



## ON THE SHAPES OF ATOMS

*Common discussions of the electronic configuration of atoms, their total angular momenta, Hartree's SCF method and nuclear quadrupole coupling constants, as well as applications of the valence-bond approach to molecular structure, imply that isolated open-shell atoms are not necessarily spherical. A critical examination of this problem is made, it being shown how quantum mechanics predicts that all isolated atoms are effectively spherical.*

### 1 — INTRODUCTION

«What is the shape of an atom?» This is a question that may seem totally trivial, especially nowadays when children soon incorporate the word «atoms» into their language and learn to think of them simply as very tiny balls of matter. Most authors of introductory chemistry textbooks and teachers certainly seem to conform to that view. In fact, the idea of spherical isolated atoms is initially tacitly accepted and even widely transferred, with some success, to situations when atoms are no longer isolated, for example, in metals and ionic crystals, thus enabling the definition of quantities such as (effective) atomic radii. In the case of covalent molecular systems, conceptual models such as covalent radii, or physical models, for example the stick-and-ball models (or even the space-filling ones), also serve to cement that idea; when it is made clear that one cannot, in such circumstances, rigorously speak of spherical individual atoms, it is usually said or implied this is only because atoms were brought too close together. So, the discussion of atomic shapes may seem of little interest. However, when discussing orbitals and the electronic configurations of atoms, or the valence-bond approach to molecular structure, it is commonly implied, often by the same authors that have before assumed atoms as spherical, that open-shell atoms are not necessarily spherical. Also, some discussions of the total angular momentum of atoms and of nuclear quadrupole coupling constants suggest the same. Hence, the question is not so trivial as it might seem. In this paper, I try to tackle these varied aspects of the problem and show that, in fact, *all* isolated atoms, including those showing orbital angular momentum or nuclear quadrupole couplings, must be regarded as effectively spherical. The same will of course be true of atoms in an environment having no preferred direction.

### 2 — CLOSED-SHELL ATOMS

The shape of an atom is, of course, determined by the electron cloud surrounding the nucleus. More precisely, it is defined by the angular (with

respect to the nucleus) dependence, if any, of the total electron probability density. If this is spherically symmetric the atom is then regarded as spherical.

The total electron density  $\rho_T$  given by quantum mechanics for a closed-shell atom has spherical symmetry. In fact (in the orbital approximation),  $\rho_T$  is given as the sum of all the one-electron densities  $\Phi_\mu^* \Phi_\mu$  (or  $\Phi_\mu^2$  if  $\Phi_\mu$  is real)

$$\rho_T = 2 \sum_{\mu}^{\text{occ.}} \Phi_\mu^* \Phi_\mu, \quad (1)$$

the various  $\Phi_\mu$  being the (doubly) occupied (orthonormal) atomic orbitals; in addition, the sum of the  $2\mu^2 + 1$   $\Phi_\mu^* \Phi_\mu$  density functions corresponding to the same orbital angular momentum quantum number  $l$  is spherically symmetric.

This latter statement is known as Unsold's theorem (1) and can easily be verified for p, d... orbitals. For example, for a set of three degenerate p-orbitals, we have the angular independent result:

$$\begin{aligned} \Phi_{p_x}^2 + \Phi_{p_y}^2 + \Phi_{p_z}^2 &= A^2(r) \cos^2 \theta_x + \\ &+ A^2(r) \cos^2 \theta_y + A^2(r) \cos^2 \theta_z = A^2(r) \end{aligned} \quad (2)$$

$\theta_x$ ,  $\theta_y$  and  $\theta_z$  being the angles defined by the position vector  $r$  with the x, y and z axes, respectively ( $\cos^2 \theta_x + \cos^2 \theta_y + \cos^2 \theta_z = 1$ ) (1). This is a conclusion that ought never to be neglected in the teaching of the orbital picture of atoms. Specially, since the emphasis given to graphical representations and models of orbitals may easily mislead the unwarned student, as far as the total electron cloud is concerned. For the purpose of graphically illustrating expression 2, for example, the usual representations of the angular parts of  $\Phi_p$  or  $\Phi_p^2$  are not adequate.

The same is true even of the isodensity contour representations (2); these correctly give the effective shape of the electron cloud associated with a given p atomic orbital (a. o.), but do not lead, in an obvious graphical manner, to the circular contours corresponding to  $A^2(r)$  in 2. For this

matter, more appropriate atomic orbital representations are the variable density clouds as illustrated in fig. 1.

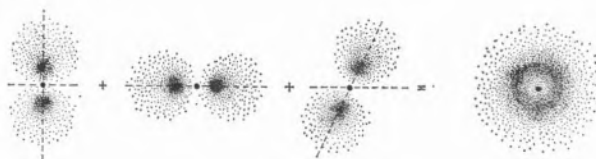


Fig. 1

Graphical illustration of the spherical symmetry of the probability density function for a set of degenerate 2p orbitals

That 1 holds (for orthonormal a. o.s.) can be proved as follows. The normalized wavefunction for a closed-shell atom ( $N$  electrons,  $N/2$  orbitals,  $N$  spin-orbitals) is given by the Slater determinant (2)

$$\begin{aligned} \Psi(1,2,\dots,N) &= \\ &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \Phi_a(1)\bar{\Phi}_a(1)\Phi_b(1)\dots\Phi_t(1)\bar{\Phi}_t(1) \\ \Phi_a(2)\bar{\Phi}_a(2)\Phi_b(2)\dots\Phi_t(2)\bar{\Phi}_t(2) \\ \dots\dots\dots \\ \Phi_a(N)\bar{\Phi}_a(N)\Phi_b(N)\dots\Phi_t(N)\bar{\Phi}_t(N) \end{vmatrix} = \\ &= \frac{1}{\sqrt{N!}} [\Phi_a(1)\bar{\Phi}_a(2)\dots\bar{\Phi}_t(N) - \Phi_a(2)\bar{\Phi}_a(1)\dots \\ &\dots\bar{\Phi}_t(N) + \dots] \end{aligned} \quad (3)$$

there being  $N!$  products in the expanded form of  $\Psi^* \Psi(1,2,\dots,N)$ . The  $N$ -electron function  $\Psi^* \Psi$  will then contain  $(N!)^2$  products of the form

$$\pm [\Phi_a^*(i) \bar{\Phi}_a^*(j) \dots \bar{\Phi}_t^*(k)] [\Phi_a(i') \bar{\Phi}_a(j') \dots \Phi_t(k')] \quad (4)$$

We now want to know the probability density function for electron 1,  $\rho_1$ , regardless of spin, the other electrons being anywhere. This is obtained by

(1) It is noted that the sum  $\Phi_{p_x} + \Phi_{p_y} + \Phi_{p_z}$  is angularly dependent.

(2)  $\Phi_a$  stands, as usually, for  $\Phi_{a\alpha}$  and  $\bar{\Phi}_a$  for  $\Phi_{a\beta}$ ,  $\alpha$  and  $\beta$  being the electron spin functions.

integrating  $\Psi^* \Psi$  over the spatial ( $\tau$ ) and spin ( $\sigma$ ) coordinates of electrons 2,3,...N and over the spin coordinates of 1:

$$\rho_1 = \int \Psi^* (1,2, \dots N) \Psi (1,2 \dots \dots N) d\sigma_1 d\sigma_2 d\tau_2 \dots d\sigma_N d\tau_N \quad (5)$$

Of the  $(N!)^2$  products (4) only those with

$$i = i' \quad j = j' \dots k = k' \quad (6)$$

have a non-zero contribution to  $\rho_1$ , because of spin-orbital orthogonality<sup>(1)</sup>. The number of products obeying 6 and having  $i = i' = 1$  is  $(N-1)!$ , corresponding to the  $(N-1)!$  permutations of the remaining  $N-1$  electrons 2,3,...N among the  $N-1$  spin-orbitals  $\bar{\Phi}_a, \Phi_b, \dots \bar{\Phi}_t$ ; each product contributes  $\Phi_a^*(1) \Phi_a(1)$  to  $\rho_1$ . We thus have a first contribution to  $\rho_1$  equal to  $(N-1)! \Phi_a^*(1) \Phi_a(1)$ . If we now consider all other products 4 obeying 6, but with  $j = j' \neq 1, \dots k = k' \neq 1$ , we get, similarly, the additional contributions:  $(N-1)! \Phi_a^*(1) \Phi_a(1)$ , twice  $(N-1)! \Phi_b^*(1) \Phi_b(1)$ , etc. Hence,

$$\rho_1 = 2[\Phi_a^*(1)\Phi_a(1) + \Phi_b^*(1)\Phi_b(1) + \dots \dots + \Phi_t^*(1)\Phi_t(1)]/N \quad (7)$$

where account has been taken of the squared normalization factor  $(N-1)!/N! = 1/N$ .

Since identical expressions are obviously obtained for  $\rho_2, \dots \rho_N$ , we have finally

$$\begin{aligned} \rho_T &= \sum_{i=1}^N \rho_i = \frac{2}{N} \sum_{i=1}^N \sum_{\mu}^{\text{occ.}} \Phi_{\mu}^*(i) \Phi_{\mu}(i) = \\ &= 2 \sum_{\mu}^{\text{occ.}} \Phi_{\mu}^* \Phi_{\mu} \end{aligned} \quad (8)$$

It must be noted that it has been assumed that the a. os. are orthogonal. Otherwise, besides the orbital populations  $\Phi_{\mu}^* \Phi_{\mu}$  there will be also overlap populations  $\Phi_{\mu}^* \Phi_{\nu}$  (e. g.  $\Phi_{1s} \Phi_{2s}, \Phi_{2p_x} \Phi_{3p_x}$ )

contributing to  $\rho_T$ . However,  $\rho_T$  is still a spherically symmetric function; it is easily understood that for example,  $\Phi_{1s} \Phi_{2s}$  has spherical symmetry and so has the sum  $\Phi_{2p_x} \Phi_{3p_x} + \Phi_{2p_y} \Phi_{3p_y} + \Phi_{2p_z} \Phi_{3p_z}$ <sup>(2)</sup>. It is, in fact, always possible to transform a set of non-orthogonal orbitals into an orthogonal set without altering the wavefunction  $\Psi$ , so that expression 1 holds when using the new orbitals. These are of the same type as the original ones, i. e.  $1s', 2s', 2p'_x, \dots$  and so the conclusion of spherical symmetry for  $\rho_T$  remains.

The density function  $\rho_T$  that is being discussed is not the exact one, even if the best a.os. — Hartree-Fock atomic orbitals — are being assumed. The wavefunction  $\Psi$  given by 3 is not exact, although it is usually taken as a good approximation as far as electron densities are concerned. In order to keep the orbital concept, the average and not the instantaneous repulsions between electrons are considered (neglect of electrostatic correlation). In so doing, the problem becomes a central field one (of spherical symmetry)<sup>(3)</sup> and it is not surprising that  $\rho_T$  so calculated is angularly independent. Although instantaneous electron repulsions do not possess spherical symmetry, they cannot lead to a preferred direction in the atom and, consequently, to any change in shape. In fact, one can only rigorously, speak of shape of an atom in terms of an average (in time) and not in terms of the instantaneous positions of electrons as self coherent particles. The magnetic interactions between electrons associated with their spin and orbital angular momenta have no effect on closed-shell atoms; the average magnetic interaction energy vanishes. These atoms have zero spin, orbital and total angular momenta.

The same is also true of the magnetic interactions between the electrons and a magnetic nucleus; certainly, the nuclear magnetic dipole moment has no preferred orientation for an isolated closed shell atom. A similar situation occurs for the electrostatic interaction of the electrons with a nucleus having an electric quadrupole moment.

<sup>(1)</sup> For example,  $\int [\Phi_a^*(3) \Phi_a^*(1) \Phi_b^*(4) \dots] [\Phi_a(4) \bar{\Phi}_a(1) \Phi_b(3) \dots] d\tau_1 d\tau_2 d\tau_3 \dots = 0$ , because  $\int \Phi_a^*(i) \Phi_b(i) d\tau_i = 0$ .

<sup>(2)</sup> Note that  $\Phi_{2p_x} = A(r) \cos \Theta_x$ ,  $\Phi_{3p_x} = B(r) \cos \Theta_x$ , etc.

<sup>(3)</sup> Even when considering nuclear motions.

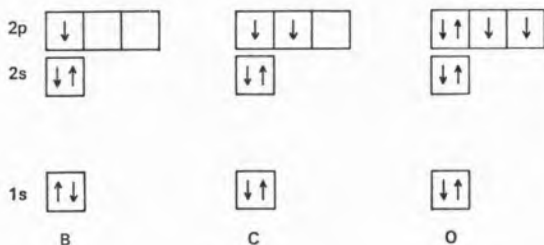
## 3 — OPEN-SHELL ATOMS

As for closed-shell atoms, there is no controversy about the shape of atoms having half-filled valence orbitals,  $s^1$ ,  $p^3$ ,  $d^5$ ,  $f^7$ . Expression 1 is taken as still applying if the population factor 2 is replaced by 1 for the singly occupied  $\Phi_\mu$  orbitals. Thus, the total electron distribution is again spherical.

Contradictory ideas appear, however, in other open-shell situations. For example, it is not uncommon to find the shape of an atom having only one electron in the outer p sub-shell regarded as arising from the superposition of a spherical distribution and a 2p ( $2p_x$ , say) dumbbell-like cloud, and that of an atom with 5 p electrons as the result of subtracting a  $2p(2p_x$ , say) cloud from the spherical electron distribution corresponding to 6 p electrons. That is, the single p electron is assumed to occupy one of the three 2p orbitals ( $2p_x$ ) the others being vacant, and, in the latter case, one of the p orbitals ( $2p_x$ ) is taken as singly occupied whereas the others are doubly occupied. This is, however, an incorrect view. It is worth mentioning that the shape of a  $d^1$  atom would even depend on the d orbital being assumed occupied, for  $d_{z^2}$  has a shape different from  $d_{x^2-y^2}$ ,  $d_{xy}$ , etc. There are several possible reasons for such a misunderstanding, which I shall now discuss.

a) *The customary graphical representation of electron configurations.*

For example, for the lowest energy configuration of boron  $1s^2$ ,  $2s^2$ ,  $2p^1$ , carbon  $1s^2$ ,  $2s^2$ ,  $2p^2$ , and oxygen,  $1s^2$ ,  $2s^2$ ,  $2p^4$  one usually finds the following diagrams, respectively,



which clearly suggest (or reflect the idea) that the populations of the  $p_x$ ,  $p_y$  and  $p_z$  a.os. for a given (isolated) atom can be different.

b) *Some aspects of the qualitative valence bond approach to molecular structure*

This approach may also lead to (or use) the idea of non-uniformly populated p, d, f orbitals. In fact, for example, a common first explanation of the bond angle in  $H_2O$  invokes the existence of two 2p orbitals of O with only one electron each.

c) *Statements related to orbital angular momentum.*

It is well known that an electron in an s orbital has no orbital angular momentum (o.a.m.) as a result of the spherical symmetry of the function  $\Phi_s$ . On the contrary, with any of the non-spherically symmetric p orbitals there is associated an orbital angular momentum. Also, the spherical closed-shell atoms have zero total o.a.m.; and so have the lowest energy terms of  $p^3$ ,  $d^5$  and  $f^7$  configurations.

From these statements it is quite often inferred that open-shell atoms having a net total o.a.m. are non-spherical. In particular, the fact that the total o.a.m. for a  $ns^2$ ,  $np^1$  valence-shell atom is just the same as that for a p orbital supports the idea of an electron occupying just one of the orbitals.

d) *The interpretation of nuclear quadrupole coupling constants.*

The situation here is almost identical to that reported in c). One electron in an s orbital<sup>(1)</sup> does not contribute to a nuclear quadrupole coupling constant (n.q.c.c.) because  $\Phi_s$  is angularly independent; as a result the corresponding field gradient at the nucleus is zero. On the contrary, an electron assumed in a given p orbital contributes to the n.q.c.c.; it creates a field gradient at the quadrupolar nucleus and an interaction energy with its electric quadrupole moment thus arises. Also, a closed-shell atom, e.g.  $Cl^-$ , has no n.q.c.c.; the total electric field gradient at the nucleus is again zero.

From this it is often deduced that atoms showing a n.q.c.c., e.g. Cl, are non-spherical.

e) *Statements related to product functions and Hartree's SCF method.*

Before the introduction of antisymmetry in atomic wavefunctions, an approximate way of defining a

<sup>(1)</sup> That is, a non-polarized s orbital.



N electron wavefunction was by a product of one-electron functions (a.o.s.):

$$\Psi = \Phi_a(1) \bar{\Phi}_a(2) \Phi_b(3) \dots \quad (9)$$

For an open shell case, boron  $1s^2, 1s^2, 2p^1$ , for example, one has

$$\Psi = \Phi_{1s}(1) \bar{\Phi}_{1s}(2) \Phi_{2s}(3) \bar{\Phi}_{2s}(4) \Phi_{2p}(5) \quad (10)$$

In this way many Hartree SCF a.o.s. were obtained and are still used. Although the Hartree method takes an averaged  $2p$  distribution over the three  $2p$  a.o.s. in the process of calculating average electron repulsions (in order to keep the problem to a central field one), (10) again suggests that the  $2p$  electron resides in one of the  $p$  orbitals. In fact, that averaging procedure over the three  $2p$  a.o.s. is often regarded, in itself, as an approximation, which again supports the mistaken view.

The misunderstanding concerning open-shell atom shapes was recently briefly commented on by COHEN (3), by rightly invoking orbital degeneracy. Let us consider the  $p^1$  case, e.g. an excited H atom with one  $p$  electron. As the three  $p$  orbitals are degenerate, no one  $p$  orbital is preferred for the location of the electron. In this case, the magnetic quantum number  $m_l$  (and also the spin quantum number  $m_s$ ) is not a good quantum number; the component of the orbital angular momentum (and also that of the spin angular momentum) along the  $z$  axis is not a constant of the motion, that is, the electron changes its  $m_l$  (and  $m_s$ ) values. The three  $2p$  a.o.s. must then be equally populated, the density function being given by

$$\rho_T = (\Phi_{p_{+1}}^* \Phi_{p_{+1}} + \Phi_{p_{-1}}^* \Phi_{p_{-1}} + \Phi_{p_0}^* \Phi_{p_0}) = \frac{1}{3} (\Phi_{p_x}^2 + \Phi_{p_y}^2 + \Phi_{p_z}^2) \quad (11)$$

which is spherically symmetric<sup>(1)</sup> ( $\Phi_{p_i}$  represents the  $2p$  a.o. associated with a  $m_l$  value  $i$ ).

There may be a tendency to explain the spherical distribution by describing the electron as a «resonance hybrid» (3)

$$\Phi_1 = (\Phi_{p_x} + \Phi_{p_y} + \Phi_{p_z})/\sqrt{3} \quad (12)$$

However, neither  $\Phi_1$  nor  $\Phi_1^2$  are spherically symmetric (the sum of the cross terms  $\Phi_{p_x} \Phi_{p_y} + \Phi_{p_x} \Phi_{p_z} + \Phi_{p_y} \Phi_{p_z}$  is angularly dependent). Although  $\Phi_1$  is certainly an eigenfunction of the hamiltonian (being a linear combination of degenerate eigenfunctions), it must be realized that a set of three degenerate functions cannot be replaced by just one linear combination of them; there are always two more functions  $\Phi$  to be considered:

$$\begin{aligned} \Phi_2 &= (\Phi_{p_x} - \Phi_{p_y})/\sqrt{2} \\ \Phi_3 &= (\Phi_{p_x} + \Phi_{p_y} - 2\Phi_{p_z})/\sqrt{6} \end{aligned} \quad (13)$$

The sum  $(\Phi_1^2 + \Phi_2^2 + \Phi_3^2)/3$  is angularly independent; it equals expression 11.

A similar situation occurs for a  $1s^2, 2s^2, 2p^1$  configuration case, boron for example. Now, instead of degenerate one-electron wavefunctions (6 spin-orbitals  $\Phi_{p_x} \alpha, \Phi_{p_x} \beta$ , etc.), we have 6 degenerate five-electron wavefunctions of the type (only the first diagonal of the Slater determinant is shown)

$$\Psi_1 = | \Phi_{1s}(1) \bar{\Phi}_{1s}(2) \Phi_{2s}(3) \bar{\Phi}_{2s}(4) \Phi_{2p_{+1}}(5) | \quad (14)$$

differing from each other in the spin-orbital  $2p$  considered. The electron density associated to  $\Psi_1$  is

$$\rho_T^{(1)} = 2(\Phi_{1s}^2 + \Phi_{2s}^2) + \Phi_{2p_{+1}}^* \Phi_{2p_{+1}} \quad (15)$$

and the total electron density  $\rho_T$  is simply

$$\begin{aligned} \rho_T &= \frac{1}{6} \sum_{i=1}^6 \rho_T^{(i)} = 2(\Phi_{1s}^2 + \Phi_{2s}^2) + \\ &+ \frac{1}{3} (\Phi_{2p_x}^2 + \Phi_{2p_y}^2 + \Phi_{2p_z}^2) \end{aligned} \quad (16)$$

<sup>(1)</sup> If the a.o.  $2s$  is regarded as having the same energy as  $2p$ , then the electronic distribution is  $\rho_T = (\Phi_s^2 + \Phi_{p_x}^2 + \Phi_{p_y}^2 + \Phi_{p_z}^2)/4$ , which is again spherical.

Actually, the degeneracy of the six wavefunctions for a sub-configuration  $p^1$  — the 6 components of a  $^2P$  term — is partially removed by spin-orbit interactions. As a result, two levels of different energy occur, according to the total angular momentum quantum number  $J$  ( $3/2$  and  $1/2$ ),  $^2P_{3/2}$  and  $^2P_{1/2}$ . The first is four-fold degenerate and the second has degeneracy two. In view of the fact that the electron spin has no preferred orientation (in isolated atoms) and that the electron distribution is already spherical in the absence of spin-orbit coupling, it is expected that the atomic shape does not change. This is, in fact, true. For  $^2P_{1/2}$ , for example, the degenerate states are (the spherical core  $1s^2$ ,  $2s^2$  is ignored without affecting the conclusion) (4):

$$\begin{aligned}\theta_1 &= (\Phi_{p_0} - \sqrt{2}\Phi_{p_{+1}})/\sqrt{3} \\ \theta_2 &= (\sqrt{2}\Phi_{p_{-1}} - \Phi_{p_0})/\sqrt{3}\end{aligned}\quad (17)$$

The electron density  $\rho_1$  associated with  $\theta_1$  is (note the integration over the spin coordinates)

$$\rho_1 = \int \theta_1^* \theta_1 d\sigma = (\Phi_{p_0}^* \Phi_{p_0} + 2\Phi_{p_{+1}}^* \Phi_{p_{+1}})/3 \quad (18)$$

and similarly for  $\theta_2$ , so that  $\rho$  has spherical symmetry:

$$\rho = (\rho_1 + \rho_2)/2 = (\Phi_{p_x}^2 + \Phi_{p_y}^2 + \Phi_{p_z}^2)/3 \quad (19)$$

If the atom possesses two  $p$  electrons, carbon for example, they must be equally distributed among the three  $p$  orbitals. The probability density for a sub-configuration  $p^2$  must then be

$$\rho = 2(\Phi_{p_x}^2 + \Phi_{p_y}^2 + \Phi_{p_z}^2)/3 \quad (20)$$

The situation is, however, more complex now. The 15 possible basic determinant functions, as 14, obeying the Pauli Principle, are not all independent of each other; they are not all eigenfunctions of the hamiltonian<sup>(1)</sup>. Due to electron repulsion, interaction between them must be taken into account. As a consequence, the configuration  $p^2$

splits into three terms of different energy and different orbital angular momentum:  $^3P$ ,  $^1D$ ,  $^1S$ . The first is nine-fold degenerate, the second shows degeneracy five and the latter is non-degenerate. Again, the total electron density associated with each of these terms, account being taken of degeneracy, is spherically symmetric. Let us consider, for example,  $^1D$ . The five components of this term are (4) ( $\Phi_{p_i}$  has been abbreviated to  $p_i$ ):

$$\begin{aligned}\Psi_1 &= |p_{+1} \bar{p}_{+1}| \\ \Psi_2 &= \{ |p_{+1} \bar{p}_{-1}| - |p_{-1} \bar{p}_{+1}| + 2 |p_0 \bar{p}_0| \} / \sqrt{6} \\ \Psi_3 &= \{ |p_{+1} \bar{p}_0| - |p_{-1} \bar{p}_0| \} / \sqrt{2} \\ \Psi_4 &= \{ |p_0 \bar{p}_{-1}| - |p_0 \bar{p}_{+1}| \} / \sqrt{2} \\ \Psi_5 &= |p_{-1} \bar{p}_{-1}| \end{aligned} \quad (21)$$

The electron density associated to  $\Psi_2$ , for example, is simply the sum of the contributions of the various determinants individually (there are no cross terms contributing to  $\rho$ ), that is

$$\rho_2 = (\Phi_{p_{+1}}^* \Phi_{p_{+1}} + \Phi_{p_{-1}}^* \Phi_{p_{-1}} + 4\Phi_{p_0}^* \Phi_{p_0})/3 \quad (22)$$

The total electron density for  $^1D$  (ignoring  $1s^2$ ,  $2s^2$ ) is then (there are two  $p$  electrons):

$$\rho_D = \frac{2}{5} \sum_{i=1}^5 \rho_i = 2(\Phi_{p_x}^2 + \Phi_{p_y}^2 + \Phi_{p_z}^2)/3 \quad (23)$$

Spin-orbit coupling splits each of the  $^3P$  and  $^1D$  terms into several levels. However, as for the  $p^1$  case, the shape of the atom for each level is again spherical<sup>(2)</sup>.

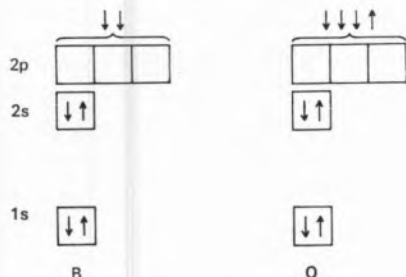
It is clear that this must be a general conclusion valid for isolated atoms both in ground and excited configurations, as might, perhaps, have been

(1) They are eigenfunctions of an hamiltonian that contains no electron repulsion terms.

(2) This must also be true for cases when the Russell-Saunders coupling scheme is not appropriate.

expected intuitively and on semi-classical and symmetry grounds (1).

In order to avoid misunderstandings among students on this matter, if a graphical representation of electron configurations (and Hund's rule) for open-shell atoms is required, then it should make clear that electrons of same  $l$  are uniformly distributed among the  $2l + 1$  degenerate a.o.s. For example, for carbon  $1s^2, 2s^2, 2p^2$  and oxygen  $1s^2, 2s^2, 2p^4$  one could have:



In the second case, one of the p electrons has spin opposite to the other three not because it is going to complete one of the p orbitals, but because no more than one electron with a given spin is allowed per each a.o. (Pauli Principle); otherwise, one would have 4/3 of electron in each a.o. with the same spin.

All this also implies special care when need is felt of electron configurations in the simple valence-bond model. For example, in order to discuss the molecular geometry of  $H_2O$  it is customary to start with the oxygen electron configurations  $1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$ . It should, definitely, be made quite clear that this is *not* the electronic distribution of the isolated atom.

#### 4—SPHERICAL ATOMIC SHAPE IN RELATION TO ORBITAL ANGULAR MOMENTUM AND NUCLEAR QUADRUPOLE COUPLING CONSTANTS

We thus have atoms that have a spherically symmetric electron distribution and simultaneously may have a net orbital angular momentum (o.a.m.). There is no contradiction because there is no relation between angular momentum and the symmetry of the total electron probability density  $\rho_T$ . The magnitude of the o.a.m. is determined

by the expectation value of the square of the corresponding quantum mechanical operator,  $M^2$ . Now, that is calculated by using any of the degenerate (with respect to energy and to o.a.m.) eigenfunctions associated with a given term, and not  $\rho_T$ ;  $\rho^{1/2}$  is certainly not an eigenfunction (except in the case  $s^1$  discussed below). For example, for the  $p^1$  configuration we have

$$\int \Phi_{p_x} M^2 \Phi_{p_x} d\tau = \int \Phi_{p_y} M^2 \Phi_{p_y} d\tau = \int \Phi_{p_z} M^2 \Phi_{p_z} d\tau = l(l+1)h^2/4\pi^2 = 1(1+1)h^2/4\pi^2 \quad (24)$$

Analogously, for the term  $^1D$  ( $L=2$ ) of a  $p^2$  configuration we could choose  $\Psi_1$  (eq. 21)

$$\int \Psi_1^* M^2 \Psi_1 d\tau_1 d\tau_2 = L(L+1)h^2/4\pi^2 = 2(2+1)h^2/4\pi^2 \quad (25)$$

but never  $\rho_D$  (eq. 23)):

$$\int M^2 \rho_D d\tau_1 d\tau_2 \quad (26)$$

or

$$\int \rho_D^{1/2} M^2 \rho_D^{1/2} d\tau_1 d\tau_2 \quad (27)$$

It is easily understood that the total density  $\rho_T$  can only be used to calculate expectation values of operators that can be written as the sum of one-electron *linear* operators (2). And even then it is  $\rho_T$  expressed as a sum of one-electron densities that must be used and not the overall  $r$ -dependent result  $\rho_T = R(r)$ . The operator  $M^2$  is not in such circumstances.

The trivial case when  $\rho^{1/2}$  may be used to calculate the expectation value of  $M^2$  is in an  $s^1$  situation, for then  $\rho^{1/2} = \Phi_s$  is the eigenfunction; then one

(1) Inclusion of nuclear spin and nuclear electric quadrupole effects would not alter the conclusion. The same is true of relativistic corrections to the electron mass and of nuclear motions.

(2) Then, the expectation value of operator  $O = \sum_i O_i$  is the sum of one-electron expectation values for occupied spin-orbitals,

$$\begin{aligned} \sum_{\mu} \int \Phi_{\mu}^* O_{\mu} \Phi_{\mu} d\tau_{\mu} &= \sum_{\mu} \int O_{\mu} \Phi_{\mu}^* \Phi_{\mu} d\tau_{\mu} = \\ &= \int \sum_{\mu} O_{\mu} \rho_{\mu} d\tau_{\mu} = \int O \rho_T d\tau_1 d\tau_2 \dots \end{aligned}$$

may say that the o.a.m. is zero because  $\rho$  is spherically symmetric. Since  $\rho_T$  cannot be used to calculate the o.a.m. of a closed-shell atom, the reason for zero o.a.m. here is different. It is found to be zero from the integral

$$\int \Psi^* \mathbf{M}^2 \Psi d\tau_1 d\tau_2 \dots d\tau_N, \quad (28)$$

$\Psi$  being given by expression 3, because all degenerate a.o.s. are doubly occupied and not directly because of spherical electron distribution.

The situation for nuclear quadrupole coupling constants (n.q.c.c.) is similar to that of orbital angular momentum. In fact, the operator for the field gradient at the nucleus is not a sum of one-electron operators and therefore it is not the classical field gradient of  $\rho_T$  at the nucleus that matters (the field of  $\rho_T$  is isotropic since  $\rho_T$  is spherically symmetric). Instead of  $\rho_T$ , is any of the eigenfunctions of same energy that must be used to calculate the field gradient and hence the n.q.c.c. For the  $p^1$  case, for example, and ignoring spin-orbit coupling, the field gradient at the nucleus is

$$\begin{aligned} q &= \int \Phi_{p+1}^* \frac{\partial^2 V}{\partial Z^2} \Phi_{p+1} d\tau = \\ &= \int \Phi_{p-1}^* \frac{\partial^2 V}{\partial Z^2} \Phi_{p-1} d\tau = \\ &= \int \Phi_{p_0}^* \frac{\partial^2 V}{\partial Z^2} \Phi_{p_0} d\tau \end{aligned} \quad (29)$$

This equality is not always fully appreciated, in the same way as the field gradient operator  $\frac{\partial^2 V}{\partial Z^2}$  (V is the electric potential and Z is the nuclear spin axis) is sometimes taken as a sum of one-electron operators. In fact,  $\frac{\partial^2 V}{\partial Z^2}$  is often taken as equal to

$$\frac{\partial^2 V}{\partial Z^2} = e \cdot \frac{3 \cos^2 \theta_z - 1}{r^3} \quad (30)$$

z being the usual z axis fixed in the atom; in this way a  $p_z$  electron appears to have a different contribution to q from  $p_x$  or  $p_y$ , which is absurd.

There is an important difference between the two operators <sup>(1)</sup>:

$$\frac{\partial^2 V}{\partial Z^2} = \frac{\partial^2 V}{\partial z^2} \left( \frac{3 \cos^2 \chi_z - 1}{2} \right) \quad (31)$$

where  $\chi_z$  is the angle between the z axis and the total orbital angular momentum of the atom  $\mathbf{M}$  (or the total angular momentum  $\mathbf{J}$  if spin-orbit coupling is taken into account). Therefore, as the expectation value of  $\frac{\partial^2 V}{\partial z^2}$  varies with the p a.o. considered in the  $p^1$  case, so does  $\chi_z$ , in such a way ( $\chi_z = 90^\circ$  for  $p_0$  and  $\chi_z = 0^\circ$  for  $p_{+1}$  and  $p_{-1}$ ) that (29) holds. It is the  $\chi_z$  dependence of the field gradient operator that makes the actual field gradient q different from that ( $q = 0$ ) classically expected from the electron distribution.

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#### RESUMO

São vulgares certas considerações sobre a configuração electrónica dos átomos, os seus momentos angulares totais, o método SCF de Hartree e sobre constantes de acoplamento quadrupolar nuclear, assim como aplicações do método das ligações de valência em estrutura molecular, que propõem que os átomos de camada incompleta isolados não são obrigatoriamente esféricos. Apresenta-se aqui uma análise crítica deste problema e demonstra-se como a mecânica quântica prevê que todos os átomos isolados sejam efectivamente esféricos.

<sup>(1)</sup> See for example, Sudgen, J. M. and Kenney, C. N., «Microwave Spectroscopy of Gases», D. Van Nostrand, New York, 1965.