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## A CRITIQUE ON SOME RECENT THEORIES OF CHEMICAL BONDING

### Part I. Quantum Mechanical Models

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**Abstract.** Since the advent of quantum mechanics, many models to explain the nature of chemical bonding have been put forward. Some of these models are based directly on quantum mechanical foundation while others involve semi-empirical parameters or ad hoc assumptions. In the following articles (Parts I and II), various bonding theories developed relatively recently have been discussed. Part I describes the concepts of the Pauli exclusion principle and the linear transformations which are prerequisite to follow the ensuing arguments. These are treated in some details because of their importance in showing correlation between different models discussed in these articles.

The models treated here have been classified as (a) quantum mechanical and (b) non-quantum mechanical on the basis of the arguments as to their foundations. The models treated under heading (a), Part I, are the Hartree-SCF scheme, the Walsh diagrams, the Linnett double spin set model, and the FSGO model.

The idea of structure in regard to matter and energy has been a very fundamental one in science. The chemists have been particularly interested in the former while the physicists in the latter. The structural concept in chemistry has been extremely helpful because it correlates seemingly unrelated phenomena and explains the behavior of chemicals under given set of experimental conditions. On the basis of their structural knowledge the chemists have been able to predict the behaviour and properties of previously unknown substances. This all goes on to show that our belief that matter is made up of smaller structural units (atoms, molecules, ions, nuclei, electrons) has rendered today's chemistry possible.

There have been numerous theories put forward by various scientists from time to time to explain the structure of atoms and molecules and the nature of the chemical bond. With the appearance of more sophisticated experimental techniques and accurate data some of the old theories have to be abandoned or modified. No theory has proved to be as revolutionary as that of quantum mechanics. It should perhaps be realized here that quantum mechanics has contributed a great deal to human thought in general and has achieved some striking successes for simple molecular systems in particular but it has been able to give only approximate answers for more complex systems than the hydrogen molecule. This has led to the formulation of new theories which, in spite of being approximate, are near to the chemists' viewpoint because of their simplicity and intuitive appeal. The aim of this paper is to discuss briefly the post-quantum mechanical theories of chemical structure and show their usefulness and limitations as compared to the better known theories like the molecular orbital and

valence bond theories. The more significant of these theories are: (a) the tangent sphere and the charge cloud model of Kimball and Bent, (b) the valence shell electron pair repulsion (VSEPR) model due to Gillespie and Nyholm, (c) the Linnett model, and (d) the floating spherical gaussian orbitals (FSGO).

In very broad terms, the models to be discussed here may be divided into two categories. On one hand there are those models which have their roots in the fundamental laws of quantum mechanics and the results here are obtained by computations of integrals which involve nuclear-nuclear, nuclear-electronic and electronic-electronic interactions. The total energy of a quantum mechanical system is, therefore, a contribution from its potential and kinetic energy components: the Hamiltonian spells out the kinetic and potential energy parts. The use of Born-Oppenheimer approximation somewhat simplifies the Hamiltonian. The quantum mechanical models include the well-known LCAO-SCF-MO scheme, the Walsh model, the Linnett 'double spin set' model, and the Frost FSGO model.

On the other hand, the Kimball charge cloud model, the tangent sphere model, and the VSEPR models aim primarily to explain the space filling properties of particles with special emphasis on the ground state bond distances and bond angles. By and large, the conclusions arrived at with the help of these models are qualitative depicting the trends rather than the extent of change in an observable property. These models are not based on quantum mechanical postulates *per se* although they all use the Pauli exclusion principle as the starting point. The division in categories, namely (a) quantum mechanical and (b) non-quantum mechanical is, therefore, justified.



Prerequisite to the discussion of the above-mentioned models are the following two important quantum mechanical principles, namely (1) the Pauli exclusion principle and (2) the principle of 'linear transformations'. These will now be discussed in some detail.

*The Pauli Exclusion Principle.* In its most general form the Pauli exclusion principle can be arrived at from the principle of antisymmetry.

A system of many identical particles may be described in terms of the space-spin coordinates for each particle. If two particles are labelled as 1 and 2, then  $X_1$  and  $X_2$  are their coordinates (space and spin) so that

$$X_1 = r_1, \sigma_1 \text{ and } X_2 = r_2, \sigma_2$$

Here  $r_1$  and  $r_2$  may be Cartesian coordinates  $(x_1, y_1, z_1)$  and  $(x_2, y_2, z_2)$  and  $\sigma_1$  and  $\sigma_2$  the spin coordinates.

Another important aspect of the particles under consideration is that they are indistinguishable. They may be electrons, neutrons, protons or other such particles and their indistinguishability, according to quantum mechanics, is a fundamental and indisputable property. It, therefore, immediately follows from this that the probability for configuration in which particle 1 is at position  $X_1$  and particle 2 at position  $X_2$  must always be equal to the probability of the configuration in which the particles are interchanged. This may be represented as:

$$\left| \psi \left[ X_1, X_2 \right] \right|^2 = \left| \psi \left[ X_2, X_1 \right] \right|^2$$

The above expression means that measurable physical properties such as energy and density would be invariant under the coordinate transformation and hence are symmetric with respect to the interchange of coordinate.

It also follows from the above expression that:

$$\psi \left[ X_1, X_2 \right] = + \psi \left[ X_2, X_1 \right]$$

or

$$- \psi \left[ X_2, X_1 \right]$$

in which the wave-function is either symmetric or antisymmetric with respect to the particle interchanged.

It is a basic postulate of quantum mechanics that particles belong to either one of the above categories and never cross over from one category to the other. Electrons and atoms that contain particles with odd number of mass units and show odd spin belong to the antisymmetric category while those with zero or integral spin belong to the symmetric category. Those particles with the odd spin obey Fermi-Dirac statistics and are called Fermions. On the other hand particles with zero or even spin follow Bose-Einstein statistics and are, therefore, known as Bosons.

It is experimentally established that the electrons are Fermions and are, therefore, described by an antisymmetric wave-function which changes sign on the interchange of coordinates for any two electrons. This is perhaps the most general statement of the Pauli exclusion principle.

Let us suppose that an  $N$  electron system is subjected to test in accordance with the Pauli exclusion principle then

$$\psi(X_1, X_2, \dots, X_N) = -\psi(X_2, X_1, \dots, X_N)$$

results if the coordinates of electron 1 and 2 are interchanged. Now suppose that electrons 1 and 2 have the same coordinate  $X$ , then their indistinguishability implies that  $\psi(X, X, \dots, X_N) = -\psi(X, X, \dots, X_N)$  which means that  $\psi$  is necessarily zero

$$\psi(X, X, \dots, X_N) = 0$$

We conclude, therefore, that no two electrons can occupy the same position and have the same spin. This is another statement of the Pauli exclusion principle. It also follows from the above that no two electrons in an atom or a molecule can have all four quantum numbers the same, which is perhaps the most popular statement regarding the exclusion principle. The restriction that no two electrons can have the same spin orbital may be interpreted by saying that two electrons will stay apart in momentum space if they occupy the same coordinate space. This requirement is related to the uncertainty principle expressed in a six dimensional space—three momentum coordinates and three spatial coordinates. It means that each electron needs a minimum volume to be occupied given by  $\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z \cong h^3$ .

*Linear Transformations and Localized Molecular Orbitals.* The molecular orbitals that form eigenfunctions to the Hartree-Fock Hamiltonian are commonly called the canonical molecular orbitals (CMO) or canonical Hartree-Fock orbitals. The CMO wave-function in a molecule is delocalized to encompass the entire molecule. In theory, more than one such molecular orbital are present on a single molecule, symmetry and the linear combinations of the AO's primarily determine their number and shape. Although some CMO's are more delocalized than others, the basic picture of delocalization is a fundamental one. Each CMO is unique in the sense that it forms an irreducible representation which is transformable to other more localized orbitals by a unitary transformation which leaves the electron density,  $\rho$ , unchanged.<sup>1,2</sup> One, therefore, arrives at localized molecular orbitals, LMO, from CMO by a unitary matrix transformation. It must be emphasized here, however, that the above argument is only pertinent to cases of 'closed shells'.

Furthermore a many-electron wave-function without configuration interaction is represented by a single determinantal wave-function. This makes the mathematics of molecular orbital theory comparatively simple. On the contrary in the valence bond approximation the wave-function has to be written down as a linear combination of Slater determinants which make the VB wave-functions cumbersome to deal with. CMO's have been particularly useful in the calculation of ionization energies and in the interpretation of molecular spectra. However, they do not lend themselves to easily imaginable physical pictures. LMO on the other hand give meaning to concepts such as



independent bonds in molecules, bond dissociation energy, and force constant.

Let us see, for example, how the ideas developed above explain some fundamental structural notions in simple molecules. A typical molecule whose CMO and LMO structures are well understood is that of methane. With the use of minimal basis set, namely the  $2s$ ,  $2p_x$ ,  $2p_y$ , and  $2p_z$  on carbon and  $1s$  on hydrogen, the following linear combinations yield molecular orbitals for  $\text{CH}_4$  (Fig. 1).

$$\begin{aligned}\sigma_s &= C_1 2s + C_2 (1s_a + 1s_b + 1s_c + 1s_d) \\ \sigma_x &= C_3 2p_x + C_4 (1s_a - 1s_b + 1s_c - 1s_d) \\ \sigma_y &= C_3 2p_y + C_4 (1s_a - 1s_b - 1s_c + 1s_d) \\ \sigma_z &= C_3 2p_z + C_4 (1s_a + 1s_b - 1s_c - 1s_d)\end{aligned}$$

The coefficients  $C_1$  to  $C_4$  are determined to give SCF-LCAO-MO. The molecule belongs to the symmetry group  $T_d$  and  $\sigma_s$ ,  $\sigma_x$ ,  $\sigma_y$ , and  $\sigma_z$  form irreducible representation of the group;  $\sigma_x$ ,  $\sigma_y$ , and  $\sigma_z$  being degenerate. The energy diagram for  $\text{CH}_4$  is given in Fig. 2. The ground state configuration of  $\text{CH}_4$  turns out to be  $\text{CH}_4(\sigma_s)^2(\sigma_x, \sigma_y, \sigma_z)^6$  in which two electrons accommodate in a molecular orbital of one symmetry

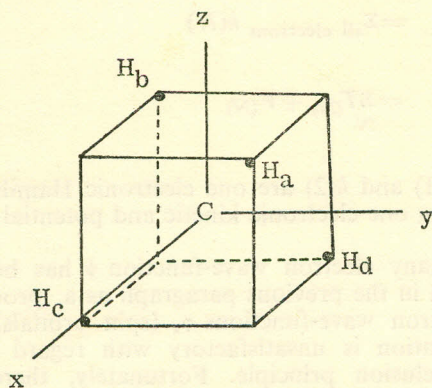


Fig. 1. Positions of hydrogen nuclei for LCAOs' in methane.

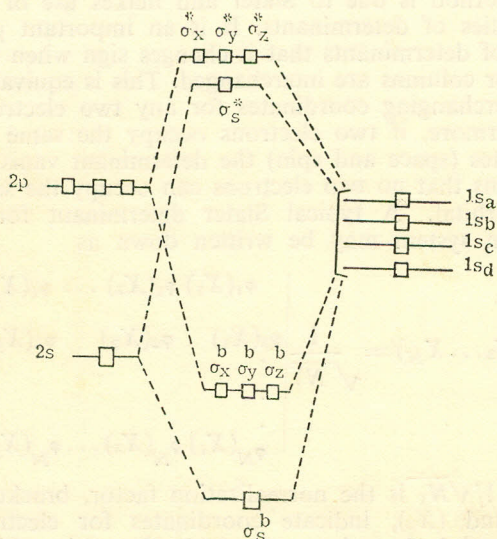


Fig. 2. Atomic and molecular orbital energies in methane.

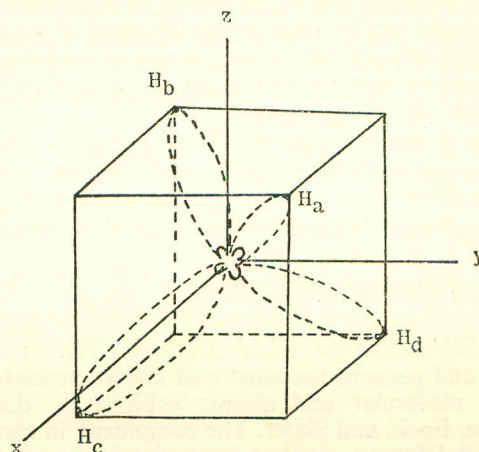


Fig. 3. Four localized hybrid orbitals ( $lmo_1$ ,  $lmo_2$ ,  $lmo_3$  and  $lmo_4$ ) in methane.

and the remaining six in three degenerate orbits of another symmetry. In other words the CMO picture of  $\text{CH}_4$  does not formulate four equivalent tetrahedral bonds for  $\text{CH}_4$ . Here electron density distribution is no doubt tetrahedral, still it does not obviously lead to a model where electron density concentration is greatest between C—H nuclei. Also, it is not immediately apparent that the bond properties of  $\text{CH}_4$  are transferable to other hydrocarbons of different symmetry species. These molecular orbitals are very helpful to predict the ionization potential and spectra of  $\text{CH}_4$ . On the other hand they are not effective to explain the equivalence of four bonds—their bond length and bond dissociation energy.

The LMO model for  $\text{CH}_4$  is best arrived at through hybridization of the AO's on carbon. This yields four equivalent orbitals arranged tetrahedrally in space, called  $sp^3$  hybridized orbitals. The orthonormal  $sp^3$  wave-functions constructed by mixing together the  $s$  and the  $p$  orbitals may be represented by the following (Fig. 3):

$$\begin{aligned}sp_d^3 &= \frac{1}{2}2s + \frac{1}{2}(px + py + pz) \\ sp_b^3 &= \frac{1}{2}2s + \frac{1}{2}(-px - py + pz) \\ sp_c^3 &= \frac{1}{2}2s + \frac{1}{2}(px - py - pz) \\ sp_a^3 &= \frac{1}{2}2s + \frac{1}{2}(-px + py - pz)\end{aligned}$$

The four equivalent LMO are now constructed as

$$\begin{aligned}\text{LMO}_1 &= \dot{C}_1 sp_a^3 + \dot{C}_2 1s_a \\ \text{LMO}_2 &= \dot{C}_1 sp_b^3 + \dot{C}_2 1s_b \\ \text{LMO}_3 &= \dot{C}_1 sp_c^3 + \dot{C}_2 1s_c \\ \text{LMO}_4 &= \dot{C}_1 sp_d^3 + \dot{C}_2 1s_d\end{aligned}$$

Where  $1 = a, b, c, d$ .

It can be shown that linear transformation of CMO's of  $\text{CH}_4$  changes them into LMO's. Unlike the CMO's, the LMO of a molecule are not eigen-function to the Hartree-Fock Hamiltonian and hence yield poor



estimates of the ionization energies. Also, the LMO model is less effective for molecules where degeneracies occur and the idea of resonance has to be brought in artificially to explain the inadequate representation of localized bond structures.

After going through the Pauli exclusion principle and the principle of 'linear transformation' we now divert our attention to the actual description of various structural models that are based on these principles.

### Quantum Mechanical Models

1. *Self-Consistent Field Method.* The most accurate and perhaps the most well-known procedure to obtain molecular and atomic orbitals is due to Hartree, Fock, and Slater. The complexity in choosing an orbital for an electron immediately arises as one goes from a simple hydrogen atom to a helium atom. The spherical  $1s$  orbital of hydrogen seems to have lost its meaning when the two electron helium atom is carefully examined. The Hamiltonian of electronic nuclear interactions looks pretty much the same here as in the hydrogen atom but an additional  $e^2/r_{12}$  electron-electron repulsion term appears in the potential energy part of the Hamiltonian. This makes it difficult for each electron to retain its original spherical potential and the orbital concept for electrons becomes ambiguous. In such a situation the validity of assigning two electrons to  $1s$  orbital in helium atom may be seriously questioned. An attempted solution of the problem leads one to arrive at the idea of one electron self-consistent field wave-functions in many electron systems.

It is realized at the outset that any electron in a system of  $N$  electrons moves in the potential field of the nucleus plus the field generated by  $N-1$  electrons, and this helps us in determining some effective potential  $V(r_1)$  for that electron. It is assumed that  $V(r_1)$  has spherical symmetry which resembles the true potential of electron 1. This is not strictly true but as it turns out  $V(r_1)$  approximates the best potential for that electron 1 is able to get at. The electron 1 now moves in an average field of all the  $N-1$  electrons and there are no instantaneous interactions of electron 1 with all other electrons. It allows one to write down the wave-function of electron 1 in terms of its own coordinates and the coordinates of all other electrons are neglected. The influence of  $N-1$  electrons, however, is built in the potential energy function of electron 1. This brings us to a situation where we can write down the wave equation for any one electron if wave-functions for all other electrons are known. Now this really does not solve our problem. A solution of the problem was suggested by Hartree.

In the Hartree scheme, the wave-functions for all the electrons are first written down as a mere conjecture. We may now choose one electron out of the lot and determine the field provided by all others. This helps us in giving a potential to this electron and solve the Schrödinger equation for our chosen electron. This revised function may now be used to compute the average field for the second electron giving improved wave-function for the second electron. The same process is repeated for the third electron and so on until a set of first improved orbital for all

the  $N$  electrons is obtained. The procedure is repeated and second improved orbitals for all the electrons appear. The revision of orbitals is carried out until the interaction procedure leaves the orbitals almost unchanged. This finally gives us orbitals for any one electron which are determined by the nuclear field and the root mean square potential of all other electrons. This is true of any electron we happen to choose. The method is, therefore, called the self-consistent field method or Hartree SCF.

According to the SCF scheme, a many electron wave-function  $\psi$  may now be written down as a product of one electron wave-function

$$\psi(X_1, X_2 \dots X_N) = \varphi_1(X_1)\varphi_2(X_2) \dots \varphi_N(X_N)$$

Here  $\varphi_1(X_1)$  represents orbital (space and spin) for electron 1 only. This in fact follows from the assumption that each electron has a self-consistent potential field  $V(r)$  which enables us to write down the Hamiltonian for an atom as the sum of one electronic Hamiltonians of its kinetic energy  $T$  and potential energy  $V$  components in the following way

$$\begin{aligned} H &= h(1) + h(2) + \dots h(N) \\ &= \sum_{\text{all electrons}} h(N) \\ &= \sum_N T_{(N)} + V_{(N)} \end{aligned}$$

where  $h(1)$  and  $h(2)$  are one electronic Hamiltonians containing one electronic kinetic and potential energy terms.

The many electron wave-function  $\psi$  has been represented in the previous paragraph as a product of one electron wave-functions  $\varphi_i$  (spin orbitals). This representation is unsatisfactory with regard to the Pauli exclusion principle. Fortunately, there is a shorthand method for representing a many electronic wave-function in accordance with the Pauli principle. The method is due to Slater and makes use of the properties of determinants. It is an important property of determinants that it changes sign when two rows or columns are interchanged. This is equivalent to interchanging coordinates for any two electrons. Furthermore, if two electrons occupy the same coordinates (space and spin) the determinant vanishes. It means that no two electrons can occupy the same spin orbital. A typical Slater determinant for  $N$  electron system may be written down as

$$\psi(X_1, X_2 \dots X_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(X_1) & \varphi_1(X_2) & \dots & \varphi_1(X_N) \\ \varphi_2(X_1) & \varphi_2(X_2) & & \varphi_2(X_N) \\ \vdots & \vdots & & \vdots \\ \varphi_N(X_1) & \varphi_N(X_2) & \dots & \varphi_N(X_N) \end{vmatrix}$$

where  $1/\sqrt{N!}$  is the normalization factor, bracketed  $(X_1)$  and  $(X_2)$ , indicate coordinates for electrons numbered 1, 2, and  $\varphi_1, \varphi_2$ , stand for spin-orbitals numbers 1 and 2.



In these terms the Hartree-Fock SCF method may be described as finding those spin-orbitals that minimize the average energy calculated from a single Slater determinantal wave-function using the well-known variation principle.

2. *Walsh Diagrams.* A useful method for the correlation of orbital energies and molecular geometries has been developed by Walsh.<sup>3</sup> The Walsh diagrams give curves which show variation in binding energy of molecules with their bond angles. A triatomic molecule of the type  $AH_2$  may be assumed to be linear or bent. Walsh diagrams predict that  $AH_2$  molecules with 4 valency electrons should have a linear geometry in their ground states while those with 5-8 valency electrons should be bent.

A typical Walsh diagram for triatomic molecules is given in Fig. 4. The molecule HAH belongs to the symmetry group  $D_{\infty h}$  when HAH angle is  $180^\circ$  and to the point group  $C_{2v}$  for  $90^\circ$  angle. Increase in the HAH angle from  $90$  to  $180^\circ$ , transforms the bent molecule to its linear form, and the orbitals  $a_1$  and  $b_2$  of  $C_{2v}$  point group eventually become  $\sigma_g$  and  $\sigma_u$  respectively of the linear molecule. The molecule with the  $(\sigma_g, \sigma_u)$  configuration should therefore be more stable as these lie lower in energy than their  $(a_1, b_2)$  counterparts. This may be explained with the help of LMO or CMO model. In terms of the localized orbital picture, the bonding in a bent molecule at a  $90^\circ$  angle is solely due to the  $p$  orbitals of the central atom overlapping into the  $s$  orbital on hydrogen. As the angle is increased,  $s$  orbital on  $A$  starts mixing with the  $p$  orbital and takes part in the bond formation. In other words, an  $s-p$  hybrid orbital in the linear molecules makes a stronger bond than a pure  $p$  orbital in the bent molecule.

In the delocalized model, the following combinations for orbitals  $a_1-\sigma_g$  and  $b_2-\sigma_u$  are possible

linear	bent
$\sigma_g = s_A, (1s_a + 1s_b)$	$a_1 = p_z, (1s_a + 1s_b)$
$\sigma_u = p_y, (1s_a - 1s_b)$	$b_2 = p_y, (1s_a - 1s_b)$

The energy correlation of these orbitals with the variation of bond angle may be explained with the help of the following assumptions: (i) the orbital  $s_A$  does not participate in bonding for a  $90^\circ$ -bent molecule; (ii) the participation of  $s_A$  orbital along with a  $p$  orbital in the formation of a molecular orbital lowers the energy of the molecular orbital in comparison to the orbital obtained from a pure  $p$  orbital; (iii) all other effects being equal, those orbitals which are antibonding between the end atoms yield the strongest bonds when the end atoms are farthest apart (linear). If the orbital is bonding between the end atoms, the most effective bonding occurs for the cases where the end atoms are nearest, namely in the  $90^\circ$  bent molecule. Orbitals  $s_A$  and  $1s_a + 1s_b$  are responsible for bonding in  $\sigma_g$  and  $p_z$  and  $1s_a + 1s_b$  in  $a_1$ , while a mixture of  $s_A, p_z$ , and  $1s_a + 1s_b$  will take part in bonding for molecules with an HAH angle  $>90^\circ$  and  $<180^\circ$ . It, therefore, follows that  $\sigma_g$  lies lower in energy than  $a_1$  which means that the linear configuration is energetically more stable than the

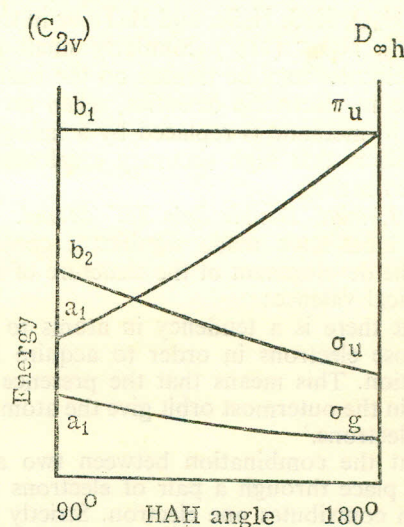


Fig. 4. The Walsh diagram for molecules of the type HAH.

nonlinear configuration. The  $\sigma_u-a_2$  orbitals involve the combination of  $1s_a-1s_b$  and  $p_y$  for both linear and bent molecules and since  $1s_a-1s_b$  is antibonding between the end atoms, it should yield a lower energy structure in which the end atoms are farthest apart (linear).

On the basis of the argument developed above, it is expected that molecules of the type  $AH_2$  with less than five valence electrons should be linear in the ground state and  $BeH_2$  and  $HgH_2$  are found to be so. Furthermore, molecules in which the  $b_1$  orbital is full or partially occupied, makes the bent configuration more probable. Hence molecules containing 5, 6, 7, or 8 valency electrons are likely to be bent in the ground state. Consequently,  $BeH_2$  and  $HgH_2$  should be bent in the first excited state.

The steepness of the curves  $a_1-\sigma_g$ ,  $b_2-\sigma_u$ , and  $a_1-\pi_u$  may vary from molecule to molecule. For example in a series like  $H_2O, H_2S, H_2Se$ , if the bonding curves fall less steeply from  $H_2O$  to  $H_2Te$ , the bond angle would perhaps tend to decline. A similar effect would result if the  $a_1-\pi_u$  curve rises more steeply.

A less common, perhaps more general way to arrive at the molecular geometries is to arrange repelling nuclei in the charge density of electrons in such a way that the internuclear repulsion forces are neutralized. This brings into play the Hellmann-Feynman electrostatic theorem, according to which the force on nuclei  $a$  and  $b$  is given by

$$\text{Force} = \frac{Z_a Z_b}{R^2} - \frac{1}{2} \left[ \int \rho \frac{Z_a}{r_a^2} \cos \theta_a dv + \int \rho \frac{Z_b}{r_b^2} \cos \theta_b dv \right]$$

Here the first term is the repulsion between the nuclei, and the expression in brackets contains two attractive terms between the nuclei and the electronic density distribution  $\rho$ . Any changes in  $\rho$  will perturb the force on the nuclei and consequently this causes the molecular geometry to change. The perturbation in charge densities causes the variation in angles of mole-



cules like  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ , and  $\text{H}_2\text{Te}$  or in the species  $\text{NO}_2$  ( $132^\circ$ ),  $\text{NO}_2^-$  ( $115^\circ$ ). Similarly small perturbation in molecules may be treated on the basis of  $\Delta\rho$ , the change in electronic densities, when an atom of hydrogen in methane is replaced by a halogen atom. The trouble is that high accuracy  $\rho$  calculations are not easy to make.

3. The Linnett 'Double Spin Set' Model. Historically, two ideas have made significant contributions towards the development of the structure of the atom and chemical valence:

(1) That there is a tendency in atoms to react or gain or lose electrons in order to acquire inert gas configuration. This means that the presence of eight electrons in the outermost orbit give the atom a 'stable shell of electrons.'

(2) That the combination between two atoms or ions take place through a pair of electrons in which each atom contributes one electron. Strictly speaking it is a 'shared pair' that is responsible for bonding.

The first idea is due to Kossel<sup>4</sup> while the second was proposed by Lewis<sup>6</sup> and developed by Langmuir.<sup>6</sup> Through years the above concepts developed into the 'octet rule' and the 'electron pair bond' as rules of thumb for structural arguments in chemistry, until 'single electron bonds, inert gas compounds, and paramagnetic  $\text{O}_2$ , demanded a more sophisticated picture of the structure of molecules to be constructed. Quantum mechanics came to the rescue but the simple classical ideas of Kossel, Lewis, and Langmuir are still intuitively appealing to the chemist. The Linnett 'double spin set' model is in fact a revival of the days gone by and has much scientific as well as nostalgic value. Undoubtedly, the Linnett representation for molecules has many advantages over classical representation as will become evident from the following discussion.

Linnett<sup>7,8</sup> starts with an argument based on the exclusion principle and makes the additional observation that the effect on the particle (neutral) spin correlation is enhanced by making the particles electrically charged. This makes the electrons avoid each other more than would be expected on the basis of spin correlation alone. This puts some restriction as to the extent of electron pairing. On the basis of his quantum mechanical reasoning, Linnett proposed that eight electrons in neon may be considered to be occupying two tetrahedra, four of each spin-set, instead of the assumption that they are present as 'four pairs'. Quantum mechanical justification for such a viewpoint may be given in the following words by Berry:<sup>9</sup>

'The tendency of one electron to repel another and to force the wave-functions of the two electrons to have low amplitudes when the electrons are near gives rise to the concept of the *correlation hole*. This hole takes the form of a region around each electron, the region where the fluctuation potential is very large, where no other electron is likely to be. The Pauli exclusion principle establishes this hole moderately well for electrons of the same spin, but it has no effect on the spatial distribution of electrons with opposite spins, so it does not help to introduce any correlation effect. In this case the correlation hole must be a pure coulomb hole and can only be introduced in a wave-function by in-

clusion of specific terms above and beyond the Hartree-Fock function.'

Eight electrons may be arranged in pairs at the corners of a tetrahedron\* which is equivalent to cubic arrangement with only opposite corners occupied (Fig. 5a), or in two tetrahedra where each electron sits at each corner of a cube (Fig. 5b). It is remarkable that cubic and tetrahedral electronic configuration of atoms were intuitively derived before the development of ideas about electron spin. In the Linnett double spin set model the cubic representation holds with the modification that opposite corners of a cube are occupied with electrons of opposite spin (Fig. 5c). This helps each electron to avoid its nearest neighbour (electron of the opposite spin) by a length equal to the edge of a cube and to repel electrons of the same spin even at a greater distance as next nearest neighbours. This is equivalent to superimposing two tetrahedra as shown in Fig. 5d. The overall effect of such an electron correlation is that the electronic structure for molecules has to be represented by two 'spin sets' thus leading to some interesting observations.

According to the Linnett scheme the tetrahedral arrangement of electrons of one spin set may be 'coincident' or 'non-coincident' to the other spin set. In the Lewis scheme it was always coincident thus leading to 'electron pairs', in the new scheme the electrons may or may not be paired. For example, the fluorine molecule is represented by the following two spin set pictures. These pictures are superimposed to account for all 14 valence shell electrons, 7 of each spin set

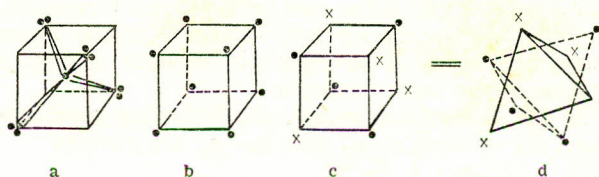


Fig. 5. Various electron distributions for eight electrons: (a) tetrahedral arrangement for 'electron pairs'; (b) cubic arrangement, each electron occupying a corner; (c) two tetrahedra (one of each spin set) arranged in a cube; (d) another way of looking at two tetrahedra of Fig. 5c.

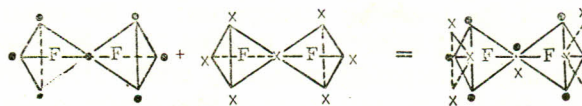


Fig. 6. Linnett structure for the  $\text{F}_2$  molecule.

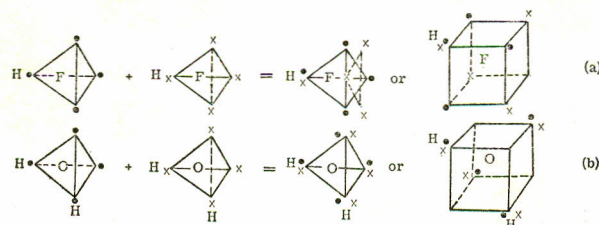


Fig. 7. Various ways to represent (a) HF and (b)  $\text{H}_2\text{O}$  molecules using Linnett double spin set model.

\*Interestingly enough, Lewis arranged four electron pairs in the middle of the edge of a cube which gives only an irregular tetrahedral configuration.



(Fig. 6). In HF and H<sub>2</sub>O, 8 valence shell electrons are arranged in two spin sets of 4 to yield the following structures (Fig. 7). Similarly, N<sub>2</sub> and O<sub>2</sub> have the following structures (Fig. 8).

This apparently tedious representation has been simplified by using a shorthand notation. A heavy line is used to stand for two electrons of opposite spin occupying the same orbital (an electron pair in the normal sense) and a light line to represent two electrons of opposite spins, occupying different orbitals. With this in mind, the formulae for some of the molecules previously described may be given as in Fig. 9. The O<sub>2</sub> molecule turns out to exhibit some interesting features.<sup>7</sup> The model predicts that O<sub>2</sub> in its ground state should be paramagnetic and it is. The excited states of O<sub>2</sub> has been shown in Fig. 10.

The Linnett 'double spin set' model, like the Lewis model, reveals clearly the number of electrons responsible for bonding in molecules and in addition gives information as to the number of electrons belonging to each 'spin set', an obvious advantage in predicting magnetic properties of molecules. The model works for most molecules without the magic of hybridization. Due to these merits, it will not be surprising if the model will enjoy increasing popularity in the future.

**4. The FSGO Model.** The gaussian orbitals have been extensively used by many authors to calculate energies and geometries of atoms and molecules.<sup>10-13</sup> In most calculations the SCF-MO scheme has been applied for gaussian type orbitals. These orbitals have the general form  $\varphi = r^{n+l} e^{-\alpha r^2}$ .

Where  $\alpha$  is the variation parameter and  $n$  takes on values 0, 1, 2, ... They differ from the Slater type orbitals (STO) in their property of decaying to zero much more quickly, particularly for large internuclear distances. This of course is obvious from the plots in Fig. 11, where  $e^{-\alpha r^2}$  is gaussian and  $e^{-\alpha r}$  represents an STO. Furthermore, the gaussian type orbitals (GTO) have no well defined 'cusps' and are, therefore, a poor approximation for an atomic orbital at small internuclear distance (Fig. 11). For a more accurate representation of atomic orbitals, however, linear combinations of several spherical gaussians are usually taken. This means that for accurate energy calculations in GTO's many more integrals are needed as

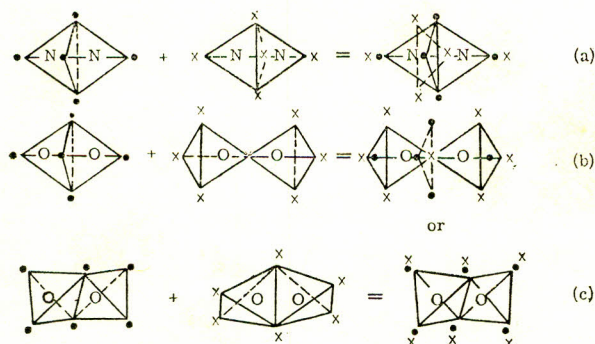


Fig. 8. Linnett structures for (a) N<sub>2</sub> molecule, (b) and (c) O<sub>2</sub> molecule. Here (b) and (c) represent two out of the three possible electronic rearrangements under the Linnett scheme. For details see Fig. 10.

compared to STO's. This difficulty is counterbalanced by the fact that integrals involving gaussians are much easier to evaluate as compared to Slater type integrals. Nevertheless, the cusp effect on the nuclei is only of secondary importance as regards energy calculations. According to Hellman-Feynmann theorem the 'charge pile up' between the nuclei is the major effect.

Both normalized and unnormalized gaussians are useful for energy and geometry calculations. All necessary integrals for the unnormalized gaussian have

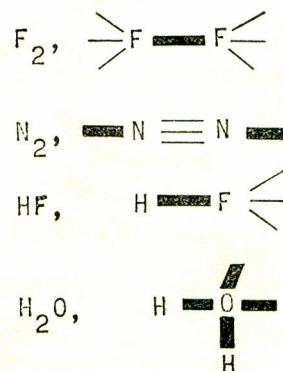


Fig. 9. Line representations for various molecules as pictured by Linnett. A heavy line stands for an 'electron pair' bond in the Lewis sense. A light line represents two electrons of opposite spin but occupying different orbitals.

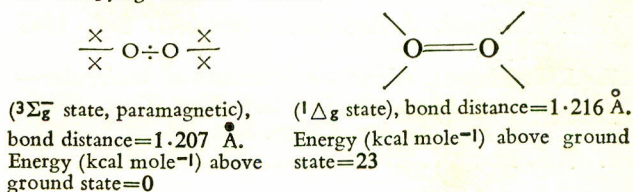


Fig. 10. Various electronic states for O<sub>2</sub> molecule.

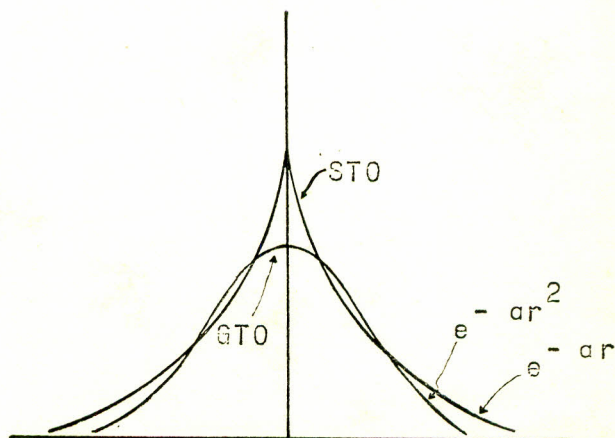


Fig. 11. Curves showing plots of  $e^{-\alpha r}$  vs  $e^{-\alpha r^2}$ . Also showing lack of 'cusp' for a GTO as compared to an STO.



been given by Boys<sup>14</sup> and in greater detail by Shavitt<sup>15</sup> while Preuss and Whitten formulas for normalized spherical gaussians are given elsewhere.<sup>16,17</sup>

More recently Frost has developed a model which uses floating spherical gaussian orbitals (FSGO) for the calculation of energies and geometries for various atomic and molecular systems.<sup>18</sup> The model is perhaps too native to give quantitative estimates of energies for molecular systems as good as the SCF-MO scheme, for example. In spite of its simplicity, the model predicts remarkably well the trends in reproducing observable properties and molecular geometries in chemical systems.

Other workers have also used floating gaussian orbitals for molecular energy and geometry computations.<sup>19</sup>

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