QUARTERLY REVIEWS

ELECTRON CORRELATION AND CHEMICAL CONSEQUENCES

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Introduction.—Two or more electrons in a system exert a mutual effect. This occurs for two reasons :

(i) Electrons repel one another because all are negatively charged, and so they tend to keep apart, *i.e.*, have a low probability of being near one another ;

(ii) There is a more subtle effect arising from the demands of the Pauli principle which governs the form of the wave function. As a result, electrons having the same spin have a low probability of being near one another, while those having opposed spins have no tendency to keep apart in this way and are often drawn together.

Since chemical properties are electronic a real appreciation of inter-electron behaviour is essential to chemists. Because the consequences of the charge repulsion can, in principle, be readily understood, this article will deal more with the Pauli principle spin effect. Four idealised systems will be considered. First, the states of helium in which the $1s$ and the $2s$ orbital are occupied ; secondly, states of helium in which the $1s$ and the $2p$ orbital are occupied ; thirdly, systems in which from two to six electrons are confined in a ring ; and lastly, 1- and 2-dimensional boxes containing two electrons. The concepts of *hybridisation* and *exchange* which arise from the operation of the Pauli principle will be examined.

Finally, a few examples in which inter-electronic effects are important will be discussed in terms of the ideas derived from the idealised systems. Effects (i) and (ii) appear to be equivalent to the inductive and mesomeric effects of organic chemistry.

Helium $1s2s$ State.—The potential energy (V) of the helium atom consisting of two electrons of charge $-e$ and a nucleus of charge $+2e$ is given by

$$V = -\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} . \qquad . \qquad . \qquad . \qquad (1)$$

r_1 and r_2 being the distances of electrons 1 and 2 from the nucleus and r_{12} the distance between the electrons. To examine the Pauli-principle electron correlation (ii) more easily, we shall, at first, ignore the effect of electron repulsion on the distribution. Thus the expression for the potential energy

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will be taken to be

$$V = -\frac{2e^2}{r_1} - \frac{2e^2}{r_2} \qquad . \qquad . \qquad . \qquad . \qquad (1a)$$

with this approximation, the wave function for a state involving one $1s$ and one $2s$ electron which satisfies the Schrödinger equation will be a simple product of two independent functions [1]

$$\Psi = 1s(1) \cdot 2s(2) \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

where $1s(1)$ denotes the wave function of electron 1 in the $1s$ orbital and is

$$1s(1) = N_{1s} \exp(-\alpha r_1) . \qquad . \qquad . \qquad . \qquad (3)$$

N_{1s} and α being constants; $2s(2)$ denotes the wave function of electron 2 in the $2s$ orbital and is

$$2s(2) = N_{2s}(2 - \alpha r_2) \exp(-\tfrac{1}{2}\alpha r_2) \qquad . \qquad . \qquad . \qquad (4)$$

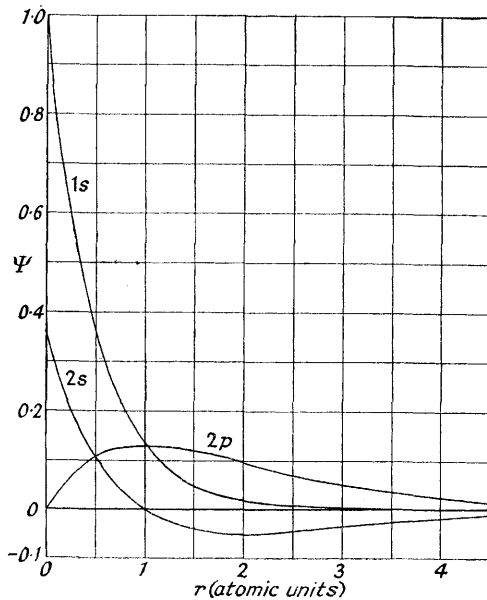N_{2s} being another constant (see Fig. 1).

Fig. 1

$1s$, $2s$, and $2p$ orbitals as functions of r (relative values of Ψ).

The electron distribution corresponding to eqn. (2) is spherically symmetrical, eqns. (3) and (4) being functions of r_1 and r_2 only. Consequently we shall plot the probability of finding simultaneously electron 1 in a spherical shell between r_1 and $(r_1 + dr_1)$ and 2 between r_2 and $(r_2 + dr_2)$ as a contour diagram. The probability $(P \, dr_1 \, dr_2)$ is given by

$$P \, dr_1 \, dr_2 = 4\pi r_1^2 \cdot 4\pi r_2^2 [1s(1)]^2 [2s(2)]^2 \, dr_1 \, dr_2 . \qquad . \qquad (5)$$

[1] Heitler, " Elementary Wave Mechanics ", Oxford Univ. Press, 1945.

Fig. 2 shows a contour diagram of P as a function of r_1 and r_2. This also gives the individual functions $4\pi r_1{}^2[1s(1)]^2$ and $4\pi r_2{}^2[2s(2)]^2$ of which P is a simple product. Fig. 2 shows that the probability of finding electron 1 at one radius and electron 2 at another is not the same as the probability of the configuration in which they are interchanged. Since the electrons are indistinguishable this is not acceptable as a solution to the problem. Clearly the solution of the wave equation in which electrons 1 and 2 are interchanged between the $1s$ and $2s$ orbitals would also satisfy the wave equations but would be equally unacceptable. There are, however, two solutions involving eqn. ($1a$) as the expression for the potential energy which would
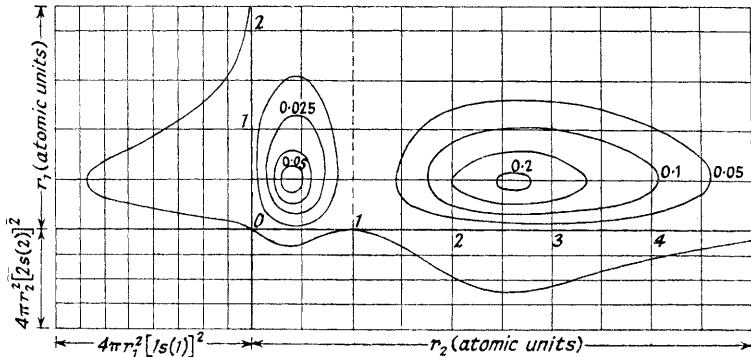

FIG. 2

Contour diagram of the probability of finding electron 1 at r_1 and 2 at r_2 for the unsatisfactory helium atom function $1s(1) \cdot 2s(2)$. On the left-hand side and below the main diagram are plotted the individual functions $4\pi r_1{}^2[1s(1)]^2$ and $4\pi r_2{}^2[2s(2)]^2$ (relative values of probabilities).

not be unsatisfactory in the above way yet still satisfy the Schrödinger equation. These are the combinations :

$$\Psi_S(1, 2) = \frac{1}{\sqrt{2}}[1s(1) \cdot 2s(2) + 1s(2) \cdot 2s(1)] \quad . \quad . \quad (6)$$

$$\Psi_A(1, 2) = \frac{1}{\sqrt{2}}[1s(1) \cdot 2s(2) - 1s(2) \cdot 2s(1)] \quad . \quad . \quad (7)$$

The factor $1/\sqrt{2}$ is included in eqns. (6) and (7) to ensure that the probability of finding electron 1 (and 2) in the whole of space is unity. The contour diagrams of probabilities

$$P_S = 4\pi r_1{}^2 \cdot 4\pi r_2{}^2 [\Psi_s(1, 2)]^2 \quad . \quad . \quad . \quad (8)$$

$$P_A = 4\pi r_1{}^2 \cdot 4\pi r_2{}^2 [\Psi_A(1, 2)]^2 \quad . \quad . \quad . \quad (9)$$

are shown in Figs. $3a$ and $3b$; for both the probability is unaltered by interchanging the positions of the two electrons and so eqns. (8) and (9) are acceptable. Figs. $3a$ and $3b$ show that eqns. (8) and (9) correspond to two different spatial distributions. For Ψ_S three configurations have high probability : two in which one electron is near the nucleus and the other further out, and the third in which both are simultaneously near the
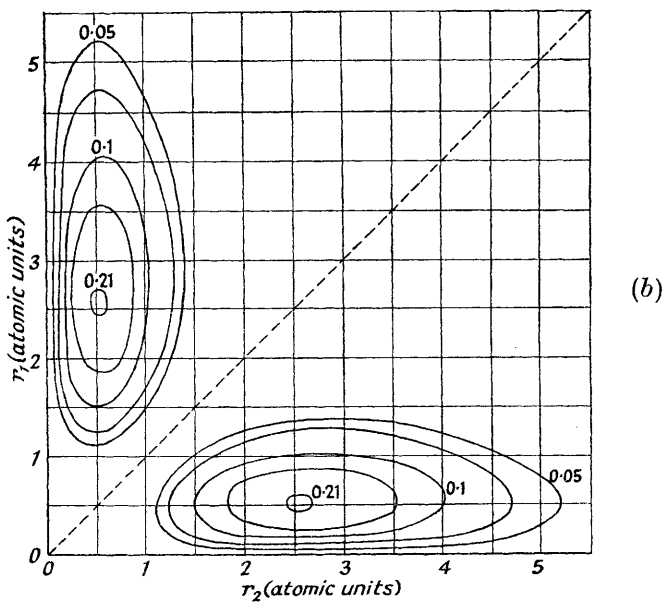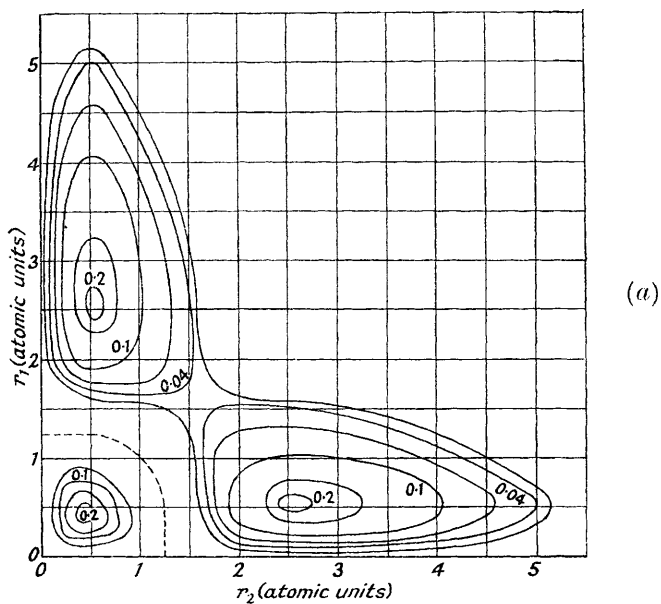
FIG. 3

Contour diagrams of the probability of finding electron 1 at r_1 and 2 at r_2 for the helium atom in the $1s^1 \cdot 2s^1$ state : (a) singlet (Ψ_S) ; (b) triplet (Ψ_A) (relative values of probabilities).

nucleus. Configurations of zero probability are shown by the dotted lines. For Ψ_A two configurations only have high probability. For both, one electron is near to and the other far out from the nucleus. The dotted line showing positions of zero probability is quite different from that for Ψ_S and is the line for which $r_1 = r_2$ so that for Ψ_A the two electrons have a zero probability of being at the same distance from the nucleus. The difference between Ψ_S and Ψ_A is therefore that for Ψ_S a configuration in which the two electrons are close together is favoured while for Ψ_A all configurations in which the electrons are close to one another have low probability.

There are two states of helium for which the $1s$ and the $2s$ orbital are both occupied. For one the electron spins are opposed (the singlet) and for the other the spins are parallel (the triplet). Ψ_S is the spatial solution when the spins are opposed and Ψ_A when they are parallel. The reason for this has been formulated in the Pauli principle which is a basic principle of quantum mechanics justified by the conclusions drawn from it. More detail as to why Ψ_S and Ψ_A are the space wave functions for the singlet and triplet states, respectively, and why the space wave function is controlled by spin states may be obtained from standard books.[1, 2] However, the important point is that the relation between the spins of the two electrons governs their spatial distribution. What consequences will this have on the energy of the two states ? Their energy, as we have considered them so far ignoring inter-electron repulsion, is the same, and is the sum of the energy of one electron in the $1s$ and one electron in the $2s$ orbital. This would be $(-4E_H) + (-E_H) = -5E_H$ where $-E_H$ is the energy of the hydrogen atom in the lowest state relative to the energy of the proton and the electron infinitely separated. Suppose that the two distributions corresponding to Ψ_S and Ψ_A are unaffected by electron repulsion, and consider what the mean electronic repulsion energy averaged over all mutual configurations will be. Because electrons mutually repel, this must be positive. It will be bigger for Ψ_S (Fig. 3a) than for Ψ_A (Fig. 3b) because Ψ_S favours configurations in which the electrons are close together, while Ψ_A favours configurations in which they are well separated, and those in which they are close together have low probability. Consequently, the energy of the singlet state (Ψ_S) will be greater than the energy of the triplet (Ψ_A). This is in accordance with Hund's empirical rule (see later).

If the energies are calculated in this way the inter-electronic repulsion energy for the singlet state (Ψ_S) is $+0.93E_H$ and that for the triplet state (Ψ_A) $+0.75E_H$. So the total energies are calculated to be $-4.07E_H$ and $-4.25E_H$ for Ψ_S and Ψ_A, respectively. The experimental energies are $-4.29E_H (\Psi_S)$ and $-4.35E_H (\Psi_A)$.

The calculated energy of the distribution represented by eqn. (2) in which there are no charge or Pauli-principle correlation effects is $-4.16E_H$. The calculated energy of the triplet state with no charge correlation but only Pauli-principle correlation corresponding to eqn. (7) is $-4.25E_H$. The

[2] Pauling and Wilson, " Introduction to Quantum Mechanics ", McGraw-Hill, New York, 1935.

true energy of the *real* state in which both types of correlation are operating is $-4\cdot35E_\mathrm{H}$. It appears that in this example the effect of Pauli-principle correlation on the energy of the triplet state is about the same as that of charge correlation.

For the singlet state the calculated energy corresponding to eqn. (6) is $-4\cdot07E_\mathrm{H}$. Because the Pauli-principle effect has brought the electrons together, the effect of charge correlation here is greater, and the true energy is $-4\cdot29E_\mathrm{H}$. The lowering by charge correlation is $0\cdot22E_\mathrm{H}$ as compared with $0\cdot10E_\mathrm{H}$ for the triplet state. This method of analysing the results might be criticised but it emphasises that the effects of charge and Pauli-principle correlations are comparable. Other methods of analysing the results would not alter this general conclusion, but the precise situation will vary from case to case.

Exchange.—The spatial distribution illustrated in Fig. 2 consists of the product of a distribution for electron 1 multiplied by a second independent distribution for electron 2. The coulomb interaction between these two distributions due to electron repulsion is easy to picture. But because of the nature of the functions (6) and (7) these states do not involve the product of two independent distributions for the two electrons. Consequently the interaction cannot be pictured simply as the coulomb interaction of two charge clouds. In one approximate treatment (the so-called first-order perturbation which we used in the previous section), the inter-electronic repulsion energy appears as the combination of two terms. The reason why two terms are involved is that the square of the wave function (giving the probability) involves terms of two types :

$$
\begin{aligned}
\Psi_S{}^2 &= \left\{ \frac{1}{\sqrt{2}}[1s(1)\cdot2s(2) + 1s(2)\cdot2s(1)] \right\}^2 \\
&= \frac{1}{2}\Big\{ [1s(1)]^2[2s(2)]^2 + [1s(2)]^2[2s(1)]^2 \\
&\qquad\quad + 2[1s(1)][2s(1)][1s(2)][2s(2)] \Big\} \quad . \quad . \quad (10)
\end{aligned}
$$

The first two terms on the right-hand side give rise to a coulomb interaction (C) and the third to the so-called exchange interaction (K), of the distributions $1s(1)\cdot2s(1)$ and $1s(2)\cdot2s(2)$. As a result the energy of the singlet state is calculated on this approximation to be $(C + K)$ and that of the triplet state $(C - K)$. In the previous section C and K were respectively $0\cdot84E_\mathrm{H}$ and $0\cdot09E_\mathrm{H}$. However, the fundamental point is that this exchange energy is the term which, in this particular treatment, takes account of the effect of mutual spin on spatial distribution, increasing the energy of the singlet and decreasing the energy of the triplet because of the tendency of the electrons to come together or keep apart in these two states, respectively.

Helium 1s2p.—The wave function of the $2p$ state (the effect of the other electrons being neglected) is

$$
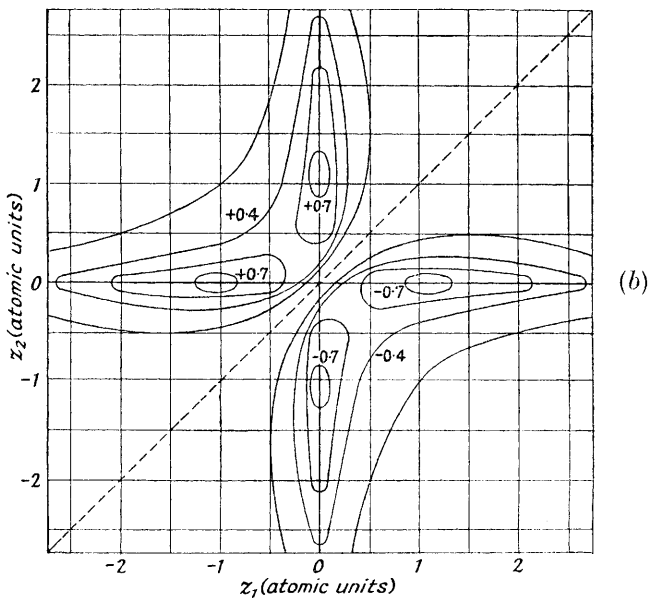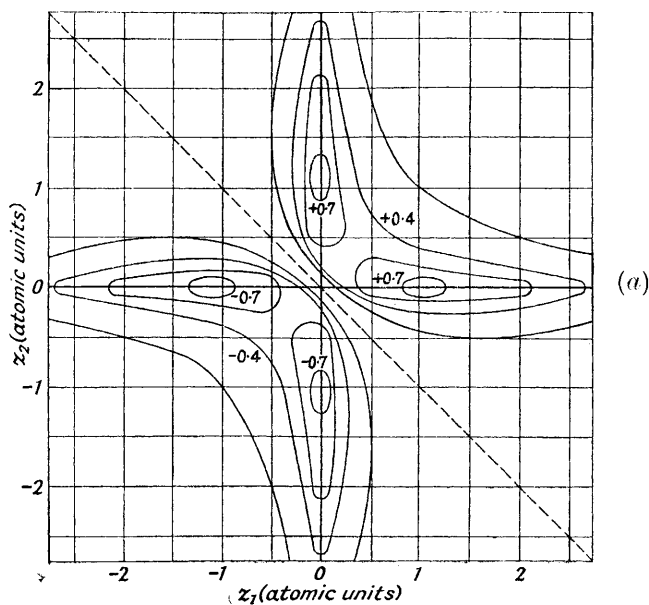2p(1) = N_{2p}r_1 \exp\left(-\alpha r_1\right)\cos\theta_1
$$

Fig. 4

*Contour diagram of the wave function as dependent on z_1 and z_2 (along the fixed axis)
for the helium atom in the $1s^1 \cdot 2p^1$ state : (a) singlet (Ψ_S) ; (b) triplet (Ψ_A) (relative
values of the wave functions).*

where N_{2p} is a constant and θ_1 is the angle between the line joining the electron to the nucleus (the origin) and a fixed axis, about which the wave function is symmetric. Our consideration will be limited to the points on the fixed axis, for it is along this that the $2p$ function is greatest, the values being shown in Fig. 1.

As in the previous example the wave function of the singlet state is

$$\Psi_S = \frac{1}{\sqrt{2}}[1s(1) \cdot 2p(2) + 1s(2) \cdot 2p(1)] \qquad . \qquad . \qquad (11)$$

and that of the triplet is

$$\Psi_A = \frac{1}{\sqrt{2}}[1s(1) \cdot 2p(2) - 1s(2) \cdot 2p(1)] \qquad . \qquad . \qquad (12)$$

The variation of these two functions with the positions of the two electrons, z_1 and z_2, along the fixed axis is shown in Figs. 4a and 4b.

For Ψ_S, configurations with the two electrons on the same side of the nucleus are favoured. For Ψ_A, the reverse is true and configurations in which electrons are on opposite sides are favoured. As with the last example the tendency of electrons having the same spin to keep apart is apparent. Here the form of the quantisation is such that they tend to be on opposite sides of the nucleus. It is this effect for s and p electrons with parallel spins that leads to such atoms as beryllium, mercury, etc., forming covalent bonds in opposite directions from the nucleus (bond angle $180°$). In molecules, negatively charged electrons bond together positively charged nuclei. Consequently if electrons with parallel spins tend to be on opposite sides of the nucleus they will be most efficient in binding other nuclei, if these are also on opposite sides of the nucleus.

Electrons in a Ring.—Systems in which the electrons are confined to a circle will now be used to illustrate these effects. Positions on the circle can be designated by an angle ϕ varying from 0 to 2π. If the potential energy of an electron is uniform for all points on the circle the wave functions for the one-electron system are

$$\Psi_m = \frac{1}{\sqrt{(2\pi)}} \exp(im\phi) \quad . \qquad . \qquad . \qquad (13)$$

where $1/\sqrt{(2\pi)}$ is the normalising constant and m, the quantum number, can be zero or any positive or negative integer ($i = \sqrt{-1}$). This can be verified by direct substitution into the appropriate wave function

$$\frac{1}{r^2}\frac{d^2\Psi}{d\phi^2} + \frac{8\pi^2\mu}{h^2}E\Psi = 0 \quad . \qquad . \qquad . \qquad (14)$$

The energy (E) is $m^2h^2/8\pi^2r^2\mu$ where μ is the electronic mass, and r the radius of the circle; the angular momentum is $mh/2\pi$.

For the one-electron case, in any state, the probability of finding the electron between ϕ and $(\phi + d\phi)$ is

$$\Psi_m\Psi_m{}^* \, d\phi = \frac{1}{\sqrt{(2\pi)}} \exp(im\phi) \cdot \frac{1}{\sqrt{(2\pi)}} \exp(-im\phi) \cdot d\phi = \frac{d\phi}{2\pi} \quad . \qquad (15)$$

The distribution is uniform as must be required. (This is one reason why

the wave functions in the imaginary rather than the real sine or cosine forms are to be preferred.)

Suppose there are two electrons, in the $m = 0$ and $m = +1$ states, the effects of inter-electronic forces being ignored as before. Then, if the electrons have opposed spins

$$\Psi_S = \frac{1}{\sqrt{2}}\left\{\left[\frac{1}{\sqrt{(2\pi)}}\right]\left[\frac{1}{\sqrt{(2\pi)}}\exp{(\mathrm{i}\phi_2)}\right] + \left[\frac{1}{\sqrt{(2\pi)}}\right]\left[\frac{1}{\sqrt{\pi(2)}}\exp{(\mathrm{i}\phi_1)}\right]\right\}. \quad (16)$$

and if they have parallel spins

$$\Psi_A = \frac{1}{\sqrt{2}}\left\{\left[\frac{1}{\sqrt{(2\pi)}}\right]\left[\frac{1}{\sqrt{(2\pi)}}\exp{(\mathrm{i}\phi_2)}\right] - \left[\frac{1}{\sqrt{(2\pi)}}\right]\left[\frac{1}{\sqrt{(2\pi)}}\exp{(\mathrm{i}\phi_1)}\right]\right\}. \quad (17)$$

then

$$\Psi_S\Psi_S{}^* = \left[\frac{1}{2\pi}\right]^2\{1 + \cos{(\phi_2 - \phi_1)}\} \quad . \qquad . \qquad . \quad (18)$$

$$\Psi_A\Psi_A{}^* = \left[\frac{1}{2\pi}\right]^2\{1 - \cos{(\phi_2 - \phi_1)}\} \quad . \qquad . \qquad . \quad (19)$$
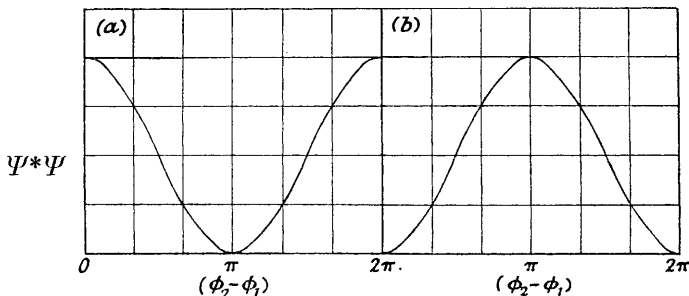

FIG. 5

$\Psi^*\Psi$ *for two electrons in a circle having* $m = 0$ *and* $m = 1$ *as a function of* $\phi_2 - \phi_1$:
(a) *singlet ;* (b) *triplet (relative values of* $\Psi^*\Psi$).

The probability distributions are shown graphically in Fig. 5. Again, when the spins are opposed the electrons tend to come together but when they are parallel they have a low probability of being near to one another. If the two electrons are in states m and n then

$$\Psi_S\Psi_S{}^* = \left[\frac{1}{2\pi}\right]^2\{1 + \cos{[(m - n)(\phi_2 - \phi_1)]}\} \quad . \qquad . \quad (20)$$

$$\Psi_A\Psi_A{}^* = \left[\frac{1}{2\pi}\right]^2\{1 - \cos{[(m - n)(\phi_2 - \phi_1)]}\} \quad . \qquad . \quad (21)$$

In this case $\Psi_S\Psi_S{}^*$ has a maximum when the electrons are coincident but there are in all $(m - n)$ similar maxima at intervals of $2\pi/(m - n)$. But $\Psi_A\Psi_A{}^*$ is at a minimum and zero when the electrons are coincident but there are in all $(m - n)$ configurations of zero probability. Again we find the situation that electrons with parallel spins have a zero probability of being in the same place. The above distribution depends on $(m - n)$ and

not on the absolute values of m and n. That is, it depends on the difference between the angular momenta of the two states. In the helium example it was noticeable that for the states in which the electrons differed in angular momentum $(1s, 2p)$ there was an angular correlation. This effect may therefore be considered as a "momentum" correlation.

When there are three electrons with parallel spins in states m, $(m + 1)$, and $(m + 2)$ (if $m = -1$ this will be the lowest quartet state), the most probable configuration is that in which the three electrons are as widely separated as possible (*i.e.*, at the corners of an equilateral triangle). Also any configuration in which two electrons are coincident has a zero probability.

For the three-electron system there are higher-energy quartet or doublet states in which the number of electrons with one spin is different from the number with the other. The spatial distributions are more complex and it is less easy to discuss any general pattern.

When there are four electrons, two having $m = 0$ and two $m = 1$, the most probable distribution is that in which two coincident pairs are at opposite sides of the circle. For configurations in which two of the electrons are separated by π and the other two by π also, there is a sinusoidal variation of probability as one pair is rotated with respect to the other. The maximum is when the pairs are coincident and the minimum when the four electrons are at intervals of $\pi/2$. However, the minimum probability is three-quarters of the maximum. Configurations in which three electrons are brought near to one another have a low probability, since in such a configuration two having the same spin must be near one another.

With six electrons in the lowest energy state (two each in $m = 0$, $+1$, and -1) the configuration of maximum probability is that in which three coincident pairs are at the corners of an equilateral triangle (cf. three- and four-electron cases). If three electrons are at the corners of one equilateral triangle and the other three at the corners of a second, the variation of probability as one triangle is rotated relative to the other is sinusoidal, the maximum being when the triangles are coincident and the minimum when the electrons are evenly distributed round the circle. The ratio of the maximum to the minimum probability is $9/5$. These last two cases exemplify the way in which, for ground states, the arrangement of maximum probability is that in which there are coincident pairs mutually oriented in the way that half the electrons distributed between the same orbitals and all having parallel spins would be oriented. This is a useful general rule. (See neon and methane later.)

Two Particles in One- and Two-dimensional Boxes.—The wave functions for a single particle restricted to a line of length L between 0 and L are $\sqrt{\dfrac{2}{L}} \sin \left[n\pi\dfrac{x}{L} \right]$, where n the quantum number is integral being the number of half-waves in the box. When there are two particles (*e.g.*, electrons) the lowest triplet state has the wave function

$$\Psi_A = \frac{\sqrt{2}}{L}\left[\sin\left(\pi\frac{x_1}{L}\right)\cdot\sin\left(2\pi\frac{x_2}{L}\right) - \sin\left(\pi\frac{x_2}{L}\right)\cdot\sin\left(2\pi\frac{x_1}{L}\right) \right] \quad . \quad (22)$$

and that for the corresponding singlet state is

$$\Psi_S = \frac{\sqrt{2}}{L}\left[\sin\left(\pi\frac{x_1}{L}\right)\cdot\sin\left(2\pi\frac{x_2}{L}\right) + \sin\left(\pi\frac{x_2}{L}\right)\cdot\sin\left(2\pi\frac{x_1}{L}\right)\right] \quad . \quad (23)$$

Contour diagrams of the squares of these functions are shown in Figs. 6a and 6b. For the first there are maxima when the particles are on opposite sides of the box and minima (zero) when the particles are in the same place. For the second there are maxima when the particles are simultaneously on the same side of the box.
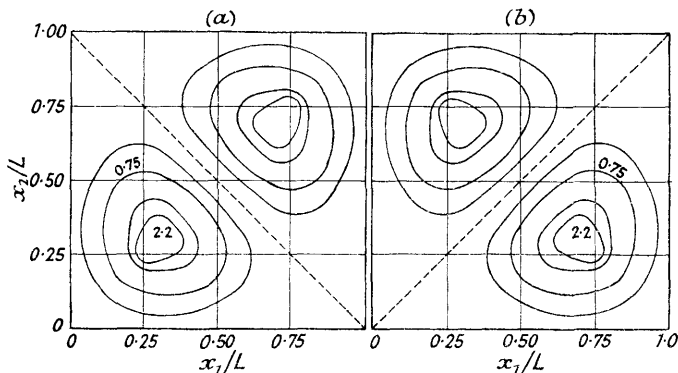

FIG. 6

Contour diagram of the relative probability of finding electron 1 at x_1 and 2 at x_2 in a one-dimensional box for the state in which the $n = 1$ and $n = 2$ levels are occupied : (a) singlet (Ψ_S) ; (b) triplet (Ψ_A).

Suppose we now represent the wave functions (22) and (23) in terms of hybrids H_+ and H_- which are

$$H_+(1) = \frac{1}{\sqrt{L}}\left[\sin\left(\pi\frac{x_1}{L}\right) + \sin\left(2\pi\frac{x_1}{L}\right)\right] \quad . \quad . \quad (24)$$

and

$$H_-(1) = \frac{1}{\sqrt{L}}\left[\sin\left(\pi\frac{x_1}{L}\right) - \sin\left(2\pi\frac{x_1}{L}\right)\right] \quad . \quad . \quad (25)$$

These are shown graphically in Fig. 7 and we find that

$$\Psi_A = \frac{1}{\sqrt{2}}[H_-(1)\cdot H_+(2) - H_-(2)\cdot H_+(1)] \quad . \quad . \quad (26)$$

and

$$\Psi_S = \frac{1}{\sqrt{2}}[H_+(1)\cdot H_+(2) - H_-(1)\cdot H_-(2)] \quad . \quad . \quad (27)$$

that is the forms (22) and (26) are *identical* and (23) and (27) are *identical*. One may ask : Which is preferable ? The answer is : It depends.

If we square Ψ_A we obtain for eqn. (26)

$$\Psi_A{}^2 = \frac{1}{2}\{[H_-(1)\cdot H_+(2)]^2 + [H_-(2)\cdot H_+(1)]^2$$
$$- 2[H_-(1)\cdot H_+(1)\cdot H_-(2)\cdot H_+(2)]\} \quad . \quad . \quad (28)$$
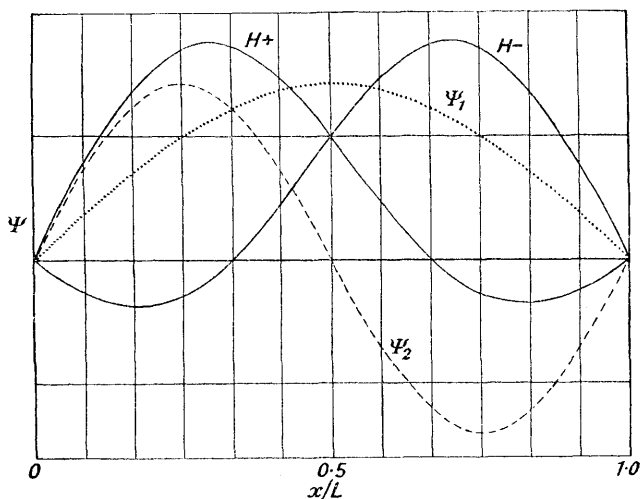
FIG. 7

The hybrid orbitals H_+ and H_- together with the basic one-particle orbitals $\sqrt{\dfrac{2}{L}} \sin\left(\pi\dfrac{x}{L}\right)$

(Ψ_1) *and* $\sqrt{\dfrac{2}{L}} \sin\left(2\pi\dfrac{x}{L}\right)$ (Ψ_2) *for a particle in a box.*

and, for (22)

$$\Psi_A{}^2 = \frac{2}{L^2}\left\{\left[\sin\left(\pi\frac{x_1}{L}\right)\cdot\sin\left(2\pi\frac{x_2}{L}\right)\right]^2 + \left[\sin\left(\pi\frac{x_2}{L}\right)\cdot\sin\left(2\pi\frac{x_1}{L}\right)\right]^2\right.$$
$$\left. - 2\left[\sin\left(\pi\frac{x_1}{L}\right)\cdot\sin\left(2\pi\frac{x_1}{L}\right)\cdot\sin\left(\pi\frac{x_2}{L}\right)\cdot\sin\left(2\pi\frac{x_2}{L}\right)\right]\right\} \quad . \qquad . \quad (29)$$

These consist of two squared terms and one exchange term. Figs. 8*a* and 8*b* show the contour diagrams for the two squared terms of eqns. (28) and of (29), respectively. It will be seen that Fig. 8*a* approximates more closely to the true distribution shown in Fig. 6*a* than does Fig. 8*b*, *i.e.*, the concept of one electron being in the H_+ and the other in the H_- orbital gives a clearer idea of the distribution than the concept of one being in the $\sin\left(\pi\dfrac{x}{L}\right)$ orbital and the other in the $\sin\left(2\pi\dfrac{x}{L}\right)$ orbital. A similar effect is found for Ψ_S. So, for the electron distribution for the state and for factors depending on this, the hybrid description presents a more convenient and revealing description (cf. shapes of molecules), but for transitions from one state to another (*e.g.*, in electronic spectra) then the description in terms of the basic one-electron function is more convenient and useful (cf. a similar treatment of the simple harmonic oscillator).[3]

Consider the corresponding two-dimensional problem of two electrons confined to a rectangular area of sides L_x and L_y. There are now two quan-

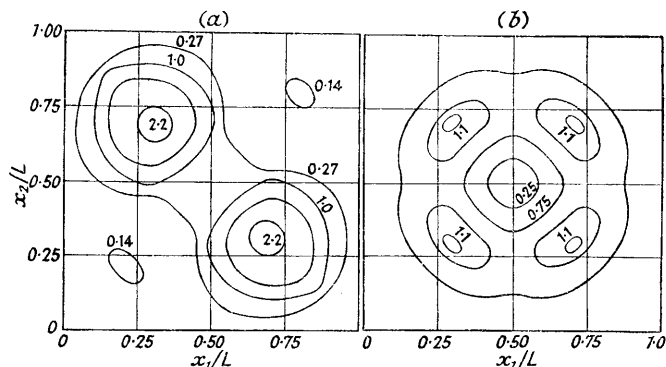[3] Lennard-Jones and Pople, *Proc. Roy. Soc.*, 1950, *A*, **202**, 166.

Fig. 8

Contour diagrams of

(a) $\{[H_-(1)\cdot H_+(2)]^2 + [H_-(2)\cdot H_+(1)]^2\}$

and

(b) $\left\{\left[\sin\left(\pi\dfrac{x_1}{L}\right)\cdot\sin\left(2\pi\dfrac{x_2}{L}\right)\right]^2 + \left[\sin\left(\pi\dfrac{x_2}{L}\right)\cdot\sin\left(2\pi\dfrac{x_1}{L}\right)\right]^2\right\}$

for two particles in a box for comparison with Fig. 6b, the diagram for the lowest triplet state (relative values of probabilities).

tum numbers n_x and n_y. Let the two occupied orbitals have (i) $n_x = 1$, $n_y = 1$, and (ii) $n_x = 1$, $n_y = 2$. For the triplet state

$$\Psi_A = \frac{2\sqrt{2}}{L_x L_y}\left\{\sin\left(\pi\frac{x_1}{L_x}\right)\cdot\sin\left(\pi\frac{y_1}{L_y}\right)\cdot\sin\left(\pi\frac{x_2}{L_x}\right)\cdot\sin\left(2\pi\frac{y_2}{L_y}\right)\right.$$
$$\left. - \sin\left(\pi\frac{x_2}{L_x}\right)\cdot\sin\left(\pi\frac{y_2}{L_y}\right)\cdot\sin\left(\pi\frac{x_1}{L_x}\right)\cdot\sin\left(2\pi\frac{y_1}{L_y}\right)\right\} . \qquad . \quad (30)$$

$$= \frac{2\sqrt{2}}{L_x L_y}\left\{\sin\left(\pi\frac{x_1}{L_x}\right)\cdot\sin\left(\pi\frac{x_2}{L_x}\right)\left[\sin\left(\pi\frac{y_1}{L_y}\right)\cdot\sin\left(2\pi\frac{y_2}{L_y}\right)\right.\right.$$
$$\left.\left. - \sin\left(\pi\frac{y_2}{L_y}\right)\cdot\sin\left(2\pi\frac{y_1}{L_y}\right)\right]\right\}$$

This equation shows that there is no spin correlation in the x direction because both n_x quantum numbers are the same. The correlation in the y direction is the same as in eqn. (22). So correlation occurs independently in the x and the y direction and is dependent on the momentum relation in the two directions. This is analogous to the case of helium. For the $1s,2s$ state in which both electrons had the same (zero) angular momentum there was no angular correlation, but only in–out (radial) correlation. On the other hand, for the $1s,2p$ state in which the angular momentum associated with each orbital is different, there is angular correlation. This form of behaviour is found in other problems.

Examples

In the remainder of the review examples from physical, inorganic, and organic chemistry of effects which are a consequence wholly or in part of electron correlation will be examined in general terms.

Hund's Rule and Russell–Saunders Coupling.—In the section dealing with helium with electrons in the $1s$ and the $2s$ orbital the energies of the triplet and singlet states were discussed. Because electrons with parallel spin tend to keep apart and those with opposed spins are drawn together when occupying different spatial orbitals, the energy of the triplet state must be less than that of the singlet. Moreover, this must be a general property of triplet and singlet states for which the orbital occupation is the same (at any rate for atoms in which direct magnetic interactions are small). This follows from the application of the Pauli principle and is the reason underlying Hund's rule.

On the basis of Russell–Saunders coupling, applied to a two-electron atomic system, states in which the electrons have the same individual n_1l_1 and n_2l_2 quantum numbers but different resultant L and S values have very different energies (coupling is large between l_1 and l_2 and between s_1 and s_2), but those having the same L and S but different J values have approximately the same energies (coupling between L and S is small). The reason why the coupling between l_1 and l_2 is large is because different L values correspond to the occupied orbitals having different relative orientations in space and so to different mean inter-electronic repulsion energies. States with different S values correspond to different spatial distributions of the electrons (for parallel and opposed spins), so the difference of energy arises again from inter-electronic charge effects and is therefore large. On the other hand, the interaction between L and S is a magnetic interaction, and is small for atoms of low atomic number. Therefore Russell–Saunders coupling is equivalent to saying that, in systems where it is applicable, charge interactions are large and magnetic ones small.

The Hydrogen Molecule and Electron-pair Bonds.—When two hydrogen atoms come together the electrons tend, as far as the electrostatic effects of the nuclei are concerned, to move into the internuclear region. The concentration of negatively charged electrons between the positive nuclei binds the nuclei together. However, electron correlation affects the extent to which this concentration can occur. Charge correlation clearly limits the extent to which the two electrons can be simultaneously in the internuclear region. If the electrons have parallel spin, spin correlation will also tend to keep them apart, and so the probability of the two electrons being simultaneously between the nuclei will be further reduced. The combined effect of these two correlation factors does, in fact, so reduce the charge concentration in the internuclear region that no bonding occurs and so this triplet state is purely repulsive. If the spins are opposed the electrons occupy the same molecular orbital of H_2 and there is no spin correlation (cf. two particles in a box). Charge correlation is alone insufficient to keep the electrons from the bonding region, and a stable molecule is formed.

The above is one way of stating the reasons why single bonds are formed by pairs of electrons with opposed spins, and consequently why the valency of an atom is equal to the number of " unpaired electrons ". Consider ammonia as an example. A nitrogen atom has three unpaired electrons. If three hydrogen atoms approach with electrons of opposed spins these

can enter the same region of space as the three electrons of the nitrogen atom, but the three pairs tend to keep apart from one another (and from the lone pair), so that the three hydrogen atoms are held in particular directions. Three directed bonds result and no more can be formed. Moreover if only two hydrogen atoms are attached it will be possible for the two NH_2 to bind together to give $NH_2 \cdot NH_2$.

Neon and Methane.—The neon atom has eight electrons in the L quantum shell, one $2s$ pair and three $2p$ pairs. For the carbon atom in the ^5S state there are four L electrons (one s, three p), having parallel spins. Because of the electrons' tendency to keep apart, by both charge and spin correlation, a regular tetrahedral configuration round the nuclei and K electrons has the highest probability. In the first part it was shown that three electrons having parallel spins in a ring tended in the lowest state ($m = 0$ and ± 1) to be equally spaced, and when there were three pairs these tended to exist with greatest probability as far as spin correlation is concerned as three close pairs. It is similarly found that spin correlation favours for neon a configuration of four close pairs at the corners of a regular tetrahedron.[4] Charge effects will tend to oppose the existence of " close " pairs just as in H_2. The electron distribution in C^{4-} will have the same general form as that of neon. Consequently methane which can be pictured as formed from C^{4-} by attaching four protons, will at equilibrium be a regular tetrahedron. The electron distribution will be most conveniently described in terms of tetrahedral, sp^3, hybrid orbitals (cf. two particles in a box), but the means of *description* (hybrid orbitals) should not be regarded as the *cause* of the molecule being tetrahedral (cf. also SiH_4, NH_4^+, and BH_4^-).

It may be that the tetrahedral character of the outer shells of neon, argon, krypton, and xenon is the reason why these elements in the solid state have the cubic close-packed structure like tetrahedral methane rather than the hexagonal one of helium, this being the form to be expected on simple theory for the Group 0 elements, the atoms being assumed to be spherical.[5]

Water, Hydrogen Sulphide, and Fluorine Monoxide.—The O^{2-} ion will have the same electron configuration as neon. To a first approximation, it would be expected, therefore, that the HOH angle would be $109\frac{1}{2}°$; in fact it is $104\frac{1}{2}°$. The four electron pairs in water are no longer equivalent. The two bonding pairs must be polarised by the presence of the protons so it is to be expected that the two bonding pairs will be " centred " further from the oxygen nucleus than the lone pairs. Consequently the four pairs will no longer tend to be oriented in the form of a *regular* tetrahedron, but both spin and charge correlations would cause the angle subtended by the bonding electrons to be less than that subtended by the lone pairs. Hence the reduction in the angle. The dipole moment of this and other molecules has been discussed in terms of such an approach to the electronic structure.[6]

With hydrogen sulphide the HSH angle is $92\frac{1}{3}°$. The S^{2-} ion is larger

[4] Linnett and Poe, *Trans. Faraday Soc.*, 1951, **47**, 1035.
[5] Cuthbert and Linnett, to be published.
[6] Coulson, " Valence ", Oxford Univ. Press, 1952, p. 209.

and more polarisable than the O^{2-} ion and sulphur is less electronegative than oxygen. Consequently the regular tetrahedral form of the electrons will tend to be distorted more in hydrogen sulphide than in water, and the angle in the former will deviate more from the regular tetrahedral angle than in the latter.

In fluorine monoxide the angle is $3°$ smaller than in water. Fluorine is more electronegative than hydrogen so that the regular tetrahedral form of the four pairs of O^{2-} is distorted more than in water. Repulsion between the lone-pair electrons on the fluorine atoms must tend to increase the inter-bond angle, and it is interesting that the effect of the four pairs round the oxygen atom seems to outweigh this. The same effect is observed in other fluorine compounds (e.g., NH_3, $106\frac{3}{4}°$; NF_3, $102°$; CH_2F_2, $\widehat{FCF} = 108°$).

Ethylene.—There are two ways of presenting the double bond of ethylene :

(a) as four electrons in one bonding σ orbital and in one bonding π orbital ; or

(b) as two electrons in an orbital which may be described as a " banana " shape and two in a second " banana " orbital equivalent to the first and a mirror image of it.

The description (b) is analogous in many ways to the Bayer formulation. It is improper to ask which of these is correct for they are in fact equal to one another. This can be seen by referring back to the case of two particles in a box for which the function written in terms of the H_+ and H_- hybrids was equal to that in terms of the one-electron orbitals. The σ and π orbitals are the basic one-electron orbitals of the ethylene system in the C–C region. But the hybrid orbitals $(\sigma + \pi)(H_+)$ and $(\sigma - \pi)(H_-)$ can be used to describe the system, and these $(H_+$ and $H_-)$ orbitals are the Bayer type equivalent " banana " orbitals. Moreover, just as the H_+ and H_- were the more suitable orbitals for describing the electron distribution for the box system, so they are also the most suitable for describing the electron distribution of the double bond. Daudel et al.[7] have shown that in ethylene two electrons with parallel spins tend to be on opposite sides of the molecular plane, a feature not brought home by the σ/π description, but which can be realised easily on the " banana " orbital description.

From the chemical point of view, which is concerned with the electronic ground state, it is possible that the σ/π description has been over-stressed, but both for electronic excitation and for ionisation the basic one-electron orbitals $(\sigma$ and $\pi)$ provide the most useful description. For the ground states the other (hybrid) description draws attention to the fact that for ethylene the tendency is for four electron pairs to be at the corners of a nearly regular tetrahedron round each carbon atom remains.

The same is true for acetylene (and nitrogen),[8] where one can describe the triple bond in terms of one σ and two π orbitals (the basic one-electron orbital) or in terms of three equivalent hybrids of these which are similar in form to the ethylene hybrids and which stress the tendency that the three

[7] Daudel, Brion, and Odiot, *J. Chem. Phys.*, 1955, **23**, 280.

[8] Lennard-Jones, *ibid.*, 1952, **20**, 1024 ; *Discuss. Faraday Soc.*, 1951, **10**, 9.

electron pairs shall tend to be symmetrically disposed round the C–C axis (cf. three electron pairs in a ring). Again, each carbon has four pairs disposed round it in a nearly regular tetrahedral configuration.

This tendency to surround itself by four tetrahedrally arranged pairs is a marked characteristic of the carbon atom. The mutual effects within this group can be stressed by further examples.

In ethylene the two electron pairs in the double bond tend to be drawn towards the C–C axis with the result that the angle they subtend at each carbon atom in the most probable configuration is less than $109\frac{1}{2}°$. As a result the other two pairs tend to subtend an angle greater than $109\frac{1}{2}°$ because of the tendency of electron pairs to separate as a result of spin and charge correlation. The consequence is that the HCH angle in ethylene is greater than $109\frac{1}{2}°$.

With *cyclo*propane because the CCC angles are 60° the electron pairs bonding the ring tend to be drawn in to subtend an angle less than $109\frac{1}{2}°$ but not as small as 60°. The result is that the bonds binding the carbon ring are " banana " bonds, while the HCH group resembles somewhat the same group as in ethylene.

The bending vibrations of methane show the same effect in that the distortion in which opposite CH_2 angles are decreased equally is more difficult (for a given angular distortion) than that in which one CH_2 angle is decreased and the opposite one is increased. The above examples show the way in which modifying the angle between two pairs has a consequent modifying effect on the other two pairs. This is usually explained in terms of hybridisation but such a formulation is only a means of representing the spin correlation.

Oxygen and Nitric Oxide.[9]—In ethane there are seven electron pairs (excluding the K electrons). Each carbon has four tetrahedral pairs, one pair being between the carbon atoms (cf. F_2). In acetylene there are five electron pairs (excluding the K electrons). Each carbon has four tetrahedral pairs, three pairs being in the region between the two carbon atoms (cf. N_2). In the oxygen molecule there are (besides the K electrons) five of one spin and seven of the other. It seems, therefore, that the seven should be distributed as the pairs in ethane (or F_2) and the five as the pairs in acetylene (or N_2). The " double " bond of oxygen in the ground state may therefore be regarded as the sum of half a triple and half a single bond. The first two excited states of oxygen, both singlets, have the same bond lengths and force constants as the ground state so that the number of bonding electrons is still four and there are two sets of six each distributed like the pairs in ethylene. (The two states differ in the mutual orientation of the two sets.) It seems that the ground state of oxygen has the lowest energy because the electrons tend to be kept apart more than in the singlet states. This description is equal to the more usual molecular-orbital description and the wave functions of one can be transformed into those of the other. The description in terms of one single- and two three-electron bonds also seems to be the same in principle. In the nitric oxide molecule also the number of

[9] Linnett, *J.*, 1956, 275.

electrons of one spin is not equal to the number with opposite spin.   Accordingly the bond may be regarded as a five-electron one, there being three of one spin and two of the other in the bond region.   This is the reason why nitric oxide does not behave chemically as a free radical like methyl and does not tend to dimerise.   To form $O=N-N=O$ both nitrogen–oxygen bonds would have to reduce their electron content by one electron in order to form the two-electron N–N bond.   The result is that there is no net gain in the number of bonding electrons.   The situation with two methyl groups combining to form ethane is entirely different and this is the reason why NO and O_2 behave quite differently from such free radicals as CH_3, CN, Cl, etc.

Diborane.—In the late forties three apparently different structures were suggested for this.   One involved resonance between the two structures (I) and (II)
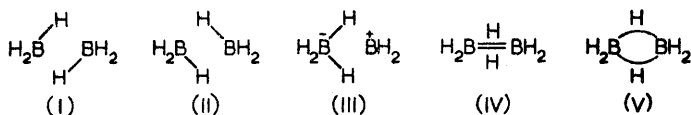

with perhaps some admixture of two ionic structures like (III).   There was also the protonated double-bonded structure (IV) and finally the structure (V) involving two three-centre bonds.   By the same argument as has been given for ethylene, we see that there is no difference between structures (IV) and (V) if full account is taken of the fact that electrons are identical and of the Pauli principle.

What is the difference between structure (V) and resonance between (I) and (II) ?   The answer is surely that there is no difference in principle ; they differ in the extent to which electron correlation is introduced and it is probable that forms (I) and (II) in resonance overemphasise electron correlation.   It will be seen that (I) and (II) in resonance allow zero probability for the configurations in which the two electron pairs are simultaneously in the two B–H bonds of one boron atom.   On the other hand formulation (V) allows this configuration equal probability with that in which the two pairs are in the B–H bonds of separate boron atoms.   For (V) the only restriction is that one pair is in one three-centre bond and the other pair in the other.   It is probable that (V) allows too little for electron correlation. Probably the best treatment is that in which an optimum proportion of two structures of type (III) is included with (I) and (II) (cf. Hamilton [10]). The various formulations are not fundamentally different.   They are different approximations to the truth and take into account to a differing degree the mutual effect of the electrons.

A similar equivalence of structures to that of (IV) and (V) is found in two apparently diverse representations of the molecular complex $(C_2H_4X)^+$, postulated as an important intermediate in the addition reactions of ethylene. Dewar [11] writes $C_2H_4Br^+$ as a " π-complex " (VI) ; this is equivalent in the

[10] Hamilton, *Proc. Roy. Soc.*, 1956, *A*, **235**, 395.
[11] Dewar, " The Electronic Theory of Organic Chemistry ", Oxford Univ. Press, 1949, p. 143.
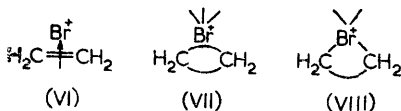
diborane sense to formulation (VII) where the straight lines represent electron pairs. Roberts and Kimball,[12] on the other hand, write this as (VIII), which differs from formulations (VI) and (VII), but the difference between the " π-complex " and " cyclic " structures is much less than sometimes assumed.

Directed Valency with Electrons in d-Orbitals.[13]—Directed valency in these systems can also be explained in terms of the configurations of maximum probability. In SF_6 the six pairs tend to be at the corners of a regular octahedron. With $Fe(CN)_6{}^{4-}$ the situation is similar, the three non-bonding d-pairs being in addition towards the edges of the octahedron. If two electrons are removed from this $Fe(CN)_6{}^{4-}$ system of 18 electrons [as in $Cr(CN)_6{}^{4-}$ and $Mn(CN)_6{}^{3-}$] there are several different ways in which the employment of the central atom orbitals might be decreased. Two electrons might be removed from one $4p$ orbital (strictly speaking, the orbital to which the $4p$ makes its contribution), leaving the system diamagnetic. This does not happen for the new ions have a paramagnetic moment corresponding to two unpaired electrons. Moreover, calculation shows that, for the system $d^2d^2d^2d^2d^2s^2p^2p^2$, there is a *zero* probability of six pairs' being simultaneously at the corners of a regular octahedron. So such an electronic system would be ill-suited for binding six cyanide ions in an octahedral configuration, and any other is probably ruled out by repulsion between the cyanide ions. A similar argument obtains for an electronic configuration $d^2d^2d^2d^2d^2s^2p^2p^2p^1p^1$. However the configuration $d^2d^2d^2d^1d^1s^2p^2p^2p^2$ does have a high probability for a configuration in which there are six pairs at the corners of an octahedron, the two electrons having, in effect, been removed from the non-bonding set directed towards the edges of the octahedron. On the other hand in $Ni(CN)_4{}^{2-}$, which has the same number of valency-shell electrons for consideration as $Cr(CN)_6{}^{4-}$ (namely 16), the ion is diamagnetic and the electronic structure is $d^2d^2d^2d^2d^2s^2p^2p^2$ as far as the employment of the nickel orbitals is concerned. This is possible for this ion since the structure which has lost two electrons from one $4p$ orbital is capable of providing with high probability four pairs at the corners of a square.

The ion $Mo(CN)_8{}^{4-}$ is interesting since the structure $d^2d^2d^2d^2d^2s^2p^2p^2$ provides, as a consequence of spin correlation, eight pairs with the highest probability in precisely the dodecahedral form found experimentally. Moreover, the calculated inter-bond angles are almost exactly the same as those observed (calc. $70°$ and $146°$; obs. $68°$ and $146°$).

The *trans*-effect in, for example, four co-ordinated platinum can be understood in general terms as a consequence of spin correlation. For

[12] Roberts and Kimball, *J. Amer. Chem. Soc.*, 1937, **59**, 947.
[13] Linnett and Mellish, *Trans. Faraday Soc.*, 1954, **50**, 665.

two particles in a rectangle, we saw that electrons could exert mutual spin-correlation effects in one direction independently of any effect in a direction at right angles.

Complex ions of the transition elements have been treated both on the basis of Pauling's valence-bond method and by crystal (or ligand) field theory. It seems that the former stresses the importance of spin correlation effects while the latter stresses electrostatic effects (*i.e.*, charge correlation). Undoubtedly both must be important.

Structure of Benzene.—The important feature of the benzene molecule is the group of six electrons in π-orbitals. In the ground state these will be paired off in the three lowest orbitals. In the first half of this Review the idealised situation of electrons confined to a circle was examined. It was shown that three electrons with parallel spins occupying the three lowest orbitals tended to be spaced equally round the ring. With three pairs the most probable configuration was that in which three close pairs were equally spaced, though the configuration in which the six electrons were equally spaced has a probability about half that of the close-pair configuration.

The molecular-orbital description of benzene is of two electrons each in the orbitals represented by (IX), (X), and (XI). [(IX) is nodeless and (X) and (XI) both have nodes as marked by the short lines on the circles.[14]]
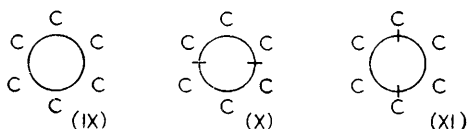
This occupation of the orbitals really implies the correlated distribution round the ring already described so there is more qualitative similarity between the molecular-orbital description and the resonance description [between structures (XII) and (XIII)] than is sometimes supposed.
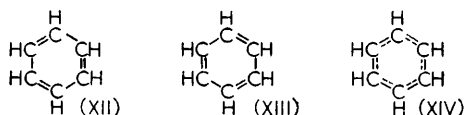
It seems that (contrary to normal consideration) resonance with structure (XIV) should also be included where each dotted line represents a single electron. Perhaps ionic structures should be included with reduced weight but the molecular-orbital treatment overweights the contributions of such structures. That is, a molecular-orbital treatment, while naturally including spin correlation if the full wave function is used, does not allow for charge correlation at all, whereas resonance by a judicious choice of contributing structures can make some allowance for this charge correlation.

Substituted Benzenes.—A group attached to the nucleus affects the electron distribution in the ring. Thus, in $C_6H_5 \cdot NH_3^+$ the electrons in the

[14] Bayliss, *Quart. Rev.*, 1952, **6**, 319.

σ bond joining the nitrogen to the ring are drawn towards the positively-charged $NH_3{}^+$ group. The result is that the effective electronegativity of the ring carbon atom attached to the nitrogen is increased. This is the inductive effect and is simply an example of charge correlation.

The inductive effect tends to favour one of the π-electron pairs being located on this carbon atom. As a consequence, the other two pairs will, by spin correlation, tend to concentrate on the two *meta* carbon atoms. This is an example of the " mesomeric " effect. Likewise a group which releases the electrons of the bond attaching it to the ring carbon atom will lower the tendency of a π-electron pair to be near that carbon atom and consequently the three pairs will tend to concentrate at the *ortho* and the *para* positions. In both cases the inductive effect directs the mesomeric effect. An important consequence of this is that ionic attacking species will be directed according to the nature of the attached group.

In pyridine there are again six π-electrons to consider but now one pair will tend to be drawn on to the nitrogen atom because of its greater electro-negativity. This will favour the other pairs' being near the β carbon atoms as a consequence of spin correlation. This is where cationoid reagents will attack, whereas anionoid reagents such as $NH_2{}^-$ will attack the α and the γ positions.

When a group such as hydroxyl or halogen is attached to the ring the situation is different since such a group possesses lone-pair electrons in a p orbital which has similar symmetry with respect to the plane of the ring to the π-orbitals. The region to be considered now is therefore a ring with an attached box which may be represented by (XV). In this the location

(XV)   (XVI)   (XVII)   (XVIII)
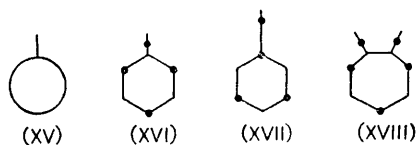
of four pairs must be considered. In phenol the tendency of the lone pair from the hydroxy-group to spread towards the ring will, by spin correlation with the other three pairs, tend to concentrate these in the *ortho* and the *para* positions (mesomeric effect). This is illustrated by (XVI). (This and the following diagrams indicate where the electrons tend to concentrate ; only a very slight localisation occurs, of course.) The inductive effect still operates in this case, tending to draw charge towards the oxygen atom. It does not direct the mesomeric effect but opposes it. If a cyano-group is attached to the ring the greater electronegativity of the nitrogen results in the π-electrons of the triple bond being drawn to that atom so that the carbon becomes an acceptor of π-electrons from the ring and the situation is as illustrated in (XVII). Here the inductive and mesomeric effects enhance one another. A more complex situation is that provided by tropolone, the correlation for which is illustrated (in XVIII).

From a naïve point of view, the permanent electron distribution in the isolated conjugated system determines the points of attack by ionic reagents,

as assumed previously. A more sophisticated theory would consider instead the stabilising influence or otherwise of the substituent group on the transition complex which is composed of both the benzene ring and the attacking species. But the general principles applied here to the isolated ring apply equally well to the transition complex and lead to identical conclusions.

Conjugated Chains.—In butadiene the four electrons in the π-orbitals can be regarded as being in a box occupying the lowest two orbitals. This situation is clearly illustrated by the one-dimensional box discussed earlier. In particular the H_+ and H_- hybrids show how the electrons will tend to be at opposite ends of the box but will spread to some extent over the central region. This situation clearly exists in butadiene : the end C–C bonds are shorter than the central C–C bond which is itself shorter than the bond in ethane. Again the correlation is illustrated by the resonance structures $CH_2{=}CH{-}CH{=}CH_2$, $\overset{..}{C}H_2{-}CH{=}CH{-}\overset{+}{C}H_2$, and $\overset{+}{C}H_2{-}CH{=}CH{-}\overset{..}{C}H_2$, the last two being weighted less than the first.

A similar situation exists in the system $C{=}C{-}C{=}O$. But here the " potential energy in the box " is not uniform so that one pair tends to move towards the oxygen atom. The other pair will therefore be drawn towards the middle carbon atom. Consequently anionoid reagents, such as $\overset{-}{C}H(CO_2Et)_2$, will tend to attack the end carbon atoms rather than the middle one. This arises because the pair of electrons tends to spread to the greatest extent it can and the correlating effect of the other pair is reduced because of the electronegativity of the oxygen atom.

It is clear that other effects of correlation (*e.g.*, alternating polarity, strengths of acids, etc.) can be discussed along these lines.

Conclusion.—The examples in this Review have been chosen from such diverse fields as atomic spectra, stereochemistry, and mechanism of organic reactions in an endeavour to illustrate the wide influence of spin- and charge-correlation effects.

The viewpoint developed is one based on cognition of three categorical principles : (1) the Coulombic law of force, (2) the Pauli principle, and (3) the indistinguishability of electrons. These are considered to be " causes " underlying problems of valency. Concepts such as " hybridisation ", " resonance ", and " exchange " are treated as convenient mathematical *descriptions* but not *explanations* of phenomena.