition is that the two products $\psi_w \psi_x$ and $\psi_y \psi_z$ have the same group-theoretical symmetry type Γ_n.

If two configurations differ by only the occupation of one spin orbital, Ca and Cb, the nondiagonal element is no longer as given in eq. (2.27), but is a summation over all spin orbitals ψ_k occurring in the common part C, *viz.*

$$
\pm \left[\sum_k \left(\int \int \frac{1}{r_{12}} \psi_a \psi_b d\tau_1 \psi_k^2 d\tau_2 - \int \int \frac{1}{r_{12}} \psi_a \psi_k d\tau_1 \psi_b \psi_k d\tau_2 \right) \right] \tag{2.29}
$$