THEORETICAL STUDY OF BINDING ENERGY AND ELECTRONIC ENERGY LEVELS IN SMALL CLUSTERS OF METAL ATOMS.

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ABSTRACT.

The theme of this research has been to investigate the structural and some of the electronic properties of various isomers for aggregates consisting of up to nine univalent atoms. The study presents a classification, by group-theoretical methods, of some of the energy levels for these systems and highlights the stability of the linear configuration. The latter result emphasizes an important difference between classical and quantum bonding theories; in the former, maximization of the number of bonds entails greatest stability.

The cause of the gradual change from the linear to the three-dimensional structures, as the most stable configuration for larger clusters, was also investigated and appears to be a consequence of the increasing ratio of volume to surface atoms for the latter isomers.

The variation of ionization potential with cluster size and shape was studied through qualitative analysis of the charge distribution in the highest occupied orbital of each system. The predicted trend for small linear complexes was found to fit into the general pattern determined by experiment.

Two distinct, but complementary, approaches have been adopted in this study. The first of these, the ENERGY formulation, analysed each system in terms of its total energy or, when detailed information concerning a particular phenomenon was desired, in terms of the appropriate component of the total energy. This approach involved the setting up of a simplified model, chosen by systematic approximations of the Hartree-Fock and Phillips-Kleinmann theories, and was used in deriving potential curves for the dimer, the trimer (equilateral triangular form) and quadramer (square and tetrahedral forms).

On the other hand, the CHARGE DENSITY formulation viewed the formation of an aggregate in terms of the accompanying redistribution of the valence charge. Symmetry arguments were used to obtain a pictorial description of this redistribution and, along with the electrostatic theory of Hellmann and Feynman, formed the basis of a qualitative Molecular Orbital theory by which the relative stability of different isomeric forms was studied.

An interesting by-product of the shift in emphasis away from purely energetic considerations and to the gross properties of the charge distribution, is the suggestion that the absence of core-electrons indirectly accounts for the non-metallic bulk properties of hydrogen. This hypothesis may be compared with the resonance theory of the Valence Bond explanation of metallic bonding.

CONTENTS.

CHAPTER I.

INTRODUCTION AND HISTORICAL REVIEW.

INTRODUCTION .

In recent years, considerable interest has been aroused in the experimental investigation of clusters of metal atoms formed by partial condensation occurring in metal vapours during their expansion through some small orifice (Nature (1971)). The ionization potentials of such clusters have been determined by the use of photo-ionization and mass-spectrometer techniques. In particular, the ionization potentials of clusters of up to eight sodium atoms have been reported (Robbins et. al. (1967)) and, despite some odd-even irregularities, show an overall reduction towards the metallic work function as the size of the aggregate increases. Furthermore, the results indicate that the occurrence of these small systems will considerably enhance the electrical conductivity of saturated vapours of alkali metals.

The importance of the roles played by small polyatomic systems, that is, systems consisting of less than one hundred atoms, in many phenomena of physical significance has been recognized for many years. Such phenomena include, for example, vapour phase nucleation and clustering in a dense fluid (Burton (1970)), as well as the anomalously small heats of vaporization of condensed films of metals on surfaces such as glass (Taylor et. al. (1933)). As pointed out by Hoare et. al. (1971), much theoretical work remains to be done in order to obtain an understanding of these micro-crystallites.

Although the theoretical investigation of the above systems is of intrinsic value, many of the techniques which have been developed have also proved adequate for the analysis of various properties of the bulk material (Messmer et. al. (1970); Inan Chen (1970); Bennett et. al. (1971)).

The developement of quantum theory has made possible, at least in principle, the explanation of the chemical and physical properties of many-particle systems. The main difficulty arises in providing a quantitative analysis of such systems. There, however, remains the possibility of introducing helpful simplifications which make quantitative investigation feasible and, in some cases, lead to quite accurate results.

In the fields of molecular and solid state physics, the basic assumption is that the nuclear and electronic motions may be considered separately. Such a simplification is possible mainly because of

i) the smallness of the electronic mass as compared with that of the nuclei; and

ii) in these systems, the electrostatic forces are dominant and other forces may, in general, be treated as perturbations with a high degree of accuracy.

Besides the abovementioned decoupling of the electronic and nuclear motions, these features also permit the Virial and Hellmann-Feynman Theorems to take on rather simple, but useful, forms.

In the following three chapters, brief reviews of various aspects of the theory of molecular quantum mechanics are given. Chapter II deals with the basic simplifying assumptions made to permit quantitative analysis and some of their implications. As the particular mathematical developement of the theory used in this research project has been mainly for use in quantum chemistry rather than in theoretical solid state physics, Chapters III and IV have been devoted to its consideration. More exhaustive accounts of the theory may be obtained from the numerous references cited.

Chapter V outlines some recent improvements of the above theory as well as attempts at modifying some of the methods of solid state theory to molecular (finite systems) problems.

Qualitative Molecular Orbital theory can be used to give a pictorial understanding of the shapes and other properties of molecular systems (Bond (1966)). Such an analysis draws upon the physical insight and experience derived from quantitative investigations of the most simple systems and, although of no direct numerical value, is not encumbered by the shortcomings of any of the present models used for studying complex systems. Thus, although the LCAO-MO framework is found to be most convenient for the analysis, the only assumptions made in the theory used here are those of the independent-particle approach. Attention is focussed on the orbitals of the system rather than on the determination of its total energy.

The gross features and relative energies of molecular orbitals can be inferred from simple symmetry arguments, the occurrence of nodal planes and/or surfaces and the resulting electronic charge distribution. None of the arbitrary assumptions of orbital hybridization prevelant in qualitative Valence Bond theory are used.

Recently, Gimarc (1973) has adopted a similar approach in his analysis of various molecular systems. The present description is, however, somewhat more physical in that it emphasizes the electronic charge distribution rather than the ' mathematical ' concept of Overlap. Thus, whereas the close relationship between the size of the overlap integral and the strength of bonding has been mentioned on many occassions (see, for example, Slater (1963)), the rule of ' maximization of overlap ' used by Gimarc is only useful for particular approximations and basis sets (McWeeny et. al. (1969)). The arguments used here are, on the other hand, more closely related to the more general force concepts originally put forward by Berlin (1951) and Clinton et. al. (1959).

The object of this research is to present some examples of the kind of information which can be derived about the properties of small clusters of univalent atoms, using qualitative Molecular Orbital theory, and to suggest a reason for the differences between aggregates of hydrogen and other monovalent atoms.

Employing a model Hamiltonian derived from systematic approximations of the Hartree-Fock and pseudopotential theories, quantum-mechanical calculations are also performed on the sodium dimer, trimer and quadramer systems. Conclusions drawn from these results and, in some cases, from semi-empirical Diatomics-In-Molecules energy expressions are compared with each other and with those of the qualitative analysis.

Chapters VI through X describe the methods used in and conclusions of this research.

Experimental Details.

Until recently, there has been very little experimental information on the properties of small clusters of atoms or molecules. The main reason for this is that, under equilibrium conditions, such systems are only stable in the presence of high pressures which, in the case of metallic vapours, also implies high temperatures. Recently, however, it was found possible to produce small clusters of molecules in the non-equilibrium conditions of an adiabatic expansion and to study them with a mass-spectrometer. Robbins et. al. (loc. cit.) have extended this technique to measure the ionization potentials of clustered alkali-metal atoms.

The alkali-metal vapour was generated in a boiler and the vapour allowed to expand through a small orifice into a vacuum chamber. Owing to the rather small mean free path in the vapour on reaching the orifice, the expansion was adiabatic and rapid cooling resulted. In the vacuum chamber, the mean free path was large and clusters were formed in the vapour because of supersaturation; the vapour flow assumed molecular character.

After being collimated, the molecular beam was passed directly through an ionization chamber to a cold trap; in the chamber, the molecular species of the beam were ionized and a mass analysis made in the usual manner. The ion beams were detected using an electron-multiplier system.

The ionization was done by focussed ultra-violet light (~2200 A°) from a prism monochromator which was first calibrated against the known ionization potentials of the monatomic alkali systems and points from the visible spectrum of a mercury discharge lamp. The threshold wavelength for ion production was then determined and the corresponding ionization potential found from the calibration curve.

Robbins et. al. have quoted an accuracy of ~0.1 e.v. in their published values. According to them, the main source of inaccuracy is the need to use large slits in the optical system in order to obtain adequate ion beams for mass-spectroscopy.

Theoretical Analysis.

As long ago as 1933, Taylor et. al. had investigated the binding energies of various isomers of three to eight sodium atoms in order to predict the most probable growth scheme for the formation of the unit cell in the bulk material. The method which they employed was based on the Valence Bond formalism but included the neglect, or semi-empirical evaluation, of a number of integrals needed for the computation of the energy.

Since then, various semi-empirical valence electron models have been developed, mainly in an effort to circumvent the mathematical and computational difficulties which arise when investigating systems with large numbers of electrons. In such models, it is assumed that the electrons of the system may be separated into two groups, the core and valence electrons, with the properties of the system being determined by the latter. Moreover, the cores are assumed to be unaffected by the presence of the valence electrons, or of other cores.

The theoretical models employed may be divided broadly into the following two classes:

1.) Molecular Orbital models in which the core electrons are neglected and where the Hartree-Fock matrix elements for determining the motion of the valence electrons (Chapter IV) are obtained from atomic information, parametrization and the neglect, or approximate evaluation, of some of the two-electron integrals (Baetzold (1972a); Sannigrahi (1972)). Although such models have been applied quite successfully to a variety of systems (Baetzold (1972b)), the identification and improvement of inadequacies is rather less straightforward than for the alternative models mentioned below.

As pointed out by Baetzold (1972b) in his review article, the results predicted using the above model seemed to be in opposition to classical concepts, where the maximum number of bonds implies greatest stability. In contrast, the relative stability of various isomers was found to depend critically upon their antibonding valence states. The destabilizing character of these states was shown to be very sensitive to the number of nearest neighbours. However, these conclusions must be considered against the assumption that the nuclear and electronic interactions cancel each other; that is, the total energy of any system is the sum of the occupied valence orbitals' energies plus the energies of its ion cores:

$$W_{Tot.} = \sum_{i}^{occ.} n_i \varepsilon_i + \sum_{\alpha} E(\alpha) \qquad \text{....(I.1)}$$

where n_i is the occupation number of the valence orbital with energy, ε_i ; $E(\alpha)$ is the energy of the α-th ion core of the system. The results also indicate that there is an overall decrease of valence level spacing and of ionization potential towards their respective values for the bulk material as the size of the aggregate increases. Furthermore, the variation of the band gap, defined as the energy separation between the highest occupied and lowest unoccupied valence states, with size appears to be a property depending on the type of atoms composing the cluster. Thus, for metal atoms, this gap decreased quite rapidly whereas, it remained rather large for semiconductors and insulators.

2.) Models in which an attempt is made to incorporate the effects of the core electrons, without their explicit consideration. Such models fit into the formalism described by Weekes et. al. (1968, 1969) and discussed briefly in Chapter V. Thus, in their studies of some alkali-metal systems, Roach et. al. (1968, 1970) and Pickup et. al. (1972) defined a model Hamiltonian for the system by the equation

$$\mathcal{H}_{model} = \begin{cases} -\sum_{i}\sum_{\alpha\neq\beta} Z''_{\alpha} e^{2}/r_{i\alpha} + \sum_{i>j} e^{2}/r_{ij} & 0 \leqslant r_{i\beta} \leqslant \sigma_{\beta} \\ -\sum_{i}\left(\hbar^{2}\nabla_{i}^{2}/2m_{e} + \sum_{\alpha} Z''_{\alpha} e^{2}/r_{i\alpha}\right) + \sum_{i>j} e^{2}/r_{ij} & r_{i\alpha} > \sigma_{\alpha} \end{cases} \qquad \text{........(I.2)}$$

with $r_{i\alpha} = | \underline{r}_{i} - \underline{R}_{\alpha} |$, $r_{ij} = | \underline{r}_{i} - \underline{r}_{j} |$

and where $\underline{r}_{i}$ and $\underline{R}_{\alpha}$ are the position vectors of the i-th valence electron and the α-th atom, respectively. $Z''_{\alpha} e$ and σ_{α} are respectively the effective nuclear charge and ionic radius of the α-th atom. The latter is treated as an empirical factor.

The justification of this model is the effective cancellation of the strong electrostatic attraction experienced by a valence electron when in the core region by the large kinetic energy which the electron possesses there. The valence electrons of the system may, therefore, be described by orbitals which are not orthogonal to those of the core electrons, when using the above model Hamiltonian.

The main conclusions to be drawn from the investigation of some alkali-metal systems using the above approach include

i) the crucial importance of adequately accounting for the orthogonality of the valence orbitals to those of the core electrons, that is, σ_{α} must be non-zero. In fact, this effect prohibits the close approach of the valence electrons to the atomic nuclei and explains the relative strengths of the one- and two-electron chemical bonds in systems such as Na_2^+ and Na_2 , respectively.

ii) It appears that p-type orbitals must be included in the basis set (Chapters IV, VI) in order to properly describe the binding in clusters of alkali-metal atoms. Equilibrium geometries and ionization potentials, however, appeared to be quite accurately determined when only s-type orbitals were included in the basis set.

In spite of its successes, the model has failed completely when applied to certain systems, for example, lithium (Pickup et. al. (loc. cit.)). The reason for this failure appears to be unknown. Furthermore, the Hamiltonian of equation (I.2) is non-Hermitian and the effect of symmetrization used by the abovementioned authors in order to retain the Hermitian property has not been investigated. Also, the non-physical aspect of the ionic radius and the discontinuity introduced into the core potential at this boundary remain unsatisfactory features of the model.

In connection with the use of the formalism of model Hamiltonians, the pseudopotential approach of Szasz and McGinn (1967, 1968) should also be mentioned. Further details of the results of this and the other methods will be given in a later chapter.

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CHAPTER II.

BACKGROUND INFORMATION.

The Born-Oppenheimer Approximation.

Consider the time-independent Schrödinger equation for any system of particles; for example, nuclei and electrons:

$$H_{Tot.}\,\Psi_{Tot.} = W_{Tot.}\,\Psi_{Tot.} \quad , \qquad ....(II.1)$$

where the Hamiltonian operator, $H_{Tot.}$, and the wavefunction, $\Psi_{Tot.}$, are functions of the electronic and nuclear coordinates.

Assume

$$\Psi_{Tot.}(\underline{R},\underline{r}) = \Psi_{Nuc.}(\underline{R})\,\Phi(\underline{R},\underline{r}) \qquad ....(II.2)$$

where $\Psi_{Nuc.}(\underline{R})$ describes the nuclear motion and depends upon the nuclear coordinates, represented collectively by the symbol, $\underline{R}$, only; $\Phi(\underline{R},\underline{r})$ describes the electronic motion and depends upon both the electronic coordinates, represented collectively by $\underline{r}$, and the nuclear positions.

If the positions of the nucleus, α, and the electron, i, relative to some chosen origin, are denoted by $\underline{R}_\alpha$ and $\underline{r}_i$ respectively, then equation (II.1) becomes

$$\Big\{ -\sum_{\alpha}(\hbar^2/2M_\alpha)\nabla_\alpha^2 - \sum_{i}(\hbar^2/2m_e)\nabla_i^2 - W_{Tot.} + \sum_{i>j} V_{ij} + \sum_{\alpha,i} V_{\alpha i} + \sum_{\alpha>\beta} V_{\alpha\beta} \Big\}\,\Psi_{Nuc.}\,\Phi = 0$$

where

$$\begin{aligned} V_{ij} &= e^2/|r_i - r_j| \quad , \\ V_{\alpha i} &= Z_\alpha e^2/|R_\alpha - r_i| \quad , \\ V_{\alpha\beta} &= Z_\alpha Z_\beta e^2/|R_\alpha - R_\beta| \quad , \qquad ....(II.3) \end{aligned}$$

m_e, M_α = mass of electron and α-th nucleus, respectively

and Z_α = atomic number of α-th nucleus.

Simplification of equation (II.3) gives

$$\Psi_{Nuc.}(\underline{R})\left\{-\sum_{i}(\hbar^2/2m_e)\,\nabla_i^2 + \sum_{i>j}V_{ij} + \sum_{\alpha,i}V_{\alpha i}\right\}\Phi(\underline{R},\underline{r})$$

$$+\ \Phi(\underline{R},\underline{r})\left\{-\sum_{\alpha}(\hbar^2/2M_\alpha)\,\nabla_\alpha^2 + \sum_{\alpha>\beta}V_{\alpha\beta}\right\}\Psi_{Nuc.}(\underline{R})$$

$$-\ \Psi_{Nuc.}(\underline{R})\sum_{\alpha}(\hbar^2/2M_\alpha)\,\nabla_\alpha^2\,\Phi(\underline{R},\underline{r})$$

$$-\ \sum_{\alpha}(\hbar^2/2M_\alpha)\,\underline{\nabla}_\alpha\Psi_{Nuc.}(\underline{R})\cdot\underline{\nabla}_\alpha\,\Phi(\underline{R},\underline{r})$$

$$=\ W_{Tot.}\,\Psi_{Nuc.}(\underline{R})\,\Phi(\underline{R},\underline{r})$$

........(II.4)

The basic assumption in the theory of molecules and solids is made possible because of the very small ratio of the electronic to nuclear masses. A straightforward argument, based on either the Uncertainty Principle of quantum mechanics or the Equipartition Principle of classical mechanics, indicates that the electronic velocities are much larger than the nuclear velocities. The Born-Oppenheimer approximation (Born and Oppenheimer (1927)), therefore, assumes that the electronic motion depends solely upon the instantaneous nuclear positions and to a much lesser extent upon the actual nuclear motions. Thus, by neglecting the last two terms on the left-hand side of equation (II.4),

$$\left\{-(\hbar^2/2m_e)\sum_{i}\nabla_i^2 + \sum_{i>j}V_{ij} + \sum_{\alpha,i}V_{\alpha i}\right\}\Phi(\underline{R},\underline{r}) = E_{elec.}(\underline{R})\,\Phi(\underline{R},\underline{r})$$

....(II.5)

and

$$\left\{-\sum_{\alpha}(\hbar^2/2M_\alpha)\,\nabla_\alpha^2 + \sum_{\alpha>\beta}V_{\alpha\beta} + E_{elec.}(\underline{R})\right\}\Psi_{Nuc.}(\underline{R}) = W_{Tot.}\,\Psi_{Nuc.}(\underline{R})$$

....(II.6)

These equations respectively determine the electronic and nuclear motions in the Born-Oppenheimer approximation. $\Phi(\underline{R},\underline{r})$ depends only upon the instantaneous nuclear configuration, denoted by $\underline{R}$, and not upon the nuclear motion since all the derivatives of Φ with respect to the nuclear coordinates have been neglected. Slater (1963a) and Longuet-Higgins (1961) have shown that the neglect of these terms is justifiable under certain conditions.

This uncoupling of the electronic and nuclear motions means that the nuclei are assigned fixed positions and the motion of the electrons in the field of the fixed nuclear framework determined by equation (II.5). The process is repeated at other fixed nuclear positions and it is assumed that the sequence of electronic distributions describes the time developement of the true electron distribution as the nuclei change their positions in time in passing through the chosen configurations.

Equation (II.5) has to be solved subject to two conditions on the wavefunction, $\Phi(\mathcal{R},r)$. These are

1.) the wavefunction and its derivatives must be square integrable; and

2.) the Pauli Exclusion Principle must be satisfied.

This latter condition follows from the requirement that the electronic wavefunction be antisymmetric with respect to interchange of the ' positions ' of any two electrons of the system. The ' position ' of the i-th electron is here specified by its spatial coordinates, $\underline{r}_i$, as well as its spin coordinate, s_i . These are collectively represented by the single coordinate, $\underline{x}_i$. It is also noted, in passing, that the generalized electronic wavefunction, $\Phi(\mathcal{R},x)$, is an eigenfunction of equation (II.5) since the operator is independent of spin effects.

The above permutation symmetry of the electronic wavefunction can be included from the outset by choosing $\Phi(\mathcal{R},x)$ to be represented by a Slater determinantal function (Slater (1929)), or some linear combination of them. In such an approximation, called the independent-particle model, the motion of each electron of the system is described by a function which depends solely upon the space and spin coordinates of the electron. Further discussions of this model is given in later sections of this chapter and in Chapters IV and V.

The Breakdown Of The Born-Oppenheimer Approximation.

The Born-Oppenheimer approximation holds as long as the electronic function is non-degenerate. Situations generally arise where degeneracy, or near degeneracy, does occur and the above analysis has to be modified (Longuet-Higgins (loc. cit.)).

In the study of highly symmetrical structures, symmetry considerations generally lead to degenerate situations which are split in the actual physical system through the nuclear motion. The small terms which were neglected above must then be considered in order to calculate the energy differences in such splitting. Furthermore, the Jahn-Teller effect, mentioned briefly in the following section, prohibits the occurrence of stable, degenerate electronic states for non-linear polyatomic structures, as may be predicted in the Born-Oppenheimer approximation.

Although linear structures with degenerate electronic states are stable against Jahn-Teller distortions, the nuclear motion again splits such degeneracies. This effect, known as the Renner effect, results in a modification of the spectra of linear, as well as non-linear, structures.

Thus, the nuclear and electronic motions are definitely inter-related and the approximation will fail in the analysis of those situations where the splitting of energy levels depends strongly upon the nuclear motion.

Jahn-Teller Effect.

It is tempting to assume that atoms in polyatomic systems would tend to occupy positions such that the configurational symmetry is a maximum. Closer analysis, however, indicates that, although this may in fact be the case at relatively high temperatures because of the higher entropy possessed by more symmetrical configurations (Kanamori (1960)), it is not generally the case at lower temperatures.

Jahn and Teller (1937, 1938) have shown that, on completely general grounds, a non-linear molecule possessing a degenerate electronic ground state is intrinsically unstable against distortions which remove the degeneracy. Thus, if in a Born-Oppenheimer calculation a configuration is assumed which gives rise to such an electronic degeneracy in the ground state, the coupling of the vibrational and electronic motions must be considered in order to determine the true molecular configuration. In such a vibronic coupling, the nuclei are displaced, the electronic degeneracy removed, and the molecule moves towards its equilibrium configuration.

The Jahn-Teller Theorem.

This states that a geometrical configuration in which the electronic state is degenerate cannot be stable except in the following cases:

1.) The system contains an odd number of electrons and the degeneracy is the two-fold Kramer's degeneracy which cannot be removed by any changes in the electrostatic field. In practice, all spin-degenerate cases are neglected because of the smallness of the Jahn-Teller distortions in such cases.

2.) The molecular structure in which the electronic state is degenerate is linear.

In every other case there exists a configuration of lower symmetry in which the degeneracy is removed to first order in the nuclear displacements from their symmetrical positions. The centre of gravity of the perturbed energies of the split levels is equal to the energy of the originally degenerate state. Thus, at least one of the split levels is more stable than before and the system can lower its energy by becoming less symmetrical and removing the degeneracy.

The mathematical formulation of the Jahn-Teller and Renner effects has been given by Longuet-Higgens (loc. cit.) and applied extensively to transition-metal complexes by Sturge (1967). More recently, these effects have been shown to explain observed data on many organic molecular systems (Coulson (1971); Englemann (1972)).

The Variational Principle.

It is mathematically impossible to obtain direct solutions of the Schrödinger equation for many-electron systems and it has therefore been necessary to resort to some approximate method of analysis; for example, the single-particle approach or independent-particle model. In such an approximation, the motion of an electron is described by a function which depends solely upon the coordinates of that electron. Thus, in effect, the motion of each electron of the system is independent of the positions of all other electrons.

However, it is yet possible to incorporate, in an average manner, the effect of the inter-electronic Coulombic repulsions through the Variational Principle (Pauling and Wilson (1935)).

If the trial wavefunction chosen to represent some state of the system is completely arbitrary, use of the variational principle to obtain the best energy can be shown to be equivalent to the statement that the trial wavefunction and energy are the eigenfunction and eigenvalue, respectively, of the time-independent Schrödinger equation. However, when some restriction is placed upon the form of the trial function, for example, the Hartree and Hartree-Fock wavefunctions, the variational principle gives the optimum function of the particular restricted form. Such a wavefunction will give the best values of those properties for which it has been optimized but there is no guarantee that it will give good values for any other properties of the system.

A brief discussion of the derivation and use of the Variational Theorem has recently been given by Shull (1970). Briefly, the theorem states that the average value of a given operator, as computed for an arbitrary trial function defined in the space spanned by the eigenfunctions of the operator, is an upper bound to its lowest eigenvalue. When applied to excited states, care must be taken to ensure orthogonality between the trial function representing the excited state and the true eigenfunctions of the lower states. The expectation value for such a trial function then converges from above to the true eigenvalue of the state being investigated (Lowdin (1959b)).

Shull (loc. cit.) has further pointed out that, in the analysis of many-electron systems, any variational trial function must be restricted to those which are antisymmetric to exchange of electrons, unless there is a priori knowledge that the eigenvalues of all symmetric functions lie above that of the state being investigated. If this is not the case, the results of the variational theorem may not be valid.

Correlation Effects.

In this section, a brief consideration of the problem of correlation is given. General reviews of this problem have been given by Lowdin (1959b) and Sinanoglu (1964).

The correlation theory of atoms, molecules and solids is an attempt to incorporate into the study of many-electron systems some treatment of the instantaneous mutual repulsions experienced by each electron of the system. The correlation energy, defined as ' the difference between the exact non-relativistic and Hartree-Fock energies of a many-electron system ' , is comparable in magnitude to many of the energy quantities of interest (Lowdin (1959b)); for example, excitation and dissociation energies. For this and other reasons mentioned by Sinanoglu (loc. cit.) it is necessary, therefore, to consider the problem of correlation between electrons.

The consequence of Coulomb correlation is to render the occurrences of close approach of any two electrons of the system energetically unfavourable. Mathematically, this may be expressed by the equation

$$\lim_{r_1 \to r_2} \rho_2(\underline{x}_1, \underline{x}_2 \,|\, \underline{x}_1, \underline{x}_2) = 0 \qquad \text{....(II.7)}$$

where

$\rho_2(\underline{x}_1, \underline{x}_2 \,|\, \underline{x}_1, \underline{x}_2)$ is the two-particle density function (equation (IV.10); McWeeny et. al. (1969a)). Each electron may then be considered as being surrounded by a ' Coulomb ' hole with respect to all other electrons of the system.

Slater (1963b) has pointed out that the antisymmetric requirement on the electronic wavefunction introduces some correlation between the motions of electrons with parallel spins. This follows directly from the two-particle density function (equation (IV.27)):

$$\begin{aligned}\lim_{\underline{x}_1 \to \underline{x}_2} \rho_2(\underline{x}_1, \underline{x}_2 \,|\, \underline{x}_1, \underline{x}_2) &= \lim_{r_1 \to r_2} \rho_2(r_1, s;\, r_2, s \,|\, r_1, s;\, r_2, s) \\ &= 0 \qquad \text{........(II.8)}\end{aligned}$$

Each electron is therefore considered to be surrounded by a ' Fermi ' hole with respect to all other electrons with parallel spin. As shown by Slater (1963b, 1968), the main property of the Fermi hole is to exclude all the charge density due to electrons with parallel spin from the region within the hole. Maslen (1956) has investigated the spatial characteristics of the hole and has shown that it extends some distance away from the actual position of the electron.

Hence, the main problem of correlation theory is to provide a better description of the instantaneous electron repulsion between the electrons of opposite spin. This can indeed be quite significant in the Hartree-Fock formalism where pairs of electrons with antiparallel spins occupy the same spatial orbital (Clementi (1963)).

Various methods have been devised to account, at least partially, for the correlation effect (Sinanoglu (loc. cit.); Parr (1963); Szasz (1968); McWeeny et. al. (1969b); Palke et. al. (1969) and Poshusta et. al. (1973), among others). The most straightforward of these is the Method of Configuration Interaction (Craig (1950)); its mathematical background is the following basic theorem as stated by Lowdin (1959b):

Every normalizable antisymmetric function can be expressed as a series expansion of Slater determinantal functions built from a complete set of one-electron functions.

Thus,

$$\Phi = \sum_{k=0}^{\infty} c_k \Phi_k \quad , \qquad ....(II.9)$$

where the set $\{\Phi_k\}$ of Slater determinants is complete.

In practice, however, such a series is found to be slowly convergent (Slater (1960)). In spite of this, use of a truncated series still provides a better description of correlation between electrons (Karo et. al. (1959); Das and Wahl (1966)) and considerable effort has been expended in determining the optimum set of determinantal functions to affect the most rapidly convergent series (Shull et. al. (1959); Hinze et. al. (1967)) for investigating various systems.

Detailed analysis of simple atoms and diatomic molecules suggests that correlation effects may be divided into three main types (Slater (1960): Shull (loc. cit.)). These are

1.) Radial Correlation: this tends to reduce the chances of the electrons of the system being near the same nucleus simultaneously.
2.) Angular Correlation: this tends to produce some polarizing effect across nodal planes of the system.
3.) ' In-Out ' Correlation: this tends to produce some polarization across nodal surfaces of the system.

The above division of correlation effects is purely conceptual, but is useful within the independent-particle model treatment of this complicated many-particle phenomenon.

The Virial And Hellmann-Feynman Theorems.

The Virial Theorem is useful because it provides a connection between certain calculable properties of any physical system. Such connections may be used in simplifying calculations and checking theoretical results. As shown by Lowdin (1959a), the theorem is valid, not only for exact treatments of the system being investigated, but also for those approximations as derived from the Variational Principle. It however does not hold for results derived from perturbation theory, as pointed out by Teller and Sahlin (1970).

The mathematical aspect of the theorem has been discussed in great detail by Lowdin (1959a), who concluded that ' the fulfillment of the Virial Theorem is a necessary but insufficient criterion that a wavefunction is an accurate solution of the Schrödinger equation corresponding to a stationary state '.

Further discussion of this theorem, especially in relation to the model Hamiltonian used in this research project, is given in Chapter VI.

Another very useful theorem is due to Hellmann (1937) and Feynman (1939). This theorem, which can be easily derived from the Schrödinger equation (II.5), for example, can be expressed mathematically by the equation

$$(\partial E_{elec.}/\partial \mu) = \int \Phi^{*}(\partial H_{op}/\partial \mu)\,\Phi\, d\underline{\tau} \qquad \text{....(II.10)}$$

where μ is some arbitrary parameter

and $\int \Phi^{*}\Phi\, d\underline{\tau} = 1$.

The usual derivation of the theorem (Lowdin (1959a); Shull (1970)) implies that Φ is an exact solution of equation (II.5). Recently, however, Coulson (loc. cit.) has pointed out that equation (II.10) is more general and also holds if Ψ is an exact Hartree-Fock wavefunction (Chapter IV). This follows from a generalization of the Brillouin theorem (McWeeny et. al. (1969c)) and the subsequent use of the Completeness theorem for the set of Slater determinants formed from the Hartree-Fock orbitals to represent $(\partial\Psi^*/\partial\mu)$ and $(\partial\Psi/\partial\mu)$.

The Hellmann-Feynman theorem has proved very useful in the study of molecular systems. Thus, Berlin (1951) has discussed the nature of chemical bonding in molecules by considering the classical Coulomb forces acting on the nuclei of the system due to the quantum-mechanical electron distribution. Other examples of its use may be found in the review paper of Deb (1973).

A variation of this theorem is the Integral Hellmann-Feynman theorem (Parr (1965)). This article may be consulted for references to its uses.

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CHAPTER III.

SYMMETRY AND SERIES EXPANSIONS.

General Considerations Of Symmetry .

Any system of regularly arranged points in coordinate space in general possesses some definite symmetry properties. The system of points may be the lattice sites of a crystal structure, the nuclear or ionic positions of a polyatomic molecule or cluster, or simply the position of a single atom or ion. For any such system, it is possible to define a number of symmetry operations which, if performed on the system, leaves it apparently unchanged. Such symmetry operations include, for example, reflections, inversions, rotations and their products.

Any set of such operations, satisfying certain conditions as specified later, forms a mathematical group and it has become natural to classify crystal structures and the various isomers of molecules and clusters by the corresponding abstract mathematical group of operations (Herzberg (1945); Koster (1957)).

As may be expected, the symmetry properties of the nuclear framework results in certain requirements upon the eigenstates of the system. This effect may be deduced by considering the properties of the Schrödinger equation for the particular system. The invariance of the Hamiltonian operator with respect to the symmetry operations implies that the Schrödinger equation possesses such invariance. Moreover, the eigenfunctions must provide a representation for the group of symmetry operations. As will be shown later, the eigenstates belonging to a given eigenvalue form bases for the various irreducible representations of the particular symmetry group. Thus, the states of the system may be classified by the particular irreducible representations for which they provide bases.

It is very convenient to have a matrix representation of the group of symmetry operations, in which each operation is represented by a matrix.

Such a representation is said to be ' faithful ' if the set of matrices is isomorphic to the set of symmetry operations; that is, there is a one-to-one correspondence between the elements of each set and, moreover, the matrix representation of any ' product ' of two, or more, symmetry operations is identical to the matrix product of the representations of the individual operations.

There is always an infinity of such representations, all of which are inter-related by similarity transformations. Representations related in such a manner are termed Equivalent.

However, there usually exists some similarity transformation which expresses some general representation as a direct sum of representations of smaller dimensionalities. (The dimensionality of a given representation is defined as the dimensionality of the matrices providing the representation of the symmetry group.) Consequently, it is only necessary to consider those representations which cannot be reduced in this manner; such representations are termed Irreducible. Irreducible representations yet remain arbitrary with respect to similarity transformations, as described above.

It has become usual to choose all irreducible representations as unitary, since the properties of such matrices result in considerable mathematical simplification in the theory of representations.

In general, approximate wavefunctions of many-particle systems are expressed as products of the orbitals of the particles of the system. Each orbital may be chosen to have a definite symmetry compatible with the nuclear configuration and thus the product wavefunction has the symmetry determined by the direct-product of the symmetry types of the individual orbitals*. Such a product

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* These orbitals are generally determined by a variational procedure (Chapter IV) and satisfy an equation of the form $h\phi = \varepsilon\phi$.

will not in general possess a definite spatial symmetry but it is quite a straightforward procedure to project its component of symmetry-adapted functions from it.

One of the most valuable applications of the theory of groups is to the approximate solutions of Schrödinger equation and certain forms of the Hartree-Fock equations (Chapter IV):

$$h(r)\,g(r) = W g(r) \qquad \text{........(III.1)}$$

The basic idea is to expand the eigenfunctions of the above equation in terms of a complete set of known functions. Since, however, such sets are in fact infinite, a truncated set is actually used. Thus,

$$g(r) \simeq \sum_{\mu}^{N} c_\mu\, g_\mu(r) \qquad \text{........(III.2)}$$

where $\{c_\mu\}$ are expansion coefficients to be determined and N denotes the size of the set of known functions, $g_\mu(r)$.

Inserting equation (III.2) into equation (III.1) gives, after pre-multiplication by $g_\mu^*(r)$ and integration

$$\sum_{\mu}^{N} c_\mu \left(h_{\nu\mu} - W S_{\nu\mu} \right) = 0 \qquad \text{........(III.3)}$$

$$(\nu = 1, 2, -- N)$$

where $$h_{\nu\mu} = \int g_\nu^*(r)\, h(r)\, g_\mu(r)\, dv$$

and $$S_{\nu\mu} = \int g_\nu^*(r)\, g_\mu(r)\, dv \, .$$

Equation (III.3) has non-trivial solutions provided that the following equation (secular equation) is satisfied:

In general, the operator, h , is invariant with respect to all the symmetry operations of the system and, therefore, the orbitals, ϕ , will possess the properties of the true eigenstates of the system, as mentioned above. Exceptional cases are generally treated in some approximate manner which results in the orbitals having the above-mentioned properties (see McWeeny et. al. (1969a)).

$$\det \left| h_{\nu\mu} - W\Delta_{\nu\mu} \right| = 0 \qquad \ldots.(\mathrm{III}.4)$$

The N roots of the secular equation determine approximations to the lowest N eigenvalues of the system specified by equation (III.1). For each value of W, the set of linear simultaneous equations (III.3) is solved for the coefficients c_μ and the corresponding approximate eigenfunction determined from equation (III.2). As N is increased, the eigenvalues converge from above to the actual values for the system.

The numerical work involved in determining the solutions of the secular equation may be considerably reduced if the set of functions, $g_\mu(x)$, are chosen to be basis functions for irreducible representations of the group of operations leaving the operator, $h(x)$, of equation (III.1) invariant. Such basis functions can be obtained from any general function by the use of the projection-operator technique, as described later.

The functions, $g_\mu(x)$, are now specified by three indices:

$$g_\mu(x) \equiv g^p_{mj}(x) ,$$

where $g^p_{mj}(x)$ transforms as the m-th row of the p-th irreducible representation of the group; the index j distinguishes the different sets of basis functions having this particular symmetry.

Thus, equations (III.2) and (III.4) become

$$g(x) = \sum_p \sum_m \sum_i c^p_{mi}\, g^p_{mi}(x) \; ; \qquad \ldots.(\mathrm{III}.5)$$

$$\det \left| h^{qp}_{nj,mi} - W S^{qp}_{nj,mi} \right| = 0 \qquad \ldots\ldots..(\mathrm{III}.6)$$

where $$h^{qp}_{nj,mi} = \int g^{q*}_{nj}(x)\, h(x)\, g^p_{mi}(x)\, dv$$

and $$\Delta^{qp}_{nj,mi} = \int g^{q*}_{nj}(x)\, g^p_{mi}(x)\, dv .$$

As will be shown later (equations (III.26) and (III.27)),

$$h^{qp}_{rj,mi} = (1/l_p)\,\delta_{pq}\,\delta_{mr} \sum_{n=1}^{l_p} h^{pp}_{nj,ni}$$

and (III.7)

$$s^{qp}_{rj,mi} = (1/l_p)\,\delta_{pq}\,\delta_{mr} \sum_{n=1}^{l_p} s^{pp}_{nj,ni} ,$$

where l_p is the dimensionality of the p-th irreducible representation; δ_{ij} is the Kronecker-delta symbol.

Thus, the secular equation takes the ' block form ' of equation (III.8) below.

$$\begin{vmatrix} \mathcal{D}(1,1) & 0 & - & - & - \\ 0 & \mathcal{D}(1,2) & - & - & - \\ | & & \ddots & & \\ 0 & & \mathcal{D}(1,l_1) & 0 & - \\ 0 & & 0 & \mathcal{D}(2,1) & - \\ | & & | & & \ddots \\ | & & | & & \end{vmatrix} = 0 \qquad \text{........(III.8)}$$

or det $|\mathcal{D}(p,m)_{ij}| = 0$ ....(III.9)
$(m = 1,2,\text{--}\, l_p;\ p = 1,2\text{--})$

with

$$\mathcal{D}(p,m)_{ij} = h^{pp}_{mi,mj} - W\, s^{pp}_{mi,mj} .$$

This is a matrix involving only the basis functions corresponding to the m-th row of the p-th irreducible representation. Furthermore, the elements of the matrix are independent of m (equation (III.7)) and thus

$$\mathcal{D}(p,1) = \mathcal{D}(p,2) = \text{--} = \mathcal{D}(p,m) = \text{--} = \mathcal{D}(p,l_p).$$

........(III.10)

It is, therefore, only necessary to consider one secular equation for each irreducible representation, each of the resulting eigenvalues being l_p-fold degenerate.

As the dimensions of $|\mathcal{D}(p,m)|$ $(p = 1,2,\text{---})$ are usually smaller than those of equation (III.4), considerably less numerical work is needed to compute the approximate eigenvalues of the system.

By the theory of linear simultaneous equations (Slater (1963a)), the eigenfunctions of the system, corresponding to the eigenvalues determined from equation (III.9), are given by

$$g^{p}_{m}(\underline{x})' = \sum_{i} c^{p}_{i}\, g^{p}_{mi}(\underline{x}), \qquad \text{........(III.11)}$$

where the expansion coefficients, c^{p}_{i} , are determined by the simultaneous equations:

$$\sum_{i} c^{p}_{i}\, \mathcal{D}(p,m)_{ji} = 0 \qquad \text{........(III.12)}$$

$$(i,j = 1,2, ---)$$

The set of functions $g^{p}_{m}(\underline{x})$ ($m = 1,2, -- l_p$) forms a basis for the p-th irreducible representation of the group of symmetry operations. This confirms the statement made earlier concerning the properties of the eigenstates of the system as a result of the spatial symmetry of its nuclear configuration.

Group Theory ..... (Finite Groups.)

The following sections give a brief review of the theory of groups. Only those aspects of the theory which specifically relate to the foregoing statements are given. More exhaustive accounts are given in the works of Slater (1963b) and Cornwell (1969), among others.

Definition Of A Group.

A group is a set of distinct elements for which an operation of combining is defined, and which has the following properties:

1.) The ' product ' of two elements of the group is itself an element of the group. (The collection of rules defining the products of any two elements is called the Multiplication Table of the group; that is, the operation of combining in this case is defined as ' multiplication '.)

2.) For any three elements, A,B and C of the group, the Associative Law:

$$(AB)C = A(BC) = ABC$$

must be obeyed.

3.) The group must contain an element, E, called the Identity, such that for any element A of the group,

$$AE = EA = A .$$

4.) For every element A of the group, there exists an element denoted by A^{-1} , and called the inverse of A, that is also a member of the group and satisfies the equation

$$A^{-1} A = AA^{-1} = E .$$

The number of elements of the group is defined as the order of the group. In general, the elements of a group do not commute with each other; that is,

$$AB \neq BA ,$$

where A and B are any two elements of the group. In the particular case when the Commutation Rule does hold, the group is said to be Abelian.

An important property of any group is the existence of Classes of elements.

Definition Of A Class.

A class is defined as a set of mutually conjugate elements of the group. A group element A is said to be mutually conjugate to an other element B if there exists a third group element X such that

$$B = XAX^{-1}$$

General Properties Of Representations.

A group of square l x l matrices, with matrix multiplication as the group operation, is said to form an l-dimensional matrix representation of the group, G, of elements if, to each element A of G, there corresponds a square matrix, $\underline{M}(A)$, from the group of square matrices and

$$\underline{M}(A)\underline{M}(B) = \underline{M}(AB)$$

for every A and B of G.

If $\underline{S}$ is any non-singular l x l matrix, the set of matrices $\tilde{\underline{M}}(A)$ defined for each A of G by

$$\tilde{\underline{M}}(A) = \underline{S}^{-1}\,\underline{M}(A)\underline{S} \qquad \text{........(III.13)}$$

also forms an l-dimensional matrix representation of G. This follows because for any A and B of G

$$\begin{aligned}\tilde{\underline{M}}(A)\tilde{\underline{M}}(B) &= \underline{S}^{-1}\,\underline{M}(A)\underline{S}\underline{S}^{-1}\,\underline{M}(B)\underline{S} = \underline{S}^{-1}\,\underline{M}(A)\underline{M}(B)\underline{S} \\ &= \underline{S}^{-1}\,\underline{M}(AB)\underline{S} = \tilde{\underline{M}}(AB) \qquad \text{........(III.14)}\end{aligned}$$

The two representations $\underline{M}$ and $\tilde{\underline{M}}$ are related by the similarity transformation of equation (III.13) and are therefore Equivalent.

The similarity transformation may be such that $\tilde{\underline{M}}(A)$ takes the ' block form ' :

$$\tilde{\underline{M}}(A) = \left[\begin{array}{c|c} \underline{M}^{\rho}(A) & \underline{0} \\ \hline \underline{0} & \underline{M}^{q}(A) \end{array}\right] \qquad \text{........(III.15)}$$

for each element A of the group G. $\underline{M}^{\rho}(A)$ is a square $l_\rho \times l_\rho$ matrix $(l_\rho < l)$.

Employing the multiplication property of partitioned matrices, it follows that for any A and B of G,

$$\begin{aligned}\tilde{\underline{M}}(A)\tilde{\underline{M}}(B) &= \begin{pmatrix} \underline{M}^{\rho}(A)\underline{M}^{\rho}(B) & \underline{0} \\ \underline{0} & \underline{M}^{q}(A)\underline{M}^{q}(B) \end{pmatrix} \\ &= \tilde{\underline{M}}(AB) \qquad \text{(using equation (III.14)}\end{aligned}$$

$$= \begin{bmatrix} \underline{M}^p(AB) & \underline{0} \\ \underline{0} & \underline{M}^q(AB) \end{bmatrix}, \text{ from equation (III.15)} \qquad \text{........(III.16)}$$

Thus,

$$\underline{M}^p(AB) = \underline{M}^p(A)\underline{M}^p(B), \text{ etc.,}$$

and the group of matrices, $\underline{M}^p$, forms a representation for the group, G. The representation $\tilde{\underline{M}}$ is then said to be Reducible into the direct sum of the representations $\underline{M}^p$ and $\underline{M}^q$:

$$\tilde{\underline{M}} = \underline{M}^p \oplus \underline{M}^q \ .$$

There are some very important theorems which help to deduce the number and dimensionalities of the non-equivalent irreducible representations of a given group from any general reducible representation for the group. These theorems are as follows:

1.) The number of non-equivalent irreducible representations* is equal to the number of classes of the group.

2.) The sum of the squares of the dimensions of the irreducible representations equals the order of the group.

3.) $$\sum_A M^p(A)^*_{\mu\nu} M^q(A)_{\alpha\beta} = (g/l_p)\,\delta_{pq}\,\delta_{\mu\alpha}\,\delta_{\nu\beta} \qquad \text{........(III.17)}$$

where g is the order of the group.

Defining the character of the group element, A, in the p-th irreducible representation by the equation

$$\chi^p(A) = \sum_{\mu=1}^{l_p} M^p(A)_{\mu\mu} \qquad \text{........(III.18)}$$

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* Hereafter, reducible representations are denoted by $\tilde{\underline{M}}$; the p-th irreducible representation is denoted by $\underline{M}^p$. Their associated properties are denoted in a similar manner.

and summing equation (III.17) over the indices μ, ν, α and β ($\mu, \nu, \alpha, \beta = 1, 2, --- l_p$) gives

$$\sum_A \chi^p(A)^* \chi^q(A) = g\delta_{pq} \qquad \text{........(III.19)}$$

Equation (III.19) provides a useful method for investigating reducible representations. Since the character of any group element is invariant under any similarity transformation, the character of the reducible representation must equal the sum of the characters of the irreducible representations appearing in the reduction of $\underline{\tilde{M}}$. Thus,

$$\tilde{\chi}(A) = \sum_p n_p \chi^p(A)$$

or

$$n_p = g^{-1} \sum_A \chi^p(A)^* \tilde{\chi}(A) \qquad \text{........(III.20)}$$

for any group element, A; n_p is the number of times that the irreducible representation, $\underline{M}^p$, occurs in the reduction of $\underline{\tilde{M}}$.

Basis Functions.

Consider a set of linearly independent functions, $g^p_{\mu\nu}$ ($\mu = 1, 2 -- l_p$), such that

$$A g^p_{\mu\nu} = \sum_{\lambda=1}^{l_p} g^p_{\lambda\nu} M^p(A)_{\lambda\mu} \qquad \text{........(III.21)}$$

for each element of the group, G. Then the functions, $\{g^p_{\mu\nu}\}$, are said to be partners in a set of basis functions for the p-th irreducible representation, $\underline{M}^p$. The function, $g^p_{\mu\nu}$, is said to transform as the μ-th row of the representation.

The set of linearly independent functions, $\{\tilde{g}^p_{i\nu}\}$, defined by the equation ($i = 1, 2 --- l_p$)

$$\tilde{g}^p_{i\nu} = \sum_{\mu}^{l_p} g^p_{\mu\nu} \beta_{\mu i} \qquad \text{........(III.22)}$$

forms a basis of a representation, $\tilde{\underline{M}}^p$, that is equivalent to $\underline{M}^p$, since

$$\tilde{\underline{M}}^p = \underline{S}^{-1}\, \underline{M}^p\, \underline{S} \qquad \text{........(III.23)}$$

Thus, similarity transformations are induced by the rearrangement of the basis functions.

There is an infinite number of sets of basis functions which are not related by transformations of the form given in equation (III.22). The different sets are specified by the index, ν .

Theorem .

The set of functions, $g^p_{\mu\nu}$ ($\mu = 1, 2 --- l_p$), will form a set of basis functions for the unitary irreducible representation, $\underline{M}^p$, where

$$g^p_{\mu\nu}(x) = \sum_{A} M^p(A)^*_{\mu\nu}\, P(A)\, \phi(x) \qquad \text{........(III.24)}$$

P(A) is the function operator corresponding to the element, A, of the group G. $\phi(x)$ is any arbitrary function (see equation (III.29)). Thus, the projection operator

$$P^p_{\mu\nu} = g^{-1} \sum_{A} l_p\, M^p(A)^*_{\mu\nu}\, P(A) \qquad \text{........(III.25)}$$

provides a powerful tool for setting up functions of definite symmetry from an arbitrary function, $\phi(x)$, provided that the matrix elements of the representation are known. The matrix elements may be determined by the method described by Cornwell (loc. cit.).

One of the most useful properties of the basis functions of unitary irreducible representations is expressed by the following:

$$\int g^{p*}_{\mu i}\, h(x)\, g^q_{\nu j}\, d\underline{r} \begin{cases} \text{is zero if } p \neq q \text{ and } \mu \neq \nu \\ \text{is independent of } \mu \text{ (or } \nu\text{).} \end{cases} \qquad \text{........(III.26)}$$

$\underline{M}^p$ and $\underline{M}^q$ are assumed non-equivalent if $p \neq q$ but are identical if $p = q$. $h(r)$ is any operator which commutes with all the elements of the group, G, for which $\underline{M}^p$ forms the p-th irreducible representation. The integration is performed over all space.

This important property follows since

$$\int g^{p*}_{\mu i}(r)\, h(r)\, g^{q}_{\nu j}(r)\, \underline{d\tau}$$

$$= g^{-1} \sum_{A} \int [P(A) g^{p}_{\mu i}(r)]^{*} h(r) [P(A) g^{q}_{\nu j}(r)]\, \underline{d\tau}$$

$$= g^{-1} \sum_{A} M^{p}_{\sigma\mu}(A)^{*} M^{q}_{\gamma\nu}(A) \sum_{\sigma}^{l_p} \sum_{\gamma}^{l_q} \int g^{p*}_{\sigma i}\, h(r)\, g^{q}_{\gamma j}\, \underline{d\tau}$$

(using equation (III.21))

$$= l_p^{-1}\, \delta_{\mu\nu}\, \delta_{pq} \sum_{\gamma=1}^{l_p} \int g^{p*}_{\gamma i}(r)\, h(r)\, g^{p}_{\gamma j}(r)\, \underline{d\tau}$$

(using equation (III.17))

........(III.27)

where the first equality holds because $P(A) g^{p}_{\mu i}(r)$ and $g^{p}_{\mu i}(r)$ are defined to have the same values at the same points in space, as explained below.

Symmetry And The Schrödinger Equation.

Consider some scalar quantity to be represented by the function, $\phi(r)$, in some coordinate frame of reference. In another frame of reference, obtained by the transformation

$$\underline{r}' = \underline{\tilde{M}}(A)\, \underline{r} \quad , \qquad ....(III.28)$$

the same quantity will be represented by a different function, denoted by $P(A)\phi(r')$, such that

$$P(A)\phi(r') = \phi(r) \qquad ....(III.29)$$

$\underline{r}$ and $\underline{r}'$ are the position vectors of the same point relative to the two coordinate frames; the relationship of equation (III.29) must hold for every point in space. P(A) is called the function operator corresponding to the transformation, A, which is represented by the matrix, $\underline{\tilde{M}}(A)$. Furthermore, it can be shown that, if the set of transformations $\{A\}$ forms a group, G, the set of associated function operators also forms a group which is isomorphic to G.

Equation (III.29) can be written in the equivalent form:

$$P(A)\,\phi(r') = \phi(\tilde{M}(A)^{-1}\underline{r}') \quad \text{........(III.30)}$$

and this equation may be used as the definition of the function, P(A) $\phi(r)$.

Consider the eigenvalue equation

$$h(r)\,g_\mu(r) = W g_\mu(r) \qquad \text{........(III.31)}$$

Under the transformation of equation (III.28), this becomes

$$P(A)\,[h(r')\,g_\mu(r')] = W\,P(A)\,g_\mu(r')$$

or

$$h(\underline{\tilde{M}}(A)^{-1}\underline{r}')\,P(A)\,g_\mu(r') = W\,P(A)\,g_\mu(r') \qquad \text{........(III.32)}$$

where equations (III.29) and (III.30) have been used.

If the transformation is such that

$$h(r') = h(\tilde{M}(A)^{-1}\underline{r}')\,, \qquad \text{........(III.33)}$$

equation (III.32) then becomes

$$h(r)\,\{P(A)\,g_\mu(r)\} = W\,\{P(A)\,g_\mu(r)\} \quad \text{........(III.34)}$$

This shows that P(A)$g_\mu(r)$ is also an eigenfunction of equation (III.31) with the same eigenvalue, W. Thus, if W is an l-fold degenerate eigenvalue with eigenfunctions $g_\nu(r)$ ($\nu = 1, 2, -- l$), P(A)$g_\mu(r)$ can be expressed in the form

$$P(A)\, g_{\mu}(x) = \sum_{\nu=1}^{l} g_{\nu}(x)\, U(A)_{\nu\mu} \qquad \text{........(III.35)}$$

for each value of μ (= $1, 2 -- l$). Equation (III.35) defines a square l x l matrix for each transformation, $\tilde{\underline{M}}(A)$, satisfying equation (III.33). Moreover, it can be shown that the set of matrices $\{\underline{U}(A)\}$ forms an l-dimensional representation for the group of function operators, P(A).

Of particular importance is the case where $h(x)$ is the Hamiltonian operator for a system. Equation (III.35) shows that the set of energy eigenfunctions corresponding to an l-fold degenerate energy eigenvalue forms a set of basis functions for an l-dimensional representation of the function operators, P(A), corresponding to each symmetry operation, A, for the nuclear configuration of the system being investigated.

' Spin Symmetry ':

In the treatment of electronic systems, the approximation of zero spin-orbit coupling may be mathematically expressed by the following commutation relations:

$$\begin{aligned} \mathcal{H}_{op}\,\mathcal{S}_{op}^{2} &= \mathcal{S}_{op}^{2}\,\mathcal{H}_{op} \\ \mathcal{H}_{op}\,\mathcal{S}_{z} &= \mathcal{S}_{z}\,\mathcal{H}_{op} \qquad \text{........(III.36)} \\ \text{and} \qquad \mathcal{S}_{op}^{2}\,\mathcal{S}_{z} &= \mathcal{S}_{z}\,\mathcal{S}_{op}^{2} \end{aligned}$$

$\mathcal{H}_{op}$ and $\mathcal{S}_{op}$ are respectively the Hamiltonian and total Spin operators of the system. $\mathcal{S}_{z}$ is the operator determining the z-component of the total spin.

The above spin operators are related to the analogous one-electron operators as follows:

$$\begin{aligned} \mathcal{S}_{op}^{2} &= \mathcal{S}_{x}^{2} + \mathcal{S}_{y}^{2} + \mathcal{S}_{z}^{2} \\ &= (\mathcal{S}_{x} + i\mathcal{S}_{y})(\mathcal{S}_{x} - i\mathcal{S}_{y}) - \mathcal{S}_{z} + \mathcal{S}_{z}^{2} \\ &= (\mathcal{S}_{x} - i\mathcal{S}_{y})(\mathcal{S}_{x} + i\mathcal{S}_{y}) + \mathcal{S}_{z} + \mathcal{S}_{z}^{2} \end{aligned}$$

........(III.37)

where $\mathcal{S}_{k} = \sum_{i=1}^{N} \mathcal{S}_{k}(i)$ (k = x, y, z)

and the summation is over all the electrons of the system.

Furthermore, in atomic units ($\hbar = 1$),

$$\begin{aligned} (\mathcal{S}_{x} + i\mathcal{S}_{y})(i)\,\alpha(S_i) &= 0 \\ (\mathcal{S}_{x} + i\mathcal{S}_{y})(i)\,\beta(S_i) &= \alpha(S_i) \\ (\mathcal{S}_{x} - i\mathcal{S}_{y})(i)\,\alpha(S_i) &= \beta(S_i) \qquad \text{........(III.38)} \\ \text{and} \quad (\mathcal{S}_{x} - i\mathcal{S}_{y})(i)\,\beta(S_i) &= 0 \end{aligned}$$

$$\mathcal{S}_{z}(i)\,\alpha(S_i) = \tfrac{1}{2}\,\alpha(S_i)\ ; \qquad \mathcal{S}_{z}(i)\,\beta(S_i) = -\tfrac{1}{2}\,\beta(S_i).$$

The spin functions, α and β , are as defined by equation (IV.7).

The consequence of the above commutation property is that the wavefunction representing a state of the system must be simultaneously an eigenfunction of the three operators $\mathcal{H}_{op}$, S^2_{op}, and S_z (Eyring et. al. (1944)). In general, however, a single determinantal function of one-electron orbitals is not an eigenfunction of the total Spin operator, S^2_{op}, although it is an eigenfunction of S_z with eigenvalue

$$M = 0.5 \, (n_\alpha - n_\beta), \qquad \text{in units of } \hbar.$$

n_α and n_β are respectively the number of electrons in spin orbitals with α - and β - spin functions.

It is possible to determine linear combinations of determinantal functions which are spin eigenfunctions for the system. Moreover, the matrix elements of the Hamiltonian operator between functions corresponding to different eigenvalues of the spin operators are identically zero (Eyring et. al. (loc. cit.)). This property can be used to further simplify the secular equation (III.9).

There are various methods of determining such spin eigenfunctions (McWeeny et. al. (1969b)). The particular method used in this research is the projection operator technique of Lowdin (1956), who has pointed out that the operator

$$O_S = \prod_{j(\neq S)} \frac{S^2_{op} - S(S+1)}{S(S+1) - j(j+1)} \quad \text{........(III.39)}$$

projects from any arbitrary function, $g(x)$, the component, $g_S(x)$, such that

$$S^2_{op} \, g_S(x) = S(S+1) \, g_S(x) \quad \text{.......(III.40)}$$

In equation (III.39), the index, j , runs over all the multiplets (denoted by distinct values of S) of the system. Each multiplet contains (2S + 1) members which, in the absence of spin orbit interaction, have the same energy. It is thus only necessary to consider one member of each multiplet and it is usual to choose the member of highest multiplicity:

$$\hat{\mathcal{S}}_z \mathcal{G}_S = \mathcal{S}\, \mathcal{G}_S$$
$$\hat{\mathcal{S}}_{op}^2 \mathcal{G}_S = \mathcal{S}(\mathcal{S}+1)\, \mathcal{G}_S . \qquad \text{........(III.41)}$$

Evaluation Of Matrix Elements. (Lowdin (1955); Slater (1931))

As mentioned in Chapter II , the exact or approximate solutions of equation (II.5) for the electronic motion are generally sought in terms of a series expansion of Slater determinantal functions. The expansion coefficients and eigenvalues of the system are determined from the solutions of the linear simultaneous equations (III.3) or (III.12). In this section, the problem of evaluating the matrix elements between the determinantal functions is briefly considered.

The required matrix elements are defined by the following equations:

$$\bar{\mathcal{S}}_{\mu\nu} = \int \Phi_\mu^*(\underline{R},\underline{x})\, \Phi_\nu(\underline{R},\underline{x})\, d\underline{x} \qquad \text{.......(III.42)}$$

$$h_{\mu\nu} = I_{\mu\nu} + G_{\mu\nu} \qquad \text{........(III.43)}$$

where

$$I_{\mu\nu} = \int \Phi_\mu^*(\underline{R},\underline{x}) \sum_{i=1}^{N} h(i)\, \Phi_\nu(\underline{R},\underline{x})\, d\underline{x}$$

and

$$G_{\mu\nu} = \int \Phi_\mu^*(\underline{R},\underline{x})\, \Phi_\nu(\underline{R},\underline{x}) \sum_{i>j} V_{ij}\, d\underline{x}$$

with $$h(i) = -(\hbar^2/2m_e)\nabla_i^2 + \sum_\alpha V_{\alpha i}$$

$\underline{dx} = \underline{dx}_1 \underline{dx}_2 \ldots\ldots \underline{dx}_N$ represents a volume element in the N-dimensional phase (coordinate-spin) space of the system.

The remaining notation is explained in equations (II.2) and (II.3).

The determinantal functions*, $\Phi_\mu(x)$, are defined in terms of the single-electron functions by the following equation:

$$\Phi_\mu(\underline{x}) = (N!)^{-1/2} \sum_{\mu_1-\mu_N}^{N} \varepsilon_{\mu_1--\mu_N} \, \phi^{\mu}_{\mu_1}(x_1)--\phi^{\mu}_{\mu_N}(x_N) \quad \text{....(III.44)}$$

where the summation is over the numbers 1 to N . $\varepsilon_{\mu_1--\mu_N}$ is the Levi-Civita symbol and is defined by

$$\varepsilon_{\mu_1\mu_2--\mu_N} = \begin{cases} 0 & \text{if any two of the indices } (\mu_1--\mu_N) \text{ are identical.} \\ 1 & \text{if the set } (\mu_1--\mu_N) \text{ is an even permutation of the set (1, 2, 3...N).} \\ -1 & \text{if the set } (\mu_1--\mu_N) \text{ is an odd permutation of the set (1, 2, 3...N).} \end{cases}$$

Equation (III.44) may be written in the form

$$\Phi_\mu(x) = (N!)^{-1/2} \sum_{\mu_1-\mu_N}^{N} \varepsilon_{\mu_1--\mu_N} \quad \phi^{\mu}_1(x_{\mu_1})---\phi^{\mu}_N(x_{\mu_N})$$

$$= (N!)^{-1/2} \sum_{P} (-1)^p \, P(\phi^{\mu}_1(x_1)\,\phi^{\mu}_2(x_2)--\phi^{\mu}_N(x_N)) \quad \text{........(III.45)}$$

where P is an operator which permutes the coordinates of the electrons and p is the parity of the permutation.

Theorem.

If O is an arbitrary operator which is symmetric in the electronic coordinates so that

PO = O ,

where P is the permutation operator as defined above, then

$$\int \Phi^{*}_\mu(x)\, O(\underline{x})\, \Phi_\nu(x)\, d\underline{x} = (N!)^{1/2} \int \Phi^{*}_\mu(x)\, O(x)\, \phi^{\nu}_1(x_1)--\phi^{\nu}_N(x_N)\, d\underline{x} \quad \text{....(III.46)}$$

---

* The dependence of Φ_μ on the nuclear configuration (equation (II.2)) has been suppressed in the following analysis for convenience only.

Proof.

From equation (III.45),

$$\int \Phi^*_\mu(\underline{x})\, O(\underline{x})\, \Phi_\nu(\underline{x})\, \underline{dx} = (N!)^{-1/2} \sum_P (-1)^p \int \Phi^*_\mu\, O(\underline{x})\, P(\phi^\nu_1(\underline{x}_1) - - \phi^\nu_N(\underline{x}_N))\, \underline{dx}$$

$$= (N!)^{-1/2} \sum_P (-1)^p P \int [P^{-1}\Phi^*_\mu]\, O(\underline{x})\, \phi^\nu_1(\underline{x}_1) - - \phi^\nu_N(\underline{x}_N)\, \underline{dx}$$

But $P^{-1}\, \Phi^*_\mu = (-1)^p\, \Phi^*_\mu$

Thus,

$$\int \Phi_\mu(\underline{x})\, O(\underline{x})\, \Phi_\nu(\underline{x})\, \underline{dx} = (N!)^{-1/2} \sum_P P \int \Phi^*_\mu\, O(\underline{x})\, \phi^\nu_1(\underline{x}_1) - - \phi^\nu_N(\underline{x}_N)\, \underline{dx}$$

$$= (N!)^{1/2} \int \Phi^*_\mu(\underline{x})\, O(\underline{x})\, \phi^\nu_1(\underline{x}_1) - - \phi^\nu_N(\underline{x}_N)\, \underline{dx}$$

........(III.46)

after summation over the N! permutations.

Using equations (III.44) and (III.46), equation (III.42) becomes

$$\bar{S}_{\mu\nu} = (N!)^{1/2} \int \Phi^*_\mu(\underline{x})\, \phi^\nu_1(\underline{x}_1) - - - \phi^\nu_N(\underline{x}_N)\, \underline{dx}$$

$$= \sum^N_{\mu_1 - - \mu_N} \varepsilon_{\mu_1 - - \mu_N} \left(\int \phi^{\mu *}_{\mu_1}(\underline{x}_1)\, \phi^\nu_1(\underline{x}_1)\, \underline{dx}_1\right) - - - \left(\int \phi^{\mu *}_{\mu_N}(\underline{x}_N)\, \phi^\nu_N(\underline{x}_N)\, \underline{dx}_N\right)$$

$$= \sum^N_{\mu_1 - - \mu_N} \varepsilon_{\mu_1 - - \mu_N}\, S^{\mu\nu}_{\mu_1,1}\, S^{\mu\nu}_{\mu_2,2} - - - S^{\mu\nu}_{\mu_N,N}.$$

or

$$\bar{S}_{\mu\nu} = \det \left| S^{\mu\nu}_{i,j} \right| \qquad \text{....(III.47)}$$

where

$$S^{\mu\nu}_{i,j} = \int \phi^{\mu *}_i(\underline{x}_1)\, \phi^\nu_j(\underline{x}_1)\, \underline{dx}_1 .$$

Similarly,

$$I_{\mu\nu} = \sum^N_{\mu_1 - - \mu_N} \varepsilon_{\mu_1 - - \mu_N} \sum^N_i S^{\mu\nu}_{\mu_1,1} - - \langle \phi^\mu_{\mu i} | h | \phi^\nu_i \rangle - - S^{\mu\nu}_{\mu_N,N}$$

$$= \sum^N_{\mu i, i} (-1)^{\mu i + i}\, d^{\mu\nu}_{\mu i, i} \langle \phi^\mu_{\mu i} | h | \phi^\nu_i \rangle$$

........(III.48)

where $\langle \phi^\nu_i | h | \phi^\mu_j \rangle = \int \phi^{\nu *}_i(\underline{x}_1)\, h(1)\, \phi^\mu_j(\underline{x}_1)\, \underline{dx}_1$,

$d^{\mu\nu}_{i,j}$ is the minor formed when the i-th row and j-th column are removed from the determinant of equation (III.47).

$$\mathcal{G}_{\mu\nu} = \tfrac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}}^{N} \sum_{\mu_1 \cdots \mu_N}^{N} \varepsilon_{\mu_1 \cdots \mu_N} \, \mathcal{S}^{\mu\nu}_{\mu_1,1} \, \mathcal{S}^{\mu\nu}_{\mu_2,2} \cdots$$
$$\langle \phi^{\mu}_{\mu_i} \phi^{\nu}_{i} | \phi^{\mu}_{\mu_j} \phi^{\nu}_{j} \rangle \cdots \mathcal{S}^{\mu\nu}_{\mu_N,N}$$

$$= \sum_{i>j} \sum_{\mu_i > \mu_j} (-1)^{\mu_i + \mu_j + i + j} \, d^{\mu\nu}_{\mu_i\mu_j;\, ij} \left(\langle \phi^{\mu}_{\mu_i} \phi^{\nu}_{i} | \phi^{\mu}_{\mu_j} \phi^{\nu}_{j} \rangle - \langle \phi^{\mu}_{\mu_i} \phi^{\nu}_{j} | \phi^{\mu}_{\mu_j} \phi^{\nu}_{i} \rangle \right)$$

........(III.49)

with $\langle \phi^{\mu}_{i} \phi^{\nu}_{j} | \phi^{\mu}_{k} \phi^{\nu}_{l} \rangle = \int \phi^{\mu *}_{i}(\underline{x}_1) \, \phi^{\nu}_{j}(\underline{x}_1) \, V_{12} \, \phi^{\mu *}_{k}(\underline{x}_2) \, \phi^{\nu}_{l}(\underline{x}_2) \, d\underline{x}_1 \, d\underline{x}_2$.

$d^{\mu\nu}_{ij;\,kl}$ is the minor formed when the i-th and j-th rows along with the k-th and l-th columns are removed from the determinant of equation (III.47).

The above expressions for the matrix elements are greatly simplified if the determinantal functions are constructed from an orthonormal set of one-electron functions. Then, it is convenient to consider the four possible cases separately:

Case One. $\Phi_{\mu}(\underline{x}) \equiv \Phi_{\nu}(\underline{x})$

$$\bar{\mathcal{S}}_{\mu\mu} = 1$$

$$\mathcal{I}_{\mu\mu} = \sum_{i}^{N} \langle \tilde{\phi}^{\mu}_{i} | h | \tilde{\phi}^{\mu}_{i} \rangle$$

and

$$\mathcal{G}_{\mu\mu} = \sum_{i>j} \left(\langle \tilde{\phi}^{\mu}_{i} \tilde{\phi}^{\mu}_{i} | \tilde{\phi}^{\mu}_{j} \tilde{\phi}^{\mu}_{j} \rangle - \langle \tilde{\phi}^{\mu}_{i} \tilde{\phi}^{\mu}_{j} | \tilde{\phi}^{\mu}_{j} \tilde{\phi}^{\mu}_{i} \rangle \right).$$

........(III.50)

Case Two. $\Phi_{\mu}(\underline{x})$ and $\Phi_{\nu}(\underline{x})$ differ in one function, with $\tilde{\phi}^{\mu}_{m}$ entering Φ_{μ} where $\tilde{\phi}^{\nu}_{p}$ enters Φ_{ν}.

$$\bar{\mathcal{S}}_{\mu\nu} = 0$$

$$\mathcal{I}_{\mu\nu} = \langle \tilde{\phi}^{\mu}_{m} | h | \tilde{\phi}^{\nu}_{p} \rangle$$

and

$$\mathcal{G}_{\mu\nu} = \sum_{i}^{N} \left(\langle \tilde{\phi}^{\mu}_{i} \tilde{\phi}^{\nu}_{i} | \tilde{\phi}^{\mu}_{m} \tilde{\phi}^{\nu}_{p} \rangle - \langle \tilde{\phi}^{\mu}_{i} \tilde{\phi}^{\nu}_{p} | \tilde{\phi}^{\mu}_{m} \tilde{\phi}^{\nu}_{i} \rangle \right).$$

........(III.51)

Case Three. $\Phi_{\mu}(\underline{x})$ and $\Phi_{\nu}(\underline{x})$ differ in two functions, with $\tilde{\phi}^{\mu}_{m}$ and $\tilde{\phi}^{\mu}_{n}$ entering Φ_{μ} where $\tilde{\phi}^{\nu}_{p}$ and $\tilde{\phi}^{\nu}_{q}$ enter Φ_{ν}.

$$\bar{\mathcal{S}}_{\mu\nu} = 0$$

$$\mathcal{I}_{\mu\nu} = 0$$

and

$$\mathcal{G}_{\mu\nu} = \left(\langle \tilde{\phi}^{\mu}_{m} \tilde{\phi}^{\nu}_{p} | \tilde{\phi}^{\mu}_{n} \tilde{\phi}^{\nu}_{q} \rangle - \langle \tilde{\phi}^{\mu}_{m} \tilde{\phi}^{\nu}_{q} | \tilde{\phi}^{\mu}_{n} \tilde{\phi}^{\nu}_{p} \rangle \right).$$

Case Four. $\Phi_\mu(x)$ and $\Phi_\nu(x)$ differ in three or more functions.

$$\bar{S}_{\mu\nu} = I_{\mu\nu} = G_{\mu\nu} = 0. \qquad \text{........(III.53)}$$

Orthonormal Orbitals.

In the preceding section, the mathematical problem involved in determining the matrix elements for the secular equation (III.4) or (III.12) was briefly discussed. A comparison of equations (III.47) to (III.49) with equations (III.50) to (III.53) shows the considerable simplification arising from the use of orthonormal orbitals, $\tilde{\phi}_i(x)$. In most problems of molecular and solid state physics, the most naturally occurring set of basis orbitals are non-orthogonal. Symmetry requirements do introduce some orthogonality (equation (III.27)) but, in general, different orbitals having identical symmetry properties are non-orthogonal and possess overlap integrals of the form

$$S_{ij} = \int \phi_i^*(x_1)\, \phi_j(x_1)\, dx_1 \qquad \text{........(III.54)}$$

Since $S_{ij} = S_{ji}^*$, it is possible to determine a new set of orbitals $\{\tilde{\phi}_i(x_1)\}$ such that

$$\int \tilde{\phi}_i^*(x_1)\, \tilde{\phi}_j(x_1)\, dx_1 = \delta_{ij} \qquad \text{........(III.55)}$$

The most general procedure for doing this has been given by Lowdin (1947).

Defining
$$\tilde{\phi}_j = \sum_i \phi_i U_{ij} ,$$

then, using equations (III.54) and (III.55),

$$\int \tilde{\phi}_i^*(x_1)\, \tilde{\phi}_j(x_1)\, dx_1 = \sum_{k,l} U_{ki}^* U_{lj} S_{kl}$$
$$= \delta_{ij}$$

Thus,

$$\underline{U}^{+}\,\underline{S}\,\underline{U} = \underline{I} \qquad \text{........(III.56)}$$

where $\underline{U}^{+}$ is the Hermitian conjugate of $\underline{U}$ and $\underline{I}$ is the Unit matrix.

The most general solution of the above equation is

$$\underline{U} = \underline{S}^{-1/2}\,\underline{A} \qquad \text{........(III.57)}$$

provided that $\underline{S}^{-1/2}$ exists and $\underline{A}^{+}\underline{A} = \underline{I}$; that is, $\underline{A}$ is Unitary. Choosing in particular, $\underline{A} = \underline{I}$, equation (III.57) becomes

$$\underline{U} = \underline{S}^{-1/2} \qquad \text{........(III.58)}$$

In the majority of cases, the orthogonal orbitals have been found to retain the properties of the non-orthogonal orbitals from which they were compounded. Their use has become very widespread and provides a formal justification for the neglect of certain ' overlap ' integrals in approximate calculations (McWeeny et. al. (1969c)).

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CHAPTER IV.

BASIC MOLECULAR QUANTUM MECHANICS.

In this chapter, a summary of the Molecular Orbital method used in obtaining approximate many-electron wavefunctions is given. Extensive discussions of this method have been given by many authors, including McWeeny et. al. (1969a), whose article forms the main reference for this chapter. The alternative Valence Bond formalism is also briefly considered.

In the Born-Oppenheimer approximation, the electronic structure and properties of any many electron system in a stationary state may be obtained from the solutions of the time-independent Schrödinger equation (see equation (II.5)):

$$\mathcal{H}_{op}\,\Phi(\underline{x}_1,\underline{x}_2--\underline{x}_N) = E_{elec.}\,\Phi(\underline{x}_1,\underline{x}_2--\underline{x}_N)$$

........(IV.1)

where $\underline{x}_i$ represents the space and spin coordinates of the i-th electron.

$$\mathcal{H}_{op} = \sum_{i=1}^{N} h(i) + \sum_{i>j}^{N} g(ij)$$

with $$h(i) = -\nabla_i^2/2 - \sum_{\alpha} Z_\alpha/|\underline{r}_i - \underline{R}_\alpha|$$

and $$g(ij) = 1/|\underline{r}_i - \underline{r}_j|$$

........(IV.2)

In the definitions of the above equation, atomic units (Cohen et. al. (1965) have been used:

$$e = \hbar = m_e = 1.$$

Unit of Energy: 1 a.u. = 27.209 e.v.

Unit of Length: 1 b.u. = 0.5292 A .

(The dependence of Φ and $E_{elec.}$ on the nuclear configuration has been suppressed in the notation of this chapter.)

The total energy of the system is then given by

$$W_{Tot.} = E_{elec.} + \sum_{\alpha>\beta} Z_\alpha Z_\beta/|\underline{R}_\alpha - \underline{R}_\beta|$$

........(IV.3)

The occurrence of the interelectronic terms in equation (IV.2) makes the Hamiltonian too complicated to obtain exact solutions of equation (IV.1) for all but the simplest systems (Lowdin (1959)). As already mentioned in Chapter II, an approximation to the true solution is usually constructed from antisymmetrized products of one-electron functions, either in the form of a single product:

$$\Phi(\underline{x}_1, \underline{x}_2, --- \underline{x}_N) = (N!)^{-1/2} \,\mathrm{det}\, |\phi_1(\underline{x}_1)\phi_2(\underline{x}_2) --- \phi_N(\underline{x}_N)|$$

$$= (N!)^{-1/2} (\phi_1 \phi_2 --- \phi_N)$$

........(IV.4)

or a linear combination of them:

$$\Phi(\underline{x}_1, \underline{x}_2, --- \underline{x}_N) = \sum_K C_K \, \Phi_K(\underline{x}_1, \underline{x}_2, --- \underline{x}_N)$$

........(IV.5)

Further discussion of such series expansions is given in the relevant sections of Chapters II and III.

As the operator of equation (IV.2) is spin independent, each one-electron function or spin-orbital, ϕ_i , may be expressed as a product of space- and spin-dependent functions:

$$\phi_i(\underline{x}) = \psi_{p_i}(\underline{r})\, \eta(s)$$

........(IV.6)

where $\underline{r}$ and s are as defined previously. s can have any one of two values and it is usual to define (McWeeny et. al. (1969b)):

$$\eta(s = 1/2) = \alpha(1/2) \;; \quad \eta(s = -1/2) = \beta(-1/2)$$

with

$$\alpha(-1/2) = \beta(1/2) = 0 \quad ;$$

$$\int \alpha^*(s)\alpha(s)\, ds = \int \beta^*(s)\beta(s)\, ds = 1$$

and

$$\int \alpha^*(s)\beta(s)\, ds = \int \beta^*(s)\alpha(s)\, ds = 0$$

........(IV.7)

The optimal approximations of the forms given in equations (IV.4) and (IV.5) are obtained by the application of the Variational Principle (Chapter II) to the energy expectation value:

$$\delta[\langle \Phi | \mathcal{H}_{op} | \Phi \rangle / \langle \Phi | \Phi \rangle] = 0$$

........(IV.8)

where

$$\langle \Phi | \mathcal{H}_{op} | \Phi \rangle = \int \Phi^*(\underline{x}_1 - - \underline{x}_N)\, \mathcal{H}_{op}\, \Phi(\underline{x}_1 - - \underline{x}_N)\, d\underline{x}_1 - - d\underline{x}_N$$

and

$$\langle \Phi | \Phi \rangle = \int \Phi^*(\underline{x}_1 - - \underline{x}_N)\, \Phi(\underline{x}_1 - - \underline{x}_N)\, d\underline{x}_1 - - d\underline{x}_N .$$

Density Matrices.

Following McWeeny et. al. (1969a), generalized one- and two-electron density functions are, respectively, defined by the equations:

$$\rho_1(\underline{x}_1; \underline{x}_1') = N \int \Phi(\underline{x}_1, \underline{x}_2, - - \underline{x}_N)\, \Phi^*(\underline{x}_1', \underline{x}_2, - - \underline{x}_N)\, d\underline{x}_2 - - d\underline{x}_N$$

........(IV.9)

and

$$\rho_2(\underline{x}_1, \underline{x}_2; \underline{x}_1', \underline{x}_2') = N(N-1) \int \Phi(\underline{x}_1, \underline{x}_2, \underline{x}_3, - - \underline{x}_N)\, \Phi^*(\underline{x}_1', \underline{x}_2', \underline{x}_3, - - \underline{x}_N)\, d\underline{x}_3 - - d\underline{x}_N$$

........(IV.10)

where it is assumed that the N-electron wavefunction, Φ, is normalized; that is,

$$\langle \Phi | \Phi \rangle = 1.$$

$\rho_1(\underline{x}_1 | \underline{x}_1)$ is the probability of finding an electron at the point, $\underline{x}_1$, and $\rho_2(\underline{x}_1, \underline{x}_2 | \underline{x}_1, \underline{x}_2)$ is the probability of finding an electron at the point, $\underline{x}_1$, when one is at the point, $\underline{x}_2$.

From equations (IV.9) and (IV.10), the corresponding spin-independent probability functions are

$$P_1(\underline{r}_1 | \underline{r}_1') = \int \rho_1(\underline{x}_1; \underline{x}_1')\, ds_1\, ds_1'$$

and

$$P_2(\underline{r}_1,\underline{r}_2|\underline{r}_1',\underline{r}_2') = \int \varrho_2(\underline{x}_1,\underline{x}_2;\underline{x}_1',\underline{x}_2')\,ds_1\,ds_2\,ds_1'ds_2'$$

........(IV.11)

For an arbitrary one-electron operator, $\sum_i^N A(i)$, the expectation value in the state represented by the wavefunction, Φ , is then conveniently defined by

$$\langle A\rangle = \int_{\underline{x}_1=\underline{x}_1'} A(1)\,\varrho_1(\underline{x}_1;\underline{x}_1')\,d\underline{x}_1$$

........(IV.12)

with the convention that A(1) operates only on the functions of unprimed coordinates and the primes are removed before integration is performed. A similar definition holds for the expectation value of a two-electron operator of the form, $\sum_{i>j}^N B(i,j)$.

Because of the double indexing in the generalized density functions, they are generally referred to as density ' matrices '. Moreover, the procedure outlined above in equation (IV.12) is formally equivalent to forming the trace of a matrix product:

$$\langle A\rangle = \mathrm{tr}\,A\varrho_1$$

........(IV.13)

In particular, from equations (IV.1) and (IV.2),

$$E_{elec.} = \langle\Phi|\mathcal{H}_{op}|\Phi\rangle = \mathrm{tr}\,h\varrho_1 + \tfrac{1}{2}\,\mathrm{tr}\,g\varrho_2$$

........(IV.14)

Molecular Orbital Theory.

The approximation of equation (IV.4) to the exact solution of equation (IV.1) forms the basis of the Molecular Orbital theory. The generalized one-electron density function (equation (IV.9)) is then defined by the equation

$$\varrho_1(\underline{x}_1;\underline{x}_1') = \sum_{r,s}^{N} \varrho_{1rs}\,\phi_r(\underline{x}_1)\,\phi_s^*(\underline{x}_1')$$

....(IV.15)

where ρ_{1rs} are numerical coefficients given by

$$\rho_{1rs} = (\hat{S}^{-1})_{rs} \qquad \text{........(IV.16)}$$

and $\hat{\underline{S}}$ is the matrix of overlap integrals between the spin-orbitals.

In particular, if the spin-orbitals are chosen orthonormal,

$$\begin{aligned} \rho_{1rs} &= 1 \quad r = s \\ &= 0 \quad r \neq s , \end{aligned}$$

and equation (IV.15) becomes

$$\rho_1(x_1; x_1') = \sum_{r}^{N} \phi_r(x_1)\, \phi_r^*(x_1') \qquad \text{........(IV.17)}$$

Similarly, assuming an orthonormal set of spin-orbitals, the two-electron density function (equation (IV.10)) is given by

$$\begin{aligned} \rho_2(x_1, x_2; x_1', x_2') = \sum_{r,s}^{N} [\, & \phi_r(x_1)\, \phi_r^*(x_1')\, \phi_s(x_2)\, \phi_s^*(x_2') \\ & - \phi_r(x_1)\, \phi_s^*(x_1')\, \phi_s(x_2)\, \phi_r^*(x_2') \,] \end{aligned} \qquad \text{........(IV.18)}$$

Closer investigation of the above equation shows that the two-electron density function can be expressed in terms of the single-electron density function:

$$\rho_2(x_1, x_2; x_1', x_2') = \rho_1(x_1; x_1')\, \rho_1(x_2; x_2') - \rho_1(x_1; x_2')\, \rho_1(x_2; x_1') \qquad \text{........(IV.19)}$$

Thus, all the information contained in a single determinantal function of orthonormal spin orbitals is obtainable from its single-electron density function. In general, however, this is not so.

Substituting equations (IV.17) and (IV.18) into (IV.14) gives

$$\begin{aligned} E_{elec} = \sum_{r}^{N} \langle \phi_r | h | \phi_r \rangle + \tfrac{1}{2} \sum_{r,s}^{N} [\, & \langle \phi_r \phi_r | \phi_s \phi_s \rangle \\ & - \langle \phi_r \phi_s | \phi_s \phi_r \rangle \,] \end{aligned} \qquad \text{....(IV.20)}$$

where $$\langle \phi_i | h | \phi_j \rangle = \int \phi_i^*(\underline{x}_1)\, h(1)\, \phi_j(\underline{x}_1)\, d\underline{x}_1$$

and

$$\langle \phi_i \phi_j | \phi_k \phi_l \rangle = \iint \phi_i^*(\underline{x}_1)\, \phi_j(\underline{x}_1)\, g(12)\, \phi_k^*(\underline{x}_2)\, \phi_l(\underline{x}_2)\, d\underline{x}_1\, d\underline{x}_2 ,$$

for the total electronic energy.

The density functions may also be separated into their different spin contributions by using equations (IV.6) and (IV.7). Thus, for example,

$$\begin{aligned} \rho_1(\underline{x}_1; \underline{x}_1') = & \sum_r^{\alpha} \psi_r(\underline{r}_1)\, \psi_r^*(\underline{r}_1')\, \alpha(s_1)\, \alpha^*(s_1') \\ & + \sum_r^{\beta} \psi_r(\underline{r}_1)\, \psi_r^*(\underline{r}_1')\, \beta(s_1)\, \beta^*(s_1') \end{aligned}$$

....(IV.21)

The spinless one-electron density function is then given by

$$P_1(1;1') = \int_{s_1 = s_1'} \rho_1(\underline{x}_1; \underline{x}_1')\, ds_1 = P_1^{\alpha}(1;1') + P_1^{\beta}(1;1')$$

........(IV.22)

where $$P_1^{\alpha}(1;1') = \sum_r^{\alpha} \psi_r(\underline{r}_1)\, \psi_r^*(\underline{r}_1')$$

and $$P_1^{\beta}(1;1') = \sum_r^{\beta} \psi_r(\underline{r}_1)\, \psi_r^*(\underline{r}_1')$$

....(IV.23)

In the above equations, $\sum_r^{\alpha}$ and $\sum_r^{\beta}$ indicate summations over the spatial (molecular) orbitals, defining the determinantal function of equation (IV.4), associated with α- and β-spin functions, respectively.

Similarly, the spinless two-electron density functions may be decomposed as follows:

$$\begin{aligned} P_2(1,2;1',2') = & P_2^{\alpha\alpha}(1,2;1',2') + P_2^{\alpha\beta}(1,2;1',2') \\ & + P_2^{\beta\alpha}(1,2;1',2') + P_2^{\beta\beta}(1,2;1',2') \end{aligned}$$

........(IV.24)

where

$$P_2^{\alpha\alpha}(1,2;1',2') = P_1^{\alpha}(1;1')\, P_1^{\alpha}(2;2') - P_1^{\alpha}(1;2')\, P_1^{\alpha}(2;1')$$

........(IV.25)

and $$P_2^{\alpha\beta}(1,2;1',2') = P_1^{\alpha}(1;1')\, P_1^{\beta}(2;2')$$

....(IV.26)

with similar definitions for $P_2^{\beta\alpha}$ and $P_2^{\beta\beta}$.

$P_2^{\alpha\beta}(1,2|1,2)$ can be interpreted as the probability of an electron being at the point, $\underline{r}_1$, with spin up when another is at the point, $\underline{r}_2$, with spin down. Equation (IV.26) indicates that these two ' events ' are independent of each other and there is, therefore, no spatial correlation between electrons of opposite spin for a wavefunction of the form given by equation (IV.4).

However, from equation (IV.25)

$$\lim_{\underline{r}_1 \to \underline{r}_2} P_2^{\alpha\alpha}(1,2|1,2) = 0 , \qquad \text{....(IV.27)}$$

and there is some spatial correlation between electrons with parallel spin (Chapter II).

A single determinantal function of the form given by equations (IV.4) and (IV.6) has the important property of being invariant under any linear transformation which mixes the molecular orbitals with α-spin function, and those with β-spin function, respectively, among themselves. This property, which is reflected in the invariant nature of the associated one- and two-electron density functions, is of considerable value (McWeeny et. al. (1969c)) as it permits different interpretations of the electron density in terms of localized or delocalized states. Edmiston et. al. (1963) and Rothenberg (1969, 1970), among others, have made use of such flexibility in their investigations of various molecular systems.

<u>The Roothaan-Hartree-Fock SCF Theory:</u> Closed-Shell Systems.

Closed-shell systems, that is, systems which can be represented by a single determinantal function with doubly-occupied molecular orbitals (Roothaan (1951)), are of particular interest in the theory of molecules.

From equation (IV.20), the total electronic energy for such systems is given by

$$E_{elec.} = 2\sum_{r}^{N/2} \langle r|h|r\rangle + \sum_{r,s}^{N/2} [2\langle rr|ss\rangle - \langle rs|sr\rangle]$$

$$\langle i|h|j\rangle = \int \psi_i^*(x_1)\, h(1)\, \psi_j(x_1)\, dx_1 , \quad \text{etc.}$$

........(IV.28)

In actual computations, the molecular orbitals, $\psi_p(x)$, extend, in principle, over the whole structure. Near each atomic site, however, it is expected that they will strongly resemble atomic functions centred on the particular atom. Thus, it is customary to expand the orbitals as follows:

$$\psi_p(x) = \sum_{\nu}^{m} \chi_\nu(x)\, c_{\nu p}$$

....(IV.29)

or, in matrix form,

$$\underline{\psi} = \underline{\chi}\ \underline{T}$$

........(IV.30)

$\underline{\psi}$ and $\underline{\chi}$ are row vectors consisting of the molecular orbitals and basis functions, respectively; m is the size of the basis set. $\underline{T}$ is the matrix of expansion coefficients:

$$\underline{T} = (\ \underline{c}_1 \mid \underline{c}_2 \mid \ldots\ldots \mid \underline{c}_p \mid \ldots\ldots \mid \underline{c}_{N/2}\ )$$

where

$$\underline{c}_p = \begin{pmatrix} c_{1p} \\ c_{2p} \\ | \\ | \\ c_{mp} \end{pmatrix}$$

........(IV.31)

The above expansion is quite general, there being no restriction on the type nor origin of the basis functions, $\underline{\chi}$. Usually, they are chosen to be atomic-type functions centred on the nuclei of the molecule or aggregate but it may be more advantageous, for example, to choose them as a set of floating orbitals, that is, orbitals whose origins are considered as variable parameters (Gurnee et. al. (1950); Frost et. al. (1968)). Further discussion relevant to the series expansion of equation (IV.29) is given in Chapter III.

Defining

$$h_{\mu\nu} = \langle \chi_\mu | h | \chi_\nu \rangle \ ;$$

$$G(2\underline{R})_{\mu\nu} = J(2\underline{R})_{\mu\nu} - K(\underline{R})_{\mu\nu}$$

with

$$J(2\underline{R})_{\mu\nu} = \sum_{\gamma,\sigma}^{m} 2R_{\sigma\gamma}\langle \chi_\mu \chi_\nu | \chi_\gamma \chi_\sigma \rangle ,$$

$$K(\underline{R})_{\mu\nu} = \sum\nolimits_{\gamma,\sigma}^{m} R_{\sigma\gamma}\langle \chi_\mu \chi_\sigma | \chi_\gamma \chi_\nu \rangle$$

and

$$R_{\mu\nu} = \sum_{r}^{N/2} c_{\mu r} c_{\nu r}^{*} \qquad \text{....(IV.32)}$$

equation (IV.28) may be written in the form

$$E_{elec.}(\underline{R}) = 2\,\mathrm{tr}\,\underline{h}\underline{R} + \mathrm{tr}\,\underline{G}(2\underline{R})\underline{R} \qquad \text{........(IV.33)}$$

As shown by the above equation, the total electronic energy is determined entirely by the matrix, $\underline{R}$. Furthermore, this equation is invariant under any transformation of the basis set. Thus, consider a new basis set, $\underline{\tilde{\chi}}$, such that

$$\underline{\tilde{\chi}} = \underline{\chi}\,\underline{U} \qquad \text{........(IV.34)}$$

where $\underline{U}$ is some transformation matrix. Then it can be shown that

$$E_{elec.}(\underline{\tilde{R}}) = 2\,\mathrm{tr}\,\underline{\tilde{h}}\underline{\tilde{R}} + \mathrm{tr}\,\underline{\tilde{G}}(2\underline{\tilde{R}})\underline{\tilde{R}} \qquad \text{........(IV.35)}$$

where

$$\underline{\tilde{R}} = \underline{U}^{-1}\underline{R}\,(\underline{U}^{-1})^{+} ;$$

$$\tilde{h}_{\mu\nu} = \langle \tilde{\chi}_\mu | h | \tilde{\chi}_\nu \rangle ;$$

$$\tilde{G}(2\underline{\tilde{R}})_{\mu\nu} = \tilde{J}(2\underline{\tilde{R}})_{\mu\nu} - \tilde{K}(\underline{\tilde{R}})_{\mu\nu}$$

with

$$\tilde{J}(2\underline{\tilde{R}})_{\mu\nu} = \sum_{\gamma,\sigma}^{m} 2\tilde{R}_{\sigma\gamma}\langle \tilde{\chi}_\mu \tilde{\chi}_\nu | \tilde{\chi}_\gamma \tilde{\chi}_\sigma \rangle$$

and

$$\tilde{K}(\underline{\tilde{R}})_{\mu\nu} = \sum_{\gamma,\sigma}^{m} \tilde{R}_{\sigma\gamma}\langle \tilde{\chi}_\mu \tilde{\chi}_\sigma | \tilde{\chi}_\gamma \tilde{\chi}_\nu \rangle \qquad \text{........(IV.36)}$$

Of particular importance are those transformations relating orthogonal and non-orthogonal basis sets (Chapters III and X). In such cases, the matrix, $\underline{U}$, can be represented by the equation

$$\underline{U} = \underline{S}^{-1/2} \qquad \text{........(IV.37)}$$

where

$$\underline{S} = \int \underline{\chi}^{+}\underline{\chi}\ d\tau \qquad \text{....(IV.38)}$$

is the matrix of overlap integrals between the basis functions of the non-orthogonal set.

The optimum set of expansion coefficients, $\underline{c}_r$ (r = 1,2,...N/2), is determined, in general, by applying the Variational Theorem to equation (IV.33), subject to the constraint that the molecular orbitals remain orthonormal; that is,

$$\underline{T}^{+}\underline{S}\,\underline{T} = \underline{I} \qquad \text{........(IV.39)}$$

This constraint may also be expressed in terms of the matrix, $\underline{R}$, leading to a different formulation of the variational problem (McWeeny (1960)).

The stationary value of equation (IV.33), subject to the conditions of equation (IV.39), is determined by the solution of the equation

$$\delta\left[\, E_{elec.}(\underline{R} = \underline{T}\,\underline{T}^{+}) - 2\,\mathrm{tr}\,(\,\underline{T}^{+}\underline{S}\,\underline{T}\,\underline{\varepsilon}\,)\,\right] = 0 \qquad \text{........(IV.40)}$$

where $2\underline{\varepsilon}$ is a matrix of Lagrangian multipliers.

Equation (IV.40) gives

$$2\,\mathrm{tr}\,\underline{h}\,\delta\underline{R} + \mathrm{tr}\,\underline{G}(2\underline{R})\,\delta\underline{R} + \mathrm{tr}\,\underline{G}(2\delta\underline{R})\,\underline{R} - 2\,\delta\left[\mathrm{tr}\,(\,\underline{T}^{+}\underline{S}\,\underline{T}\,\underline{\varepsilon}\,)\right] = 0 \qquad \text{....(IV.41)}$$

From the definitions of equation (IV.32),

$$\mathrm{tr}\,\underline{G}(2\delta\underline{R})\,\underline{R} = \mathrm{tr}\,\underline{G}(2\underline{R})\,\delta\underline{R} \qquad \text{........(IV.42)}$$

and thus equation (IV.41) becomes

$$\mathrm{tr}\,\underline{h}^{F}\,\delta\underline{R} - \delta\left[\mathrm{tr}\,(\,\underline{T}^{+}\,\underline{S}\,\underline{T}\,\underline{\varepsilon}\,)\right] = 0 \qquad \text{........(IV.43)}$$

where

$$\underline{h}^{F} = \underline{h} + \underline{G}(2\underline{R}) \qquad \text{........(IV.44)}$$

is the matrix representation of the Hartree-Fock operator, $\underline{h}^{F}$, in the basis, $\underline{\chi}$:

$$h^{F}_{\mu\nu} = \langle \chi_{\mu} |\, h^{F} \,| \chi_{\nu} \rangle$$

where $h^{F}(1) = h(1) + j(1) - 0.5k(1)$

with

$$j(1)\,\chi_{\mu}(x_1) = \chi_{\mu}(x_1)\int P_1(x_2; x_2')\,g(12)\,dx_2 \quad ,$$

$$k(1)\, \chi_\mu(\underline{r}_1) = \int P_1(\underline{r}_1;\underline{r}_2')\, g(12)\, \chi_\mu(\underline{r}_2)\, \underline{dr_2},$$

$$P_1(1;2') = 2\, \underline{\chi}(1)\, \underline{R}\, \underline{\chi}^+(2') \qquad \text{........(IV.45)}$$

and h(1) is as defined previously in equation (IV.2).

The Hartree-Fock operator represents the motion of an electron in the field of the nuclei and the average charge density distribution of all the other electrons of the system (Chapter II; Slater (1963a)).

Simplification of equation (IV.43) then gives

$$\underline{h}^F\, \underline{T} = \underline{S}\, \underline{T}\, \underline{\mathcal{E}} \qquad \text{........(IV.46)}$$

provided

$$\underline{\mathcal{E}} = \underline{\mathcal{E}}^+ \qquad \text{........(IV.47)}$$

As there are only N(N + 2)/8 orthonormality constraints embodied in the matrix equation (IV.39), there need only be this number of distinct Lagrangian multipliers. Therefore, the matrix, $\underline{\mathcal{E}}$, may be chosen to satisfy equation (IV.47) above (Slater (1963b)), without loss of generality.

Consider, finally, a transformation of the form

$$\tilde{\underline{\Psi}} = \underline{\Psi}\, \underline{V} \qquad \text{........(IV.48)}$$

where

$$\underline{V}^+\, \underline{V} = \underline{I} \quad .$$

From equation (IV.30),

$$\underline{\Psi} = \underline{\chi}\, \underline{T}$$

and, therefore,

$$\tilde{\underline{\Psi}} = \underline{\chi}\, \tilde{\underline{T}} \qquad \text{........(IV.49)}$$

where

$$\tilde{\underline{T}} = \underline{T}\, \underline{V} \qquad \text{........(IV.50)}$$

As in equation (IV.32), the ' new ' matrix, $\tilde{\underline{R}}$, in the given basis, $\underline{\chi}$, is defined as

$$\tilde{\underline{R}} = \tilde{\underline{T}}\, \tilde{\underline{T}}^+ = \underline{T}\, \underline{V}\, \underline{V}^+\, \underline{T}^+ = \underline{T}\, \underline{T}^+ = \underline{R} \quad .$$

Thus, the Hartree Fock matrix, which depends on $\underline{\chi}$ and $\underline{R}$, remains unchanged under the Unitary transformation, $\underline{V}$.

Substituting equation (IV.50) into equation (IV.46) then gives

$$\underline{h}^F \, \underline{\tilde{T}} \, \underline{V}^+ = \underline{S} \, \underline{\tilde{T}} \, \underline{V}^+ \, \underline{\varepsilon}$$

or

$$\underline{h}^F \, \underline{\tilde{T}} = \underline{S} \, \underline{\tilde{T}} \, \underline{\tilde{\varepsilon}} \qquad \text{........(IV.51)}$$

where

$$\underline{\tilde{\varepsilon}} = \underline{V}^+ \, \underline{\varepsilon} \, \underline{V} \quad .$$

Since $\underline{\varepsilon}$ is Hermitian, there exists some Unitary transformation, $\underline{V}$, such that $\underline{\tilde{\varepsilon}}$ is diagonal. Then, equation (IV.51) may be written as

$$\underline{h}^F \, \underline{\tilde{c}}_r = \underline{\tilde{\varepsilon}_r} \, \underline{S} \, \underline{\tilde{c}}_r \qquad \text{........(IV.52)}$$

which is Roothaan's form of the Hartree-Fock equations.

From equations (IV.33) and (IV.44), the minimum total electronic energy is

$$E_{elc.} = 2 \, \mathrm{tr} \, \underline{h}^F \underline{R} - \mathrm{tr} \, \underline{G}(2\underline{R}) \, \underline{R} \qquad \text{........(IV.53)}$$

Since $\underline{h}^F$ depends upon $\underline{R}$ and, hence, upon the solution of the problem, equation (IV.52) must be solved iteratively. Further discussion on the method of solution used herein is given in Chapter X.

It is clear that any system with an odd number of electrons cannot have a closed-shell state. However, there is yet the possibility of representing such systems by single determinantal functions in which some of the molecular orbitals are singly occupied. Such wavefunctions are then said to represent ' Open-Shell ' systems (McWeeny et. al. (1969a)). Furthermore, certain systems with even numbers of electrons are better described, within the Molecular Orbital formalism, by such single determinantal functions, especially in situations of near, or actual, orbital degeneracies (Teller et. al. (1970)); this is called the Unrestricted H-F theory.

Group theoretical analysis (Chapter III) shows that such functions will have definite spin and spatial symmetry properties and be suitable for representing real spectroscopic states, provided that

1.) all of, or none of, the orbitals defining an irreducible representation of the point group for the nuclear framework are occupied, for each choice of spin function; and

2.) all the singly-occupied orbitals are associated with the same spin function.

This latter condition implies that such functions are only suitable for representing states of maximum spin multiplicities.

When determining the molecular orbitals which minimize the energy for such a wavefunction, a constraint must be imposed from the outset upon the form of variation in order to maintain the spin symmetry during iteration. To understand the reason for this, consider the wavefunction defined by

$$\Phi(\underline{x}_1, \underline{x}_2, -- \underline{x}_N) = (N!)^{-1/2} (\psi_1^+ \psi_1^- -- \psi_i^+ \psi_i^- -- \psi_k^+ \psi_l^+ --) \qquad \text{........(IV.54)}$$

where the indices (i,j) specify molecular orbitals which are doubly-occupied and (k,l) those which are singly-occupied. (r,s) will be used to specify any of the orbitals of the set defining Φ .

Also

$$\psi_r^+(\underline{x}) = \psi_r^\alpha(\underline{r})\, \alpha(1/2)$$

and

$$\psi_s^-(\underline{x}) = \psi_s^\beta(\underline{r})\, \beta(-1/2) \qquad \text{....(IV.55)}$$

Thus, for double-occupancy, the constraint

$$\psi_i^\alpha(\underline{r}) = \psi_i^\beta(\underline{r}) \qquad \text{........(IV.56)}$$

must be obeyed.

Analysis, similar to that previously outlined for the closed-shell case, indicates that the molecular orbitals associated with different spin functions are, in general, solutions of distinct Hartree-Fock equations and, therefore, the above constraint of equation (IV.56) cannot be satisfied.

There is, however, no absolute need to require that the wavefunction be of the form given in equation (IV.54). In fact, it is known that, by relaxing the constraint of double-occupancy and using a projected wavefunction of the form given in equation (IV.5), or its equivalent, considerable improvement can be made in the description of many systems, even those which may be quite adequately classified as being of closed-shell form (Chapter V; Palke et. al. (1969); Lunell (1972)).

<u>The Hartree-Fock SCF Theory:</u> Open-Shell Systems.

The constraint of double-occupancy is imposed upon the ensuing minimization process by explicitly resolving the expression for the total energy into terms arising from the electrons in the doubly- and singly-occupied molecular orbitals. The energy expression then becomes

$$
\begin{aligned}
E_{elec.} = {} & \nu_1 \left\{ \sum_{i} \langle i|h|i\rangle + \nu_1/2 \sum_{i,j} \left(\langle ii|jj\rangle - 1/2 \langle ij|ji\rangle \right) \right\} \\
& + \frac{\nu_1 \nu_2}{2} \left\{ \sum_{i,k} \left(\langle ii|kk\rangle - 1/2 \, \langle ik|ki\rangle \right) \right\} \\
& + \nu_2 \left\{ \sum_{k} \langle k|h|k\rangle + \nu_2/2 \sum_{k,l} \left(\langle kk|ll\rangle - \langle kl|lk\rangle \right) \right\} \\
& + \frac{\nu_2 \nu_1}{2} \left\{ \sum_{k,i} \left(\langle kk|ii\rangle - 1/2 \, \langle ki|ik\rangle \right) \right\}
\end{aligned}
\qquad \text{........(IV.57)}
$$

where (i,j) and (k,l) are as defined previously in equation (IV.54) ν_1 (= 2) and ν_2 (= 1) are the corresponding occupation numbers.

The doubly- and singly-occupied orbitals are, respectively, defined in terms of a suitable basis set by the matrices $\underline{T}_1$ and $\underline{T}_2$ and the corresponding $\underline{R}$-matrices are given by

$$\underline{R}_1 = \underline{T}_1 \, \underline{T}_1^{+} \quad ; \qquad \underline{R}_2 = \underline{T}_2 \, \underline{T}_2^{+} \qquad \ldots\ldots\ldots(IV.58)$$

The energy expression of equation (IV.57) then becomes

$$E_{elec.} = \nu_1 \, tr \, \underline{h}'_1 \underline{R}_1 + \nu_2 \, tr \, \underline{h}'_2 \underline{R}_2 \qquad \ldots\ldots\ldots(IV.59)$$

where $\underline{h}'_r = \underline{h} + 0.5\underline{G}_r \qquad (r = 1, 2);$

$\underline{G}_1 = \underline{G}(\nu_1 \underline{R}_1) + \underline{G}(\nu_2 \underline{R}_2)$

and $\underline{G}_2 = \underline{G}(\nu_1 \underline{R}_1) + \underline{G}'(\nu_2 \underline{R}_2)$

with

$\underline{G}(\underline{R}) = \underline{J}(\underline{R}) - 0.5\underline{K}(\underline{R})$

and $\underline{G}'(\underline{R}) = \underline{J}(\underline{R}) - \underline{K}(\underline{R})$

$$\ldots\ldots\ldots(IV.60)$$

$\underline{J}(\underline{R})$ and $\underline{K}(\underline{R})$ are as defined in equation (IV.32).

Assuming an orthonormal basis set*, the orthonormality constraints between the molecular orbitals may be represented in terms of the $\underline{R}$-matrices as follows:

$$\tilde{\underline{R}}_1^{2} = \tilde{\underline{R}}_1 \quad ; \quad \tilde{\underline{R}}_2^{2} = \tilde{\underline{R}}_2 \quad ; \quad \tilde{\underline{R}}_1 \tilde{\underline{R}}_2 = \tilde{\underline{R}}_2 \tilde{\underline{R}}_1 = \underline{0} \qquad \ldots\ldots\ldots(IV.61)$$

The first and second conditions, respectively, express the orthonormality of the doubly- and singly-occupied orbitals; the third condition expresses the orthogonality between the orbitals belonging to different sets.

---

* This assumption greatly simplifies the following analysis but does not affect the final result since $E_{elec.}$ and the operators h'_r ($\underline{h}'_r = \int \underline{\chi}^{+} h'_r \, \underline{\chi} \, dv$; cf. equation (IV.45)) are independent of the choice of the basis set. Under the transformation of equations (IV.34) and (IV.37), the matrix eigenvalue equations

$$\tilde{\underline{h}} \, \tilde{\underline{T}} = \tilde{\underline{T}} \, \underline{\varepsilon} \qquad (\text{orthogonal basis})$$

and

$$\underline{h} \, \underline{T} = \underline{S} \, \underline{T} \, \underline{\varepsilon} \qquad (\text{non-orthogonal basis}),$$

where $\underline{h} = \underline{S}^{1/2} \tilde{\underline{h}} \, \underline{S}^{1/2}$ and $\underline{T} = \underline{S}^{-1/2} \tilde{\underline{T}}$, are equivalent.

The stationary value of equation (IV.59), with respect to arbitrary variations of the matrices $\tilde{\underline{R}}_1$ and $\tilde{\underline{R}}_2$, is given by

$$\nu_1 \, \mathrm{tr} \, \tilde{\underline{h}}_1 \, \delta\tilde{\underline{R}}_1 + \nu_2 \, \mathrm{tr} \, \tilde{\underline{h}}_2 \, \delta\tilde{\underline{R}}_2 = 0$$

where

$$\tilde{\underline{h}}_r = \tilde{\underline{h}} + \tilde{\underline{G}}_r \qquad (r = 1, 2)$$

........(IV.62)

The orthonormality constraints of equation (IV.61) require that

$$\tilde{\underline{R}}_1 \delta\tilde{\underline{R}}_1 + \delta\tilde{\underline{R}}_1\tilde{\underline{R}}_1 - \delta\tilde{\underline{R}}_1 = \underline{0}$$

$$\tilde{\underline{R}}_2 \delta\tilde{\underline{R}}_2 + \delta\tilde{\underline{R}}_2\tilde{\underline{R}}_2 - \delta\tilde{\underline{R}}_2 = \underline{0}$$

and

$$\tilde{\underline{R}}_1 \delta\tilde{\underline{R}}_2 + \delta\tilde{\underline{R}}_1\tilde{\underline{R}}_2 = \underline{0}$$

........(IV.63)

The orthonormality constraints can be shown to be also equivalent to the conditions that $\tilde{\underline{R}}_1$ and $\tilde{\underline{R}}_2$ be matrix representations, with respect to the basis, $\tilde{\underline{\chi}}$, of projection operators, θ_1 and θ_2, which respectively define subspaces spanned by the doubly- and singly-occupied molecular orbitals (McWeeny et. al. (1969d)):

$$\theta_r \psi(x_1) = \int \theta_r(\underline{x}_1; \underline{x}_1') \, \psi(\underline{x}_1') \, d\underline{x}_1'$$

....(IV.64)

where

$$\theta_1(\underline{x}; \underline{x}') = \sum_i \psi_i(\underline{x}) \psi_i^*(\underline{x}') = \tilde{\underline{\chi}}(\underline{x}) \, \tilde{\underline{R}}_1 \, \tilde{\underline{\chi}}^+(\underline{x}')$$

and

$$\theta_2(\underline{x}; \underline{x}') = \sum_k \psi_k(\underline{x}) \psi_k^*(\underline{x}') = \tilde{\underline{\chi}}(\underline{x}) \, \tilde{\underline{R}}_2 \, \tilde{\underline{\chi}}^+(\underline{x}')$$

(cf. equations (IV.29) to (IV.32))

As before, i and k specify doubly- and singly-occupied orbitals, respectively.

With the remaining unoccupied molecular orbitals, a complementary projection operator and its matrix representation may be defined by:

$$\theta_3(\underline{x}; \underline{x}') = \sum_v \psi_v(\underline{x}) \psi_v^*(\underline{x}) = \tilde{\underline{\chi}}(\underline{x}) \, \tilde{\underline{R}}_3 \, \tilde{\underline{\chi}}^+(\underline{x})$$

........(IV.65)

where v specifies unoccupied molecular orbitals.

Furthermore, since

$$\theta_1 + \theta_2 + \theta_3 = \text{identity operator},$$

$$\underline{\tilde{R}}_1 + \underline{\tilde{R}}_2 + \underline{\tilde{R}}_3 = \underline{I} .$$

Also,

$$\underline{\tilde{R}}_3^2 = \underline{\tilde{R}}_3 \qquad \text{and} \qquad \underline{\tilde{R}}_r \underline{\tilde{R}}_3 = \underline{\tilde{R}}_3 \underline{\tilde{R}}_r \qquad (r = 1, 2)$$

........(IV.66)

From equations (IV.61), (IV.66) and (IV.63), the arbitrary variations in the $\underline{R}$-matrices must satiafy the following equations:

$$\underline{\tilde{R}}_1 \, \underline{\delta\tilde{R}}_2 \, \underline{\tilde{R}}_2 = - \underline{\tilde{R}}_1 \, \underline{\delta\tilde{R}}_1 \, \underline{\tilde{R}}_2$$

$$\underline{\tilde{R}}_1 \, \underline{\delta\tilde{R}}_2 \, \underline{\tilde{R}}_3 = \underline{\tilde{R}}_2 \, \underline{\delta\tilde{R}}_1 \, \underline{\tilde{R}}_3 = \underline{0}$$

and

$$\underline{\tilde{R}}_s \, \underline{\delta\tilde{R}}_r \, \underline{\tilde{R}}_s = \underline{0} \qquad (r = 1,2;\ s = 1,2,3)$$

........(IV.67)

By using the general properties of expanding matrices, associated with the full space spanned by the basis $\underline{\tilde{\chi}}$ or by the full set of molecular orbitals, into their projected parts, the arbitrary variations, $\underline{\delta R}_1$ and $\underline{\delta R}_2$, which satisfy equation (IV.67) above, are given by

$$\underline{\delta\tilde{R}}_1 = (\underline{x} + \underline{x}^{+}) + (\underline{y} + \underline{y}^{+})$$

$$\underline{\delta\tilde{R}}_2 = (\underline{z} + \underline{z}^{+}) - (\underline{y} + \underline{y}^{+})$$

........(IV.68)

where

$$\underline{x} = \underline{\tilde{R}}_1 \, \underline{\delta\tilde{R}}_1 \, \underline{\tilde{R}}_3 \ ;$$

$$\underline{y} = \underline{\tilde{R}}_1 \, \underline{\delta\tilde{R}}_1 \, \underline{\tilde{R}}_2 \ ;$$

$$\underline{z} = \underline{\tilde{R}}_2 \, \underline{\delta\tilde{R}}_2 \, \underline{\tilde{R}}_3 \ ;$$

and $\underline{\delta R}_1$ and $\underline{\delta R}_2$ are Hermitian matrices.

Substituting equation (IV.68) into equation (IV.62) then gives

$$\nu_1 \, \mathrm{tr} \, \underline{\tilde{h}}_1 \underline{x} + \nu_2 \, \mathrm{tr} \, \underline{\tilde{h}}_2 \underline{z} + \mathrm{tr}(\nu_1 \underline{\tilde{h}}_1 - \nu_2 \underline{\tilde{h}}_2) \underline{y}$$

$$+ \text{ complex conjugate } = 0 ,$$

and since $\underline{x}$, $\underline{y}$ and $\underline{z}$ are linearly independent, then

$$\begin{aligned} &\mathrm{tr}\ \underline{\delta\tilde{R}}_1\, \underline{\tilde{R}}_3\, \underline{\tilde{h}}_1\, \underline{\tilde{R}}_1 = 0 \\ &\mathrm{tr}\ \underline{\delta\tilde{R}}_2\, \underline{\tilde{R}}_3\, \underline{\tilde{h}}_2\, \underline{\tilde{R}}_2 = 0 \\ \text{and}\quad &\mathrm{tr}\ \underline{\delta\tilde{R}}_1\, \underline{\tilde{R}}_2\, (\nu_1 \underline{\tilde{h}}_1 - \nu_2 \underline{\tilde{h}}_2)\, \underline{\tilde{R}}_1 = 0 \end{aligned}$$

........(IV.69)

The above equation is only satisfied if

$$\begin{aligned} &\underline{\tilde{R}}_3\, \underline{\tilde{h}}_1\, \underline{\tilde{R}}_1 = \underline{0}\ ; \\ &\underline{\tilde{R}}_3\, \underline{\tilde{h}}_2\, \underline{\tilde{R}}_2 = \underline{0}\ ; \\ \text{and}\quad &\underline{\tilde{R}}_2\, (\nu_1 \underline{\tilde{h}}_1 - \nu_2 \underline{\tilde{h}}_2)\, \underline{\tilde{R}}_1 = \underline{0} \end{aligned}$$

........(IV.70)

As pointed out by McWeeny et. al. (1969a), the commutation relations,

$$\underline{\tilde{\hbar}}\, \underline{\tilde{R}}_r - \underline{\tilde{R}}_r\, \underline{\tilde{\hbar}} = \underline{0} \qquad (\ r = 1,2\ )$$

........(IV.71)

with

$$\underline{\tilde{\hbar}} = a\, \underline{\tilde{R}}'_2\, \underline{\tilde{h}}_1\, \underline{\tilde{R}}'_2 + b\, \underline{\tilde{R}}'_1\, \underline{\tilde{h}}_2\, \underline{\tilde{R}}'_1 + c\, \underline{\tilde{R}}'_3\, \underline{\tilde{h}}_3\, \underline{\tilde{R}}'_3$$

........(IV.72)

where $\underline{\tilde{R}}'_r = (\ \underline{I} - \underline{\tilde{R}}_r\ )$ and a, b and c are arbitrary non-zero coefficients,

are entirely equivalent to those of equation (IV.70). Using equation (IV.58), the commutation conditions may be rewritten in the form

$$\underline{\tilde{\hbar}}\, \underline{\tilde{T}}_r = \underline{\tilde{T}}_r\, \underline{\mathcal{E}_r} \qquad \text{....(IV.73)}$$

where

$$\underline{\mathcal{E}_r} = \underline{\tilde{T}}_r^{+}\, \underline{\tilde{\hbar}}\, \underline{\tilde{T}}_r\ .$$

Finally, assuming that $\underline{\mathcal{E}_r}$ is a diagonal matrix (cf. equation (IV.51)), the columns of $\underline{\tilde{T}}_r$ (r = 1,2) satisfy the equation

$$\underline{\tilde{\hbar}}\, \underline{\tilde{c}} = \underline{\varepsilon}\, \underline{\tilde{c}} \qquad \text{....(IV.74)}$$

This pseudo-eigenvalue equation must also be solved iteratively (cf. equation (IV.52)). More important, however, is the fact that the solutions of equation (IV.74) lead automatically to the orthogonality of the doubly-occupied, singly-occupied and unoccupied orbitals.

Although equations (IV.52) and (IV.74) are of similar form, their eigenvalues do not have the same physical significance. Thus, by Koopmans' theorem (1933), the eigenvalues of equation (IV.52) may be considered as approximations to the ionization potentials of the system. However, the accuracy of such approximations depends critically upon the cancellation of the correlation energy difference between the neutral and ionized systems by the renormalization energy of the latter. The renormalization energy is here defined as the lowering in the total energy of the ionized system which results when the optimum orbitals for the neutral system relax in becoming optimal for the latter. On the other hand, the eigenvalues of equation (IV.74) have no physical significance because of the arbitrary definition of the effective Hamiltonian matrix. Recently, however, Dodds et. al. (1972) have developed and used a form of Koopmans' theorem which appears to be helpful in the iterative solution of equation (IV.74) and in the discussion of the energetics of electronic transitions in Open-Shell systems.

Valence Bond Theory.

This method is a direct developement of the method used by Heitler and London (1927) in their investigation of the hydrogen molecule, and attempts to analyse any polyatomic system by the ' atoms in molecules approach ' . The theory considers the formation of molecules as arising essentially from the occurrence of chemical bonds which, in turn, results from the pairing of the spins of electrons in the singly-occupied valence orbitals of the constituent atoms. The wavefunctions for the system are then constructed to contain the information of all possible bonds as described by this spin-pairing procedure.

The above approach can be shown to be equivalent to the approximation of equation (IV.5) where

i) the one-electron functions, $\phi_i(x)$, are the spin-orbitals of the atoms constituting the molecular system and no valence atomic orbital occurs more than once in defining the determinantal function, $\Phi_K(x_1, x_2, ---x_N)$; and

ii) the determinantal wavefunction, $\Phi(x_1 - - x_N)$, is a spin eigenfunction (Chapter III). If all the valence electrons of the system are spin-paired so that the resultant electron spin of the system is zero, then the wavefunction (equation (IV.5)) represents a singlet state.

In order to interpret stereochemical properties, for example, the tetrahedral configuration of methane, it is advantageous to choose the one-electron functions, $\phi_i(x)$, for the valence electrons to be localized and to possess directional character. Generally, such orbitals are constructed by using linear combinations of the atomic valence orbitals of the atoms of the complex. Such orbitals are termed hybrid orbitals.

The Valence Bond method may also be extended to include Configuration Interaction (Chapter II). The determinantal functions are constructed from an extended basis of atomic spin-orbitals which includes some of the excited valence state orbitals of the constituent atoms. The set of determinantal functions, $\Phi_K(\underline{x}_1 -- \underline{x}_N)$, also contains those which may be constructed when the constraint of paragraph (i) above is removed. Further discussion of this method is given by McWeeny et. al. (1969d).

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CHAPTER V.

RECENT THEORETICAL APPROACHES.

Some Recent Developements .....

In many problems of atomic, molecular and solid state physics, a distinction is made between valence and core electrons, with the physical properties of the system being determined mainly by the valence electrons. Thus, for example, the atomic spectrum of sodium is determined essentially by the valence electron outside the closed-shell configuration of the neon atom. Moreover, in many molecular and solid state problems, the binding is determined mainly by the valence electrons, the core remaining essentially the same as for the free atomic system (Pickup et. al. (1972) ; Raimes (1967)).

It is therefore natural to attempt to reduce the quantum mechanical analysis of such systems by considering explictly only the valence electrons. The core electrons are then only considered in so far as they give rise to some effective potential in which the valence electrons move.

In 1933, Rosen et. al. made use of such a formalism when studying the sodium dimer. A subsequent article by James (1934) casted some doubt on the authenticity of such an approach, however, and it was only the work of Ohrn et. al. (1966) and the developement of the pseudopotential formalism which provided a mathematical justification for such an approximation.

More recently, attempts at solving the Hartree-Fock equations for molecular systems have been made using techniques developed in solid state theory. These methods include, for example, a variation of the Green's function method (Segall et. al. (1968)) for energy band calculations in solids. This particular method is briefly discussed in a later section.

All the abovementioned developements are within the basic framework of the Hartree-Fock or Valence Bond theories, each of which are known to possess certain advantages and disadvantages.

In particular, some of the advantages of the Hartree-Fock method are

1.) the enormous conceptual simplification due to the independent-particle interpretation allowed;

2.) the high accuracy of the total energy of the ground states of systems investigated;

3.) the high accuracy of some spin-independent one-electron properties; and

4.) the practicability of ab initio solutions for fairly large molecules.

However, there are some serious deficiencies in this method. These include

1.) the poor description of the spin distribution near the nuclei for non-singlet systems;

2.) despite the high accuracy of the total energy, the error is of the order of the energies of interest; for example, binding energy; and

3.) the incorrect description of the dissociation of molecules as the nuclei are moved apart to infinity (Lowdin (1959)).

Various attempts have been made to overcome these deficiencies while retaining the advantages already mentioned. The most successful of these attempts to date appears to be the method introduced by Goddard III (1967) and mentioned briefly later on.

Finally, a mention is made of a method, first introduced by Ellison (1963), which has proved quite useful for obtaining approximate numerical results for larger systems by using data for the ground and excited states of the diatomic and monatomic fragments of the polyatomic aggregate. This method has been used here to derive approximate expressions for the ground state energies of some of the systems investigated.

The Pseudopotential Formalism: Model Hamiltonians.

In the Hartree-Fock theory, the wavefunction describing a state of a many-electron system is represented by a single determinantal function in which the single-electron orbitals are the solutions of an equation of the form (Chapter IV)

$$h^F \phi = \varepsilon \phi \quad , \qquad \ldots\ldots\ldots (V.1)$$

where h^F is the Hartree Fock operator, and the orbitals, $\phi(\underline{x})$, are mutually orthogonal. In particular, each of the valence orbitals is orthogonal to each of the core orbitals.

For cores containing many electrons, the above orthogonality requirement presents large mathematical difficulties. The pseudopotential approach attempts to circumvent such difficulties by introducing a repulsive potential into the equation for the valence orbitals. This potential will simultaneously account for the deep Coulomb well inside the core of the system and the large kinetic energy of the valence electrons there, as is evident by the rapid oscillations of their orbitals in the core region. Concurrently, the Pauli Exclusion Principle is obeyed, as the repulsive potential keeps the valence electrons out of the core region.

Each valence electron is then considered to move in the resultant potential consisting of the nuclear potential, the Coulomb and Exchange potentials arising from all the other electrons (core and valence) of the system and the pseudopotential arising from the core electrons. The core electrons are considered in so far as they determine the exact form of the core potential.

Mathematical Theory.

Consider a system, consisting of (2N + 1) electrons, to be in a state represented by a single determinantal function. Assume that the electrons can be partitioned into a closed-shell core, consisting of 2N electrons, and an open shell, containing one valence electron.

Using the expressions given in equations (III.43) and (III.50), the energy of this state is given by

$$E_{elec.} = 2\sum_{i}^{N} \langle i|h|i\rangle + \sum_{i,j}^{N} \left(2\langle ii|jj\rangle - \langle ij|ji\rangle \right) + \langle v|h|v\rangle + \sum_{i}^{N} \left(2\langle ii|vv\rangle - \langle iv|vi\rangle \right) \qquad \ldots.(V.2)$$

where $\langle i|h|j\rangle = \int \psi_i^{*}(x_1)\, h(1)\, \psi_j(x_1)\, d\underline{r_1}$

and $\langle ij|kl\rangle = \iint \psi_i^{*}(x_1)\, \psi_j(x_1)\, r_{12}^{-1}\, \psi_k^{*}(x_2)\, \psi_l(x_2)\, d\underline{r_1}\, d\underline{r_2}$

The summations are over the occupied spatial orbitals, $\psi_i(x)$, of the core and $\psi_v(x)$ designates the space orbital of the valence electron.

The optimum core- and valence-electron orbitals are determined by minimizing equation (V.2) with respect to any variation of the orbitals, subject to the condition that they remain orthonormal. In particular, the variation of the valence orbital gives the equation

$$h_v(x_1)\,\psi_v(x_1) - \sum_{i}^{N} \varepsilon_{vi}\,\psi_i(x_1) - \varepsilon_{vv}\,\psi_v(x_1) = 0 \qquad \ldots.(V.3)$$

as the necessary condition for the minimum value of $E_{elec.}$, subject to the orthonormality constraint.

$$h_v(x_1) = h(1) + 2\sum_{j}^{N} \int |\psi_j(x_2)|^2\, r_{12}^{-1}\, d\underline{r_2} - \sum_{j}^{N} \frac{\psi_j(x_1)}{\psi_v(x_1)} \int \psi_j^{*}(x_2)\, r_{12}^{-1}\, \psi_v(x_2)\, d\underline{r_2}$$

and

$$\varepsilon_{vj} = \int \psi_j^{*}(x_1)\, h_v(x_1)\, \psi_v(x_1)\, d\underline{r_1}\,. \qquad \ldots\ldots\ldots(V.4)$$

$h(1)$ is as defined in equation (IV.2).

Equation (V.3) may also be written in the form

$$(1 - \hat{O})\, h_v(x_1)\,\psi_v(x_1) = \varepsilon_{vv}\,\psi_v(x_1) \qquad \ldots\ldots\ldots(V.5)$$

where $\hat{O} = \sum_{i}^{N} |\psi_i(x)\rangle\langle\psi_i(x')|$

Since the valence orbital is orthogonal to the core orbitals,

$$(1-\hat{O})\,\psi_\nu(r) = \psi_\nu(r) \qquad \text{........(V.6)}$$

and thus equation (V.5) can be written as

$$(1-\hat{O})\,h_\nu(1-\hat{O})\,\psi_\nu = \varepsilon_{\nu\nu}(1-\hat{O})\,\psi_\nu \qquad \text{........(V.7)}$$

or

$$(h_\nu + V_{pseu.})\,\psi_\nu = \varepsilon_{\nu\nu}\,\psi_\nu \qquad \text{........(V.8)}$$

where

$$V_{pseu.} = (-h_\nu\hat{O} - \hat{O}h_\nu + \hat{O}h_\nu\hat{O} + \varepsilon_{\nu\nu}\hat{O})$$

The core orbitals also satisfy equations (V.7) and (V.8) since

$$(1-\hat{O})\,\psi_i(r) = 0 \qquad \text{........(V.9)}$$

because of the orthonormality of the core orbitals.

Consider some arbitrary function, $\chi(r)$, which is not orthogonal to the core orbitals. The function, $(1-\hat{O})\chi(r)$, is however orthogonal to all the core orbitals since, for any core orbital, $\psi_i(r)$,

$$\int \psi_i^*(r)(1-\hat{O})\,\chi(r)\,dv = \int (1-\hat{O})\,\psi_i(r)\,\chi(r)\,dv$$

$$= 0, \text{ by equation (V.9).}$$

The first equality holds because of the Hermitian property of the operator, $(1-\hat{O})$.

Furthermore, if $\chi(r)$ is chosen to be of the form

$$\chi(r) = \psi_\nu(r) + \sum_i^N a_i\psi_i(r), \qquad \text{........(V.10)}$$

then

$$(1-\hat{O})\,\chi(r) = (1-\hat{O})\,\psi_\nu(r)$$

and thus the function, $(1 - O)\chi(r)$, also satisfies equation (V.7); that is, $\chi(r)$ satisfies equation (V.8).

Under the assumption that the core and valence orbitals are eigenfunctions of the same Hartree Fock operator, then the operators,

$\hat{O}$ and h_ν, commute. Therefore, from equation (V.8),

$$V_{pseu.} = (-h_\nu + \varepsilon_{\nu\nu})\,\hat{O} \qquad \ldots\ldots\ldots(V.11)$$

since $\hat{O}^2 = \hat{O}$.

Furthermore, $h_\nu \psi_i(x) = \varepsilon_i \psi_i(x)$

and, therefore,

$$V_{pseu.} = \sum_i^N (\varepsilon_{\nu\nu} - \varepsilon_i)\,|\psi_i(x)\rangle\langle\psi_i(x')| \qquad \ldots\ldots\ldots(V.12)$$

This is the Phillips-Kleinmann (1960) form of the pseudopotential.

Weekes et. al. (1968, 1969) have generalized the above form of the pseudopotential by defining

$$V_R = \sum_i^N b_i\,|\psi_i(x)\rangle\langle\psi_i(x')| \qquad \ldots\ldots\ldots(V.13)$$

Choosing, in particular, $b_i = (E - \varepsilon_i)$,

where $h_\nu \psi_i(x) = \varepsilon_i \psi_i(x)$, as before,

and E is any arbitrary number,

then the core eigenfunctions are also eigenfunctions of the operator

$$(h_\nu + V_R)$$

with eigenvalue, E. The valence spectrum, however, remains unchanged since

$$(h_\nu + V_R)\,\psi_\nu(x) = h_\nu \psi_\nu(x) = \varepsilon_{\nu\nu} \psi_\nu(x)$$

because of the orthonormality of the eigenfunctions of $h_\nu(x)$.

If the number, E, is chosen large and positive, the lowest eigenvalue of the operator

$$(h_\nu + V_R)$$

is the lowest valence eigenvalue. Thus, it is possible to use an arbitrary trial function in a variational solution of the eigenvalue equation

$$\Big\{h_\nu + \sum_{i=1}^N (E - \varepsilon_i)\,|\psi_i(x)\rangle\langle\psi_i(x')|\Big\}\,\chi(x) = \varepsilon\,\chi(x) \qquad \ldots\ldots\ldots(V.14)$$

without collapse into the core levels. The trial function converges to the true orthogonal valence function, $\psi_\nu(\underline{r})$, and does not possess the arbitrary core contribution of equation (V.10).

In order to use any of the formalisms discussed (equations (V.12) and (V.14)), it is necessary to know the exact core eigenfunctions of the Hartree-Fock operator, $h_\nu(\underline{r})$. Furthermore, the exchange and pseudopotential operators are non-local and the solution of the Hartree-Fock equation for the valence orbitals yet requires the evaluation of many two-electron integrals between the valence and core orbitals (see following discussion).

The above considerations, coupled with the difficulty of simultaneously determining smooth pseudowavefunctions and pseudopotentials (Weekes et. al. (loc. cit.)), have resulted in the pseudopotential formalism being used to suggest suitable model Hamiltonians for the investigation of large systems. By construction, the energy of the valence electron is made free from variational collapse into the core values.

Approximate Numerical Solutions Of Hartree-Fock Equations .

For a system of N electrons moving in some fixed nuclear framework, the Hartree-Fock operator of equation (V.1) is defined by

$$h^F(1) = h(1) + \sum_{j=1}^{N} \int |\phi_j(\underline{x}_2)|^2 \, r_{12}^{-1} \, d\underline{x}_2 - \sum_{j=1}^{N} \frac{\phi_j(\underline{x}_1)}{\phi(\underline{x}_1)} \int \phi_j^*(\underline{x}_2) \, r_{12}^{-1} \, \phi(\underline{x}_2) \, d\underline{x}_2 \qquad \text{........(V.15)}$$

where the summations are over the occupied spin-orbitals of the system. The second and third terms, respectively, represent the average coulomb and exchange interactions between the electrons of the system; $h(1)$ is as defined in equation (IV.2).

Thus far, it has been possible to determine, either analytically or numerically, solutions for the Hartree-Fock equations only for atoms and small molecular systems. The main hindrance to the investigation of larger systems is the large number of two-electron integrals which need to be computed in the usual Roothaan-Hartree Fock equations* (Chapter IV) and, more important, the non-local character of the exchange term. However, much progress has been made in the study of large molecules and solids by approximating the above exchange term by some suitable average over the different orbital exchange potentials (Slater (1968, 1972)):

$$V_{X\alpha}(x) = -3\alpha\left[(3/8\pi)\sum_{j=1}^{N}|\phi_j(x)|^2\right]^{1/3} \qquad \text{........(V.16)}$$

where α is a parameter (cf. theory of Free Electron Gas).

With this approximation, the Hartree-Fock operator of equation (V.15) becomes

$$\mathcal{H}^F(1) = -\nabla_1^2/2 + V_\alpha(1)$$

where

$$V_\alpha(1) = -\sum_{e} Z_e/r_{e1} + \sum_{j=1}^{N}|\phi_j(x_2)|^2 r_{12}^{-1}\,dx_2 + V_{X\alpha}(x_1) \qquad \text{........(V.17)}$$

It is then usual to replace the above potential, $V_\alpha(1)$, by another one of ' muffin-tin ' form, in which $V_\alpha(1)$ is spherically averaged. The spherically averaged potential is then used in conjunction with ' multiple-scattering ' theory (Segall et. al. (loc. cit.)) to obtain approximate numerical solutions of equation (V.1). A direct comparison of the solutions obtained by this method with those of the accurate Hartree-Fock equations is given by Slater et. al. (1969).

The main advantage of this method is the significant reduction in computational time since no two-electron or multi-centre integrals need be evaluated. However, the method is expected to give

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* See, however, Clementi (1972) where a new time-saving scheme for evaluating the two-electron integrals is proposed and tested.

poor results when applied to small molecules as the ' muffin-tin ' potential incorrectly describes the self-consistent potential in the region between the atoms (Fricker et. al. (1971)).

Goddard III Method .

Recently, Goddard III (1967) has developed a theory of many electron systems which incorporates many of the advantages of both the Valence and Molecular Orbital theories, as well as overcoming many of their deficiencies.

It has already been mentioned in Chapter IV that the removal of the constraint of double-occupancy of the molecular orbitals in the Hartree-Fock method generally results in a lower variationally determined energy for the system. However, in the unrestricted Hartree-Fock method, the single determinantal function is no longer a spin eigenfunction (see equation (IV.54) et. seq.). It is possible to project out from this unrestricted function the component of correct spin symmetry, but the one-electron orbitals will not be optimum for the projected wavefunction (Lowdin (loc. cit.)).

The correct solution is obtained by optimizing the orbitals after the projection has been performed. Unfortunately, this procedure, the spin-polarized extended Hartree-Fock method, has been rather difficult to use because of inherent non-orthogonality problems. However, Goddard III has been able to develop a method which, although giving wavefunctions which are equivalent to those which would be obtained by the above projection procedure, circumvents many of the above difficulties. This is done by the use of a projection operator having the property that it projects from any arbitrary many-electron function, a function which has a definite spin symmetry and satisfies Pauli's Exclusion Principle.

Such a function may generally be expressed as a linear combination of Slater determinantal functions:

$$\Phi^{S,M}(\text{Goddard}) = \mathcal{G}^{S}(g\chi(M)) = \sum_{k} c_k \, \Phi_k^{M}(\text{Slater}) \qquad \text{........(V.18)}$$

where

$$S_{op}^{2}\,\Phi^{S,M}(\text{Goddard}) = S(S+1)\,\Phi^{S,M}(\text{Goddard})$$
$$S_z\,\Phi^{S,M}(\text{Goddard}) = M\,\Phi^{S,M}(\text{Goddard}) \qquad \text{........(V.19)}$$
$$S_z\,\Phi^{M}(\text{Slater}) = M\,\Phi^{M}(\text{Slater})$$

and the expansion coefficients are determined by equation (V.19). g and $\chi(M)$ are products of single-electron orbital and spin-functions, respectively.

This theory is successful since it is possible to

1.) determine pseudo-eigenvalue equations, similar to those of the Hartree-Fock method, for finding the optimum orbitals of g ;

and

2.) compute expectation values of various properties for the state of the system represented by equation (V.18),

and arises* because of certain simplifications resulting from the properties of the projection operator, $\mathcal{G}^{S}$.

Other great advantages of the method are as follows:

1.) Although the Goddard function is essentially a many-determinantal function, it still permits an independent-particle description of the system. This is because of the possibility of deriving one-electron equations, entirely analogous to the Hartree-Fock equations, in which each electron may be considered to move in the potential field arising from the nuclear framework and all the other electrons of the system.

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* It is not necessary to use the series expansion of equation (V.18).

2.) The increased flexibility in the orbital part of the wavefunction allows a better description of the charge distribution in the many-electron system. In particular, such a wavefunction does dissociate properly as the nuclei of the polyatomic system move to infinity, and, therefore, can be used for investigation of the processes of binding in molecules or solids.

3.) A much better description of the spin distribution in the system, especially near the nuclei, is given.

The Diatomics-In-Molecule Method .

In the Valence Bond Description of the electronic states of a molecular system, each state function, $\Phi(x)$, is expressed in terms of a finite set of Valence Bond functions, Φ_k :

$$\Phi(x) = \sum_k c_k \Phi_k(x) \qquad \text{........(V.20)}$$

Ellison (1963) has shown that the energy matrix elements,

$$\mathcal{H}_{nm} = \int \Phi_n^* \mathcal{H}_{op} \Phi_m \, dx, \qquad \text{........(V.21)}$$

needed to solve the resulting secular equation (cf. equations (III.4) or (III.12)) may be expressed in an approximate but well-defined manner in terms of the ground- and excited-state energies of all the possible diatomic and monatomic fragments of the system and of the overlap integrals,

$$\mathcal{S}_{nm} = \int \Phi_n^* \Phi_m \, dx \qquad \text{........(V.22)}$$

This possibility arises since the Hamiltonian operator may be expressed in terms of ' diatomic ' and ' monatomic ' components as follows:

$$\mathcal{H}_{op} = \sum_{P>Q} \mathcal{H}_{op}^{PQ} - (N-2)\sum_{P} \mathcal{H}_{op}^{P} \quad \text{........(V.23)}$$

where the operator, $\mathcal{H}_{op}^{PQ}$, is defined to contain all those interactions involving electrons assigned to atoms, P and Q , in the determinantal function upon which it operates; an analogous definition holds for $\mathcal{H}_{op}^{P}$. The summation is over all the atoms of the molecule.

Equation (V.21) may then be rewritten as

$$\begin{aligned} \mathcal{H}_{nm} &= \tfrac{1}{2}\left(\int \Phi_n^* \mathcal{H}_{op} \Phi_m \, d\underline{x} + \int \Phi_m^* \mathcal{H}_{op} \Phi_n \, d\underline{x} \right) \\ &= \sum_{P<Q} \bar{\mathcal{H}}_{nm}^{PQ} - (N-2) \sum_{P} \bar{\mathcal{H}}_{nm}^{P} \end{aligned} \quad \text{....(V.24)}$$

with

$$\begin{aligned} \bar{\mathcal{H}}_{nm}^{PQ} &= \tfrac{1}{2}\left(\mathcal{H}_{nm}^{PQ} + \mathcal{H}_{mn}^{PQ} \right) \quad ; \\ \mathcal{H}_{nm}^{PQ} &= \int \Phi_n^* \mathcal{H}_{op}^{PQ} \Phi_m \, d\underline{x} \quad . \end{aligned} \quad \text{....(V.25)}$$

Similar expressions hold for $\bar{\mathcal{H}}_{nm}^{P}$.

Thus far, no approximation has been made in the theory. Any error resulting can be attributed to the use of a finite expansion set in equation (V.20).

Evaluation Of Matrix Elements.

The Valence Bond function, Φ_n , is a determinantal function, or a linear combination of them, expressible in the form

$$\Phi_n = A[\phi_n] \quad . \quad \text{....(V.26)}$$

[ϕ_n] is in general a linear combination of simple products of atomic spin-orbitals and A is the total antisymmetrization operator. This may in turn be partitioned as follows:

$$A = A_{PQ}^{(PQ)} A_{PQ} A_{(PQ)} \quad \text{........(V.27)}$$

where the operator, $A_{(PQ)}$, antisymmetrizes the set of electrons which are not originally assigned to the diatomic fragment, PQ ;

A_{PQ} antisymmetrizes the set of electrons which are originally assigned to PQ, and $A^{(PQ)}_{PQ}$ is the antisymmetrizer which completes the identity. As mentioned before, the assignment of electrons is specified by the function upon which the operator, $\mathcal{H}^{PQ}_{op}$, operates.

Equation (V.25) then becomes

$$\mathcal{H}^{PQ}_{nm} = \int \Phi^*_n \, \mathcal{H}^{PQ}_{op} \, A \, [\phi_m] \, \underline{dx}$$

$$= \int \Phi^*_n \, A^{(PQ)}_{PQ} \, \mathcal{H}^{PQ}_{op} \, A_{PQ} \, A_{(PQ)} [\phi_m] \, \underline{dx} \qquad \text{........(V.28)}$$

since $A^{(PQ)}_{PQ}$ commutes with $\mathcal{H}^{PQ}_{op}$.

Consider one of the products, ϕ_m, of [ϕ_m].

Then,

$$A_{PQ} \, A_{(PQ)} \, \phi_m = \Phi^{PQ}_m \, \Phi^{(PQ)}_m \qquad \text{........(V.29)}$$

where Φ^{PQ}_m and $\Phi^{(PQ)}_m$ are determinantal functions totally antisymmetric with respect to those electrons in the set belonging to and not belonging to the diatomic fragment, PQ, respectively.

If it is assumed that the known eigenfunctions of the ground- and excited-states of the diatomic molecule, PQ,

$$\mathcal{H}^{PQ}_{op} \, \tilde{\Phi}^{PQ}_\mu = (E^{PQ}_{elec})_\mu \, \tilde{\Phi}^{PQ}_\mu, \qquad \text{........(V.30)}$$

may be expressed in the form

$$\tilde{\Phi}^{PQ}_\mu = \sum_m \Phi^{PQ}_m \, a_{m\mu}$$

or

$$\underline{\underline{\tilde{\Phi}}}^{PQ} = \underline{\underline{\Phi}}^{PQ} \, \underline{a} \qquad \text{....(V.31)}$$

then, it follows that

$$\underline{\underline{\Phi}}^{PQ} = \underline{\underline{\tilde{\Phi}}}^{PQ} \, \underline{a}^{-1} \qquad \text{........(V.32)}$$

may provide fair approximations for the determinantal functions, Φ^{PQ}_m, in terms of the eigenfunctions of the diatomic molecule.

Thus,

$$\hat{\mathcal{H}}^{PQ}_{nm} = \int \Phi^*_n \, A^{(PQ)}_{PQ} \, \mathcal{H}^{PQ}_{op} \, A_{PQ} \, A_{(PQ)} \, \phi_m \, \underline{dx}$$

$$\hat{\mathcal{H}}_{nm}^{PQ} = \int \Phi_n^* A_{PQ}^{(PQ)} \mathcal{H}_{op}^{PQ} \Big(\sum_{\mu} \tilde{\Phi}_{\mu}^{PQ} (a^{-1})_{\mu m} \Big) \Phi_m^{(PQ)} \, dx$$

(using equation (V.32))

$$= \int \Phi_n^* A_{PQ}^{(PQ)} \Big(\sum_{\mu} (E_{elec.}^{PQ})_{\mu} \tilde{\Phi}_{\mu}^{PQ} (a^{-1})_{\mu m} \Big) \Phi_m^{(PQ)} \, dx$$

(using equation (V.30))

$$= \sum_{\mu} (E_{elec.}^{PQ})_{\mu} (a^{-1})_{\mu m} \sum_{t} \int a_{t\mu} \Phi_n^* A_{PQ}^{(PQ)} \Phi_t^{PQ} \Phi_m^{(PQ)} \, dx$$

(using equation (V.31))

But

$$A_{PQ}^{(PQ)} \Phi_t^{PQ} \Phi_m^{(PQ)} = \sum_{k} b_{tm,k} \Phi_k , \qquad \text{........(V.33)}$$

and therefore

$$\hat{\mathcal{H}}_{nm}^{PQ} = \sum_{\mu} (E_{elec}^{PQ})_{\mu} (a^{-1})_{\mu m} \sum_{t} a_{t\mu} \sum_{k} b_{tm,k} \bar{S}_{nk}$$

(using equation (V.22))

or

$$\hat{\mathcal{H}}_{nm}^{PQ} = \sum_{k} \bar{S}_{nk} \sum_{t} b_{tm,k} \sum_{\mu} a_{t\mu} (a^{-1})_{\mu m} (E_{elec.}^{PQ})_{\mu} \qquad \text{........(V.34)}$$

The energy integrals, $\hat{\mathcal{H}}_{nm}^{P}$, may also be expressed in a similar manner. Then

$$\mathcal{H}_{nm}^{PQ} = \sum_{m} b_m \hat{\mathcal{H}}_{nm}^{PQ}$$

and

$$\mathcal{H}_{nm}^{P} = \sum_{m} b_m \hat{\mathcal{H}}_{nm}^{P} \qquad \text{....(V.35)}$$

where b_m is the coefficient of the product, ϕ_m, in [ϕ_m].

The success of the above theory rests upon the validity of the expansion equations (V.31) and (V.32); that is, upon how well the actual ground- and excited-states of the diatomic and monatomic fragments are represented by the limited set of Valence Bond functions and how well the Valence Bond functions are in turn represented by the limited set of actual ground- and excited-states of the diatomic and monatomic fragments. Some cancellation of the errors of the former representation by those of the latter may be expected.

Application of the above theory to various systems has proved fairly successful. In all cases, the computed energy eigenvalues have been found to be quite insensitive to the neglect of the atomic overlap integrals (Abrams et. al. (1968)). More recently, the theory has been extended by Tully (1973) to describe the directional bonding properties of some systems.

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CHAPTER VI.

PRESENT COMPUTATIONAL MODEL.

Model Hamiltonian.

In this research project, clusters of sodium atoms have been investigated within a model-pseudopotential approximation as developed from the framework of an ab initio calculation in which all the electrons of the system are included. The useful feature of this approach is that the approximations made are directly traceable to a theoretical basis.

Employment of either the Hartree, Hartree-Fock or Goddard III schemes in conjunction with the variational principle establishes effective potentials in which each electron of the system may be considered to move. Thus, the effective one-electron Hamiltonian of the system under consideration can be generally defined by an equation of the form

$$h_{eff.}(i) = - \nabla_i^2/2 + V(i) + U(i) \qquad \text{........(VI.1)}$$

where V(i) is the electrostatic potential at the point, i , arising from the nuclei of the system; U(i) represents some average over the interelectronic interactions (Chapter IV).

Since the operator, $h_{eff.}$, is Hermitian, all of its eigenfunctions can be chosen to be mutually orthogonal, an option arising only in cases of degeneracy. The discussion of Chapter V suggests that it is usually advantageous to replace the orthogonality requirement between the core and valence eigenfunctions by some operator, $V_R(i)$. With this modification, the expression for the effective one-electron Hamiltonian for the motion of the valence electrons becomes

$$h_m(i) = h_{eff.}(i) + V_R(i) \qquad \text{........(VI.2)}$$

This Hamiltonian is chosen so as to reproduce the same valence eigenvalues of the system, as determined by the operator of equation (VI.1). Moreover, its lowest energy eigenvalue corresponds to the lowest valence eigenvalue of the original operator.

As shown by Weekes et. al. (1968, 1969), the ' orthogonality ' operator may be chosen to be of the form

$$V_R(i) = \sum_c b_c |\psi_c(r_i)\rangle\langle\psi_c(r_j)| \qquad \text{........(VI.3)}$$

where b_c are numerical coefficients; the summation is over the core eigenfunctions of the operator, h_{eff}. In practice, the true core eigenfunctions are unknown. However, progress may be made by using approximate forms for the core functions and choosing the numerical coefficients of equation (VI.3) in order that the resulting model Hamiltonian has the same eigenvalues as the ' accurate ' one.

The model Hamiltonian defined above is still rather complicated to use. Further simplification may be made by an investigation of the relative importance of the various potential operators.

Thus, consider the average two-electron potential, U(i) . This generally includes the Coulomb and Exchange potentials of the many-electron system and represents the effect of all the other electrons of the system upon a particular ' test ' electron at the point, i . There are several ways of approximating this potential (Slater et. al. (1969)). However, consider in particular the Exchange potential for a valence electron at the point, i , arising from the core electrons of the system. This potential is a non-local one, depending upon the particular orbital occupied by the valence electron under consideration. Furthermore, its ' overlap nature ' suggests that it will make a minor contribution to the total core component of U(i) and, therefore, may be safely ignored.

The argument of ' core nonpenetrability ' introduced by Weekes et. al. (loc. cit.) provides a qualitative justification for the above approximation. As pointed out by these authors, it is physically possible to define a surface such that the major portion of the core-electron density lies within this surface and the majority of the valence-electron density lies without. The Exchange potential for the valence electrons arising from the core depends strongly upon the overlap charge densities between each of the core electrons and each of the valence electrons. The above argument suggests that this overlap will indeed be small and, consequently, the essential physics of the situation appears to be included in the chosen model, in spite of the approximations made (Hameed (1969)).

Experimental results indicate that, in the study of sodium atoms, the electrons occupying the 1s-, 2s- and 2p- atomic states may be considered as constituting the core. Furthermore, the core eigenfunctions of any system consisting of a number of sodium atoms are expected to be almost identical to the core eigenfunctions of the constituent atoms (Raimes (1961)). The polyatomic system may, therefore, be regarded as consisting of a number of atomic cores with the intra-core effects being approximately the same in the cluster as in the separated atoms (see Chapter IX for further discussion).

One further simplification can be made to the above model Hamiltonian. The results of Szasz (1967) suggest that the effect of the 1s- core orbital in the potential, $V_{\ell}(i)$, will be negligible. Thus, only the 2s- and 2p- core functions are included in the summation of equation (VI.3).

The model Hamiltonian for a polyatomic system having one valence electron, therefore, becomes

$$h_m(i) = -\nabla_i^2/2 - \sum_{\alpha} \Big[Z_\alpha / r_{\alpha i} - \sum_{c} \int |\psi_c^\alpha(j)|^2 r_{ij}^{-1} \, d\tau_j - a\,|\psi_{2s}^\alpha(i)\rangle\langle\psi_{2s}^\alpha(j)| - b \sum_{k=x,y,z} |\psi_{2p_k}^\alpha(i)\rangle\langle\psi_{2p_k}^\alpha(j)| \Big] \quad \text{....(VI.4)}$$

Z_α and $\psi_c^\alpha(r)$, respectively, denote the charge and an atomic core state on the nucleus, α .

The above operator contains two parameters which must be determined. The most convenient way of doing this is by an investigation of the atomic system using the appropriately modified form of equation (VI.4). Further discussion of this procedure is given in a later section.

For systems with more than one valence electron, the model operator given above is generalized to include the mutual interactions of the valence electrons as well as their individual interactions with the core. Thus,

$$\mathcal{H}_{model} = \sum_{i}^{\text{(valence electrons)}} h_m(i) + \sum_{i>j}^{\text{(valence electrons)}} r_{ij}^{-1} \qquad \text{........(VI.5)}$$

The total energy of the cluster in the Born-Oppenheimer approximation is then given by

$$W_{Tot.} = E_{elec.} + \sum_{\alpha} E(\alpha) + \sum_{\alpha>\beta} Z''_{\alpha} Z''_{\beta} / |R_{\alpha} - R_{\beta}| \qquad \text{........(VI.6)}$$

where

$$E_{elec} = \langle \Phi(x) | \mathcal{H}_{model} | \Phi(x) \rangle / \langle \Phi(x) | \Phi(x) \rangle$$

is the energy of the valence electrons; E(α) is the energy of the atomic core (core electrons and nucleus) on the nucleus, α . The final term represents the interaction energy of the cores, which are assumed non-overlapping and, therefore, to interact as point charges. Z''_{α} is the effective charge on the nucleus, α (see equations (IX.21) to (IX.26)).

In this model, no account is taken of the intra-, inter- or valence-core correlation effects. It may be noted in passing, that in the accurate Hartree-Fock treatment, only precorrelation effects are considered (Clementi (1963)).

On qualitative grounds, the intra-core effects may be expected to be quite significant. However, their neglect is not expected to greatly affect any of the properties of the system investigated here, since these are determined mainly by the valence electrons. Also, the inter-core effects can be ignored because of the negligible overlapping of the cores of the system.

The importance of the valence-core effects can be clearly seen form the calculations of Szasz (loc. cit.) on valence orbital energies and Callaway (1957) on cohesive energies of solids. However, for consistency of the above model, for example, the argument of core-nonpenetrability, these correlation effects are ignored, although it is quite likely that some valence-core polarization will be accounted for by the particular choice of the parameters, a and b , of equation (VI.4). Thus, the extra-molecular correlation energy, as defined by Clementi (1962), arises solely from the correlation of the valence electrons of the system.

Hellmann-Feynman And Virial Theorems.

It is expected that both the Hellmann-Feynman and Virial theorems will not be satisfied in this model because of the ' neglect ' of the core electrons. In this section, these deviations are derived and discussed.

The expression for the total energy of the system in the Hartree-Fock approximation is

$$W_{Tot.} = \sum_{i} \langle i|h_{nv}|i\rangle n_i + \sum_{i>j} n_i n_j \left(\langle ii|jj\rangle - \langle ij|ji\rangle \right) + \sum_{\alpha>\beta} Z''_{\alpha} Z''_{\beta} / R_{\alpha\beta} + \sum_{\alpha} E(\alpha) \qquad \text{........(VI.7)}$$

In the above expression, $|i\rangle$ represents an orthonormal valence orbital with occupation number, n_i (= 0, 1, 2). All other quantities are as defined previously in equations (IV.28), (VI.4) and (VI.6).

The valence orbitals are determined by the variational principle (Chapter IV) and satisfy the one-electron equations:

$$h_m|i\rangle + \sum_j n_j (\langle i|jj\rangle - \tfrac{1}{2} \langle j|ji\rangle) = \varepsilon_i |i\rangle \qquad \text{........(VI.8)}$$

where

$$\langle i \mid jk \rangle = \psi_i(x_1) \int \psi_j^*(x_2)\, r_{12}^{-1}\, \psi_k(x_2)\, d\underline{x}_2$$

and

$$|i\rangle \equiv \psi_i(x_1) .$$

1.) Hellmann-Feynman Theorem.

The x-component of the force exerted by the system upon the α-th core is given by

$$-(\partial \tilde{W}_{Tot.}/\partial \bar{X}_\alpha) = \sum_i n_i \langle i|\partial V^\alpha/\partial \bar{X}_\alpha|i\rangle - \sum_{\beta\neq\alpha} \partial(Z''_\alpha Z''_\beta R^{-1}_{\alpha\beta})/\partial \bar{X}_\alpha$$
$$- \sum_i n_i (\langle(\partial i/\partial \bar{X}_\alpha)|\varepsilon_i|i\rangle + \langle i|\varepsilon_i|(\partial i/\partial \bar{X}_\alpha)\rangle) ,$$

where

$$\tilde{W}_{Tot.} = W_{Tot.} - \sum_\alpha E(\alpha) ,$$

and

$$V^\alpha(x_1) = Z_\alpha / r_{\alpha 1} - \sum_c \int |\psi^\alpha_c(x_2)|^2\, r_{12}^{-1}\, d\underline{x}_2$$
$$- a|\psi^\alpha_{2s}(x_{\alpha 1})\rangle\langle\psi^\alpha_{2s}(\underline{x}_{\alpha 2})| - b \sum_{k=x,y,z} |\psi^\alpha_{2p_k}(\underline{x}_{\alpha 1})\rangle\langle\psi^\alpha_{2p_k}(\underline{x}_{\alpha 2})|$$
$$\text{........(VI.9)}$$

It must be remembered that each valence orbital depends parametrically upon the coordinates ($\bar{X}_\alpha$, $\bar{Y}_\alpha$, $\bar{Z}_\alpha$) of the α-th nucleus.

Now

$$\langle i|\varepsilon_i|\, \partial i/\partial \bar{X}_\alpha\rangle + \langle \partial i/\partial \bar{X}_\alpha|\, \varepsilon_i|i\rangle$$
$$= \varepsilon_i\, \partial\langle i|i\rangle/\partial \bar{X}_\alpha = 0$$

since

$$\langle i|i\rangle = \int \psi_i^*(x_1)\, \psi_i(x_1)\, d\underline{x}_1 = 1 .$$

Thus,

$$-(\partial \tilde{W}_{Tot.}/\partial \bar{X}_\alpha) = \sum_i n_i \langle i|\partial V^\alpha/\partial \bar{X}_\alpha|i\rangle - \sum_{\beta\neq\alpha} \partial(Z''_\alpha Z''_\beta R^{-1}_{\alpha\beta})/\partial \bar{X}_\alpha$$
$$\text{........(VI.10)}$$

The first and second terms, respectively, represent the forces acting on the core of the α-th nucleus arising from the valence electrons and all other cores of the system. Since the core electrons are always assumed to be spherically distributed about the nucleus during its motion, the above forces may be considered to act directly upon the nucleus.

Although equation (VI.10) is in a form similar to that which expresses the Hellmann-Feynman theorem, it cannot be strictly interpreted as such since

$$\langle i|\,\partial V^{\alpha}/\partial \bar{X}_{\alpha}\,|i\rangle \neq \langle i|i\,\partial V^{\alpha}/\partial \bar{X}_{\alpha}\rangle .$$

This follows because of the presence of the projection operator (equation (VI.3)).

2.) Virial Theorem.

Let P be the operator defined by the equation

$$P = x_1\,\partial/\partial x_1 + y_1\,\partial/\partial y_1 + z_1\,\partial/\partial z_1 \qquad \text{........(VI.11)}$$

where (x_1, y_1, z_1) are the coordinates of any point in space. Premultiplying equation (VI.8) by < i | P | gives

$$\langle i|P(-\nabla_1^2 i/2)\rangle + \langle i|-\sum_{\alpha}(PV^{\alpha})|i\rangle + \langle i|-\sum_{\alpha}V^{\alpha}|Pi\rangle$$
$$+ \sum_{j} n_j\,(\langle i(Pi)|jj\rangle + [ii|(Pr_{12}^{-1})|jj] - \tfrac{1}{2}\langle i(Pj)|ji\rangle$$
$$- \tfrac{1}{2}[ij|(Pr_{12}^{-1})|ji]\,) = \varepsilon_i\langle i|Pi\rangle$$

where

$$[ij|g(1,2)|kl] = \iint \psi_i^{*}(x_1)\psi_j(x_1)\,g(1,2)\,\psi_k^{*}(x_2)\psi_l(x_2)\,d\underline{x}_1\,d\underline{x}_2 . \qquad \text{........(VI.12)}$$

Postmultiplying the complex conjugate of equation (VI.8) by | P | i > gives

$$\varepsilon_i\langle i|Pi\rangle = \langle i|-\nabla_1^2(Pi)/2\rangle + \langle i|-\sum_{\alpha}V^{\alpha}|Pi\rangle$$
$$+ \sum_{j} n_j\,(\langle i(Pi)|jj\rangle - \tfrac{1}{2}\langle j(Pi)|ij\rangle) \qquad \text{........(VI.13)}$$

where the Hermitian property of the operator, $h_m(1)$, has been used.

Combining equations (VI.12) and (VI.13) gives

$$\langle i|\rho(-\nabla_1^2 i/2)\rangle + \langle i|\nabla_1^2(\rho i)/2\rangle + \langle i|-\sum_\alpha(\rho V^\alpha)|i\rangle$$
$$+ \sum_j n_j(\langle j(\rho i)|ij\rangle - \langle i(\rho j)|ji\rangle)/2$$
$$+ \sum_j n_j([ii|(\rho r_{12}^{-1})|jj] - 1/2\,[ij|(\rho r_{12}^{-1})|ji]) = 0 \qquad \text{........(VI.14)}$$

Multiplying the above equation by $-n_i$ and summing over the valence orbitals of the system finally gives

$$2\langle K.E.\rangle = \sum_i n_i \langle i|-\sum_\alpha(\rho V^\alpha)|i\rangle$$
$$+ \sum_{ij} n_i n_j([ii|(\rho r_{12}^{-1})|jj] - 1/2\,[ij|(\rho r_{12}^{-1})|ji]) \qquad \text{........(VI.15)}$$

since
$$\langle i|\rho(-\nabla_1^2 i/2)\rangle + \langle\nabla_1^2 i|\rho i/2\rangle = 2\langle i|\nabla_1^2 i/2\rangle .$$

< K.E. > represents the average Kinetic Energy of the valence electrons.

Now

$$-\rho V^\alpha = -(x_1\partial/\partial x_1 + y_1\partial/\partial y_1 + z_1\partial/\partial z_1)\,V^\alpha(r_{\alpha 1})$$
$$= -r_{\alpha 1}(\partial V^\alpha/\partial r_{\alpha 1}) + (\bar{X}_\alpha\partial/\partial\bar{X}_\alpha + \bar{Y}_\alpha\partial/\partial\bar{Y}_\alpha + \bar{Z}_\alpha\partial/\partial\bar{Z}_\alpha)\,V^\alpha$$

and
$$\sum_\alpha\sum_i n_i\langle i|(\bar{X}_\alpha\partial/\partial\bar{X}_\alpha + \bar{Y}_\alpha\partial/\partial\bar{Y}_\alpha + \bar{Z}_\alpha\partial/\partial\bar{Z}_\alpha)V^\alpha|i\rangle$$
$$= -\sum_\alpha(\bar{X}_\alpha\partial/\partial\bar{X}_\alpha + \bar{Y}_\alpha\partial/\partial\bar{Y}_\alpha + \bar{Z}_\alpha\partial/\partial\bar{Z}_\alpha)\tilde{W}_{Tot.} - \sum_{\alpha>\beta} Z'_\alpha Z'_\beta/R_{\alpha\beta}$$

from equation (VI.10).

........(VI.16)

Furthermore,

$$\sum_{ij} n_i n_j[ii|(\rho r_{12}^{-1})|jj] = -\sum_{i>j} n_i n_j\langle ii|jj\rangle$$

and

$$\sum_{i,j} n_i n_j \, [ij|(\rho r_{12}^{-1})|ji] = -\sum_{i>j} n_i n_j \langle ij|ji\rangle \qquad \text{........(VI.17)}$$

Therefore,

$$2\langle K.E.\rangle = -\langle P.E.\rangle - \sum_{\alpha} (\bar{X}_\alpha \partial/\partial \bar{X}_\alpha + ---)\tilde{W}_{Tot.}$$

$$- \sum_{i} n_i \langle i| \sum_{\alpha} (V^\alpha + r_{\alpha 1}\, \partial V^\alpha/\partial r_{\alpha 1})|i\rangle$$

$$\text{........(VI.18)}$$

with $< P.E. >$ representing the average Potential Energy of the valence system; this includes the inter-core repulsions.

Equation (VI.18) shows that the Virial theorem will only be satisfied if the last term vanishes identically. Since it is possible to define an ionic radius, σ_α , such that

$$V^\alpha(r_{\alpha 1}) = Z_\alpha'' r_{\alpha 1}^{-1} \qquad \text{if} \quad r_{\alpha 1} \geqslant \sigma_\alpha ,$$

then

$$\langle i| \sum_{\alpha} (V^\alpha + r_{\alpha 1}\, \partial V^\alpha/\partial r_{\alpha 1})|i\rangle = \sum_{\alpha} \langle i| V^\alpha + r_{\alpha 1}\, \partial V^\alpha/\partial r_{\alpha 1} |i\rangle_{\sigma_\alpha}$$

$$\text{........(VI.19)}$$

where the integration on the right-hand side is performed over the space enclosed by the sphere of radius, σ_α , centred on the α-th nucleus. The qualitative argument of core-nonpenetrability would suggest that the above integrals will be small, especially when it is remembered that the interaction of atoms is generally accompanied by a movement of valence charge away from the core regions of the interacting atoms (Berlin (1951)). However, the integrals will be finite and, thus, the Virial theorem is not satisfied for the chosen model Hamiltonian.

Choice Of Basis Functions .

1.) Core Orbitals.

Throughout all the calculations in this research, the core orbitals were kept fixed. They were represented by the usual Slater type atomic functions, given by

$$\psi_{nlm}(\gamma,r) = R_n(\gamma,r)\, Y_{lm}(\theta,\phi) \qquad \text{........(VI.20)}$$

where

$$R_n(\gamma,r) = [(2n)!]^{-1/2}\,(2\gamma)^{n+1/2}\, r^{n-1}\, e^{-\gamma r}$$

and

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{(2l+1)(l-|m|)!}{2\pi\,(l+|m|)!}}\; P_l^{|m|}(\cos\theta) \begin{cases} 1 & m=0 \\ \cos|m|\phi & m>0 \\ \sin|m|\phi & m<0 \end{cases}$$

are the normalized real spherical harmonics.

The exponents, however, were not chosen by the well-known Slater rules (Slater (1930)), but from the tables of the ' best single-zeta exponents ' for these orbitals as given by Clementi et. al. (1963).

The normalized basis functions for the various core states were, therefore, as follows:

$$1s = (\gamma_{1s}^3/\pi)^{1/2}\, \exp(-\gamma_{1s} r)$$

$$2s = (\gamma_{2s}^5/3\pi)^{1/2}\, r\, \exp(-\gamma_{2s} r)$$

$$2p_x,\, 2p_y,\, 2p_z = (\gamma_{2p}^5/3\pi)^{1/2}\, r \exp(-\gamma_{2p} r) \begin{cases} \sin\theta & \cos\phi \\ \sin\theta & \sin\phi \\ \cos\theta & \end{cases}$$

where

$$\gamma_{1s} = 10.6259$$

and

$$\gamma_{2s} = 3.2857$$

$$\gamma_{2p} = 3.4009 \qquad \text{........(VI.21)}$$

The above functions are not all mutually orthogonal. However, in order to maintain the orthogonality property of the true core eigenfunctions, all the overlap integrals between the above functions are set equal to zero.

The restriction of a fixed core may be considered as the initial step in a self-consistent field procedure where the valence and core orbitals are alternatively optimized in the presence of a ' frozen ' form of the other. However, in view of the fact that the core functions of the polyatomic system are essentially unchanged from those of the constituent atoms and, furthermore, that Slater orbitals do give fairly good representations of atomic functions, such an SCF procedure is expected to produce mixing of the functions given in equation (VI.21) essentially because of their non-orthogonality. This will cause a renormalization of the charge-density of the core near the nuclei but will not seriously affect those properties which depend mainly upon the densities in the internuclear regions; for example, calculation of energy. The valence states will be affected mainly because of the additional flexibility introduced into any trial wavefunction by allowing mixing with the core functions.

2.) Valence Orbitals.

The trial functions for the valence states were chosen as some linear combination of Slater orbitals, hereafter referred to as basis functions, with principal quantum number, $n = 3$. These basis functions are defined by the following equations:

$$\chi^{s}_{3lms}(x) = R_3(\gamma, r) \sqrt{\frac{(2l+1)(l-|m|)!}{2\pi\,(l+|m|)!}} \; P_l^{|m|}(\cos\theta)\, f(s, |m|\phi) \qquad \text{........(VI.22)}$$

where

$$R_3(\gamma, r) = (6!)^{-1/2}\,(2\gamma)^{7/2}\, r^2 \exp(-\gamma r)$$

and

$$f(s, |m|\phi) = \begin{cases} 1 & s=0 \\ \cos|m|\phi & s=1 \\ \sin|m|\phi & s=2 \end{cases}$$

The quantitative investigation of the clusters of sodium atoms made in this research may be separated into two sections as follows:

1.) Minimal Basis Calculation.

Only one basis function ($n = 3;\ l = m = s = 0$) per atomic centre was used in determining the many-electron determinantal functions suitable to represent states of the molecular system in either the Valence Bond or Molecular Orbital approximations. A Configuration Interaction treatment was also made for some of the states studied.

2.) Extended Basis Calculation.

Here, the number of basis functions may be increased by using either

a.) two Slater 3s-orbitals, with distinct exponents, per atomic centre; or

b.) Slater 3s- and 3p-orbitals centred on each atom of the cluster. The exponent of the 3p-functions was chosen equal to that of the 3s-functions, this restriction being imposed for mathematical convenience only. The method of choosing the exponent will be described presently.

The latter procedure may be expected to be of greater value, at this level of approximation, in determining stable configurations of the aggregates investigated mainly because of the spatial properties of the p-functions. Furthermore, these functions are expected to play an important role in describing the correlation of the valence electrons (Slater (1968); Shull (1970); Roach et. al. (1970)), as they permit a better description of both the directional and lateral movement of the electronic charge during the formation of the cluster.

An alternative method of representing such polarization effects, without at the same time increasing the size of the basis set as above, has recently been used by Poshusta and Zetik (1973).

Model Parameters And Basis Function Exponents.

The parameters occurring in the model Hamiltonian of equation (VI.4) were determined from an investigation of the valence states of the sodium atom. The wavefunctions for these states were represented by double-zeta basis expansions (Richardson (1961); Clementi (1964)):

$$\psi_{nlms}(\underline{r}) = \sum_{p=1}^{2} c_p \, \chi^{S}_{nlms}(\gamma_p, \underline{r}) \qquad (n = 3) \qquad \text{........(VI.23)}$$

where $\chi^{S}_{nlms}(\gamma_p, \underline{r})$ is as defined in equation (VI.22).

Using the model Hamiltonian for the atom:

$$h_m^{atom}(i) = -\nabla_i^2/2 - Z_\alpha/r_{\alpha i} + \sum_c \int |\psi_c^\alpha(j)|^2 r_{ij}^{-1} \, d\underline{\tau}_j + a|\psi_{2s}^\alpha(i)\rangle\langle\psi_{2s}^\alpha(j)| + b \sum_{k=x,y,z} |\psi_{2p_k}^\alpha(i)\rangle\langle\psi_{2p_k}^\alpha(j)| \qquad \text{........(VI.24)}$$

where the core functions are represented by the orbitals of equation (VI.21), variational calculations were then performed for various values of the parameters (a , b) and (γ_1 , γ_2).

For given values of the above sets of parameters, the variational procedure leads to two secular equations; one for s-states and one for p-states. In this approximation, each p-state remains threefold degenerate. The secular equations were solved for various sets of parameters until the energy level term values of the $^2S_{1/2}$ and $^2P_{1/2,3/2}$ were reproduced to a sufficient degree of accuracy; the term values are given in Table II of the article by Szasz (1968).

The optimized parameters were found to be as follows:

	a = 1.648 a.u.	b = 2.069 a.u.
3s:	$\gamma_1 = 1.239$	$\gamma_2 = 0.756$
3p:	$\gamma_1 = 1.191$	$\gamma_2 = 0.591$

........(VI.25)

With the above choice of model operator for the atomic system, the 3s-atomic wavefunction was then represented by a single-zeta expansion. A variational calculation was performed in order to determine the optimum exponent of such an expansion. The results obtained were as follows:

3s:
$$\gamma_{opt.} = 0.9$$
$$\mathcal{E}(3s) = -0.1872 \text{ a.u.} \qquad ....(VI.26)$$

For comparison, the experimental value of the 3s-atomic level is given by

$$\mathcal{E}_{expt.}(3s) = -0.188943 \text{ a.u.}$$

In the investigation of molecular systems, it would have been most desirable to consider the exponent of the basis functions as a function of

1.) the particular molecule being investigated (a molecule is here specified by the number of constituent atoms as well as by its configuration); and
2.) the particular molecular state being studied.

Time, however, did not permit such an elaborate calculation. Instead, the ' molecular environment optimized ' Slater orbital, determined from the study of the ground state of the diatomic molecule in the Minimal Basis calculation, was used throughout.

In determining the optimized basis function exponent for the ground state of the dimer, the energy, $E_{elec.}$, of the valence electrons was considered as a function of the orbital exponent, γ . Furthermore, γ was treated as a function of the internuclear separation, R . The optimized value of γ , for a given value of R , was then obtained by minimizing $E_{elec.}$(R) with respect to γ . A table of $\gamma_{opt.}$(R) against R was then constructed.

There is no guarantee that the exponents $\gamma_{opt.}$(R) are truly optimal. In fact, there is no benefit gained by expending too much effort and time in determining them, in view of the approximate nature of the calculations. Moreover, an optimal exponent for a particular level of description, for example, the Molecular Orbital formalism, is not necessarily optimal for other levels, for example, Configuration Interaction, although the importance of the orbital exponent in this case decreases as the length of the series expansion (equation (IV.5)) increases (Shull et. al. (1959)). However, the variational procedure outlined above was necessary in order to obtain any binding in the analysis of the diatomic molecule (see Chapter VII).

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CHAPTER VII.

GROUP THEORETICAL ANALYSIS AND COMPUTATIONAL RESULTS.

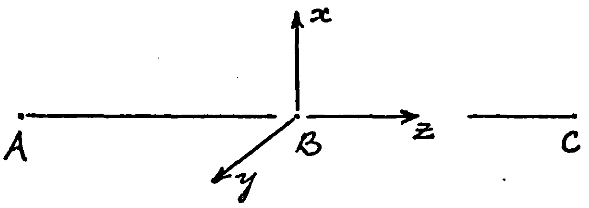
In this and the following chapter, the structural properties of various isomers for clusters consisting of up to nine univalent atoms are investigated. The analysis is within the independent-particle model discussed earlier in Chapter IV.

As pointed out by Shull (1970) and Burden and Wilson (1972), the success of numerical calculations in which the ground states, in particular, of relatively simple many-electron systems are represented by properly scaled functions of ' Molecular Orbital ' form implies that such approximations contain the essential characteristics of the average electronic distributions in these systems. Use of a small basis set for the investigation of an aggregate of atoms may be expected, therefore, to provide a meaningful picture of the charge distribution in the state of the system being investigated, although producing a rather poor description of its energy. This picture of the charge density, in conjunction with the Hellmann-Feynman theorem, is particularly useful in a qualitative discussion of the relative stability of various isomeric forms for a given cluster of atoms.

In the present chapter, a qualitative investigation is made of the symmetry and spatial properties of the charge distribution in the ground states of possible isomers for clusters of univalent atoms. Employing the LCAO-MO formalism with the s-type, or s- and p-type, atomic valence orbitals centred on each nucleus as basis functions, the gross features and relative energies of the molecular orbitals for an aggregate, of given size and shape, may be derived from simple symmetry arguments, the occurrence of nodal planes and surfaces and their resultant charge distributions, if occupied. Subsequent use of the aufbau prinzip then provides a qualitative description of the total charge distribution; its symmetry is determined by the direct product of the symmetries of the singly-occupied spin-orbitals (Chapter III).

On the same level of approximation, expressions for the energies of the ground states of some of the clusters studied are derived in the Valence Bond and the semi-empirical Diatomics-In-Molecules formalisms. Where possible, these expressions are used in determining the most stable isomeric form for a cluster of given size.

<u>The Trimer</u>: Linear Symmetric Configuration.



Such a configuration belongs to the $\mathcal{D}_{\infty h}$-point group. However, only the subgroup, consisting of sixteen operations, which is isomorphous to the $\mathcal{D}_{4h}$-point group need be considered here. This follows since the operations of the subgroup are adequate for classifying all the states of the system which can be investigated using the restricted basis of s- and p-atomic functions.

The sixteen operations are

1. Identity operation.

2 and 3. Rotations of $\pi/2$ and $3\pi/2$ about the z-axis.

4. Rotation of π about the z-axis.

5 and 6. Reflections in the two σ_d-planes: $y = \pm x$.

7 and 8. Reflections in the xz- and yz-planes.

9. Reflection in the molecular midpoint, B.

10. Reflection in the xy-plane.

11 and 12. Rotations of $\pi/2$ and $3\pi/2$ about the z-axis, each followed by a reflection in the xy-plane.

13 and 14. Rotations of π about the x- and y-axes.

15 and 16. Rotations of π about axes parallel to the σ_d-planes, each followed by a reflection in the xy-plane.

Molecular Orbital Description.

Using the projection operator techniques described in Chapter III, and the Character Table (Table (VII.1)) for the $\mathcal{D}_{4h}$-point group, the symmetry orbitals for the system are as follows:

Σ_g^+ : ($s_a + s_c$), s_b, ($z_a - z_c$)
Σ_u^+ : ($s_a - s_c$), ($z_a + z_c$), z_b
Π_g : ($x_a - x_c$)/($y_a - y_c$)
Π_u : ($x_a + x_c$)/($y_a + y_c$), x_b/y_b ....(VII.1)

The notation in the first column specifies particular irreducible representations of the $\mathcal{D}_{\infty h}$-point group.

The molecular orbitals of the system are then given by linear combinations of the above symmetry orbitals, the coefficients being determined by the self-consistent field procedure outlined in Chapters IV and X. The only exceptions to this are the π_g-orbitals, which are determined uniquely by symmetry in this treatment.

Qualitative arguments indicate that, when the system is in its ground state, the lowest-energy σ_g - and σ_u-molecular orbitals will be doubly- and singly-occupied, respectively. This follows since electrons in these states (see Figure (VII.1)) have the largest probabilities of being in those regions between the nuclei where the potential energy is lowest. Furthermore, using the spatial variation of an orbital function as an indication of the size of the kinetic energy of an electron occupying that orbital, it follows that the above states will have the lowest kinetic energies and, hence, be the two most stable for the system.

The ground state of the system will therefore have ${}^2\Sigma_u^+$-symmetry.

Table (VII·1).

Irred. Repr^{n}	Symmetry Operations 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
$^*\Sigma_g^+$ A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$^*\Sigma_u^-$ A_{1u}	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1
$^*\Sigma_g^-$ A_{2g}	1	1	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1
$^*\Sigma_u^+$ A_{2u}	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1
B_{1g}	1	-1	-1	1	-1	-1	1	1	1	1	-1	-1	1	1	-1	-1
B_{1u}	1	-1	-1	1	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1
B_{2g}	1	-1	-1	1	1	1	-1	-1	1	1	-1	-1	-1	-1	1	1
B_{2u}	1	-1	-1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1
$^*\Pi_g$ E_g	2	0	0	-2	0	0	0	0	2	-2	0	0	0	0	0	0
$^*\Pi_u$ E_u	2	0	0	-2	0	0	0	0	-2	2	0	0	0	0	0	0

The Character Table For The Symmetry Point Group D_{4h}.

[taken from Jaffé H.H. and Orchin M. (1965) Symmetry In Chemistry, Appendix 1, Wiley and Sons, Inc., New York.]

* The corresponding representation of the $D_{\infty h}$-point group.

Valence Bond Description.

Employing the Minimal Basis set of functions, it is possible to construct nine Slater determinantal functions for the system, each of which is an eigenfunction of the spin-operator, S_z , with eigenvalue given by m = 0.5 (in atomic units, $\hbar = 1$). These are as follows:

$$\begin{array}{lll}
\Phi_1 = 6^{-1/2}(\overset{+}{s}_a\overset{+}{s}_b\overset{-}{s}_c) & \Phi_4 = 6^{-1/2}(\overset{+}{s}_a\overset{+}{s}_b\overset{-}{s}_a) & \Phi_7 = 6^{-1/2}(\overset{+}{s}_b\overset{+}{s}_c\overset{-}{s}_b) \\
\Phi_2 = 6^{-1/2}(\overset{+}{s}_a\overset{+}{s}_c\overset{-}{s}_c) & \Phi_5 = 6^{-1/2}(\overset{+}{s}_a\overset{+}{s}_b\overset{-}{s}_b) & \Phi_8 = 6^{-1/2}(\overset{+}{s}_b\overset{+}{s}_c\overset{-}{s}_c) \\
\Phi_3 = 6^{-1/2}(\overset{+}{s}_a\overset{+}{s}_c\overset{-}{s}_a) & \Phi_6 = 6^{-1/2}(\overset{+}{s}_b\overset{+}{s}_c\overset{-}{s}_a) & \Phi_9 = 6^{-1/2}(\overset{+}{s}_a\overset{+}{s}_c\overset{-}{s}_b)
\end{array} \qquad \text{........(VII.2)}$$

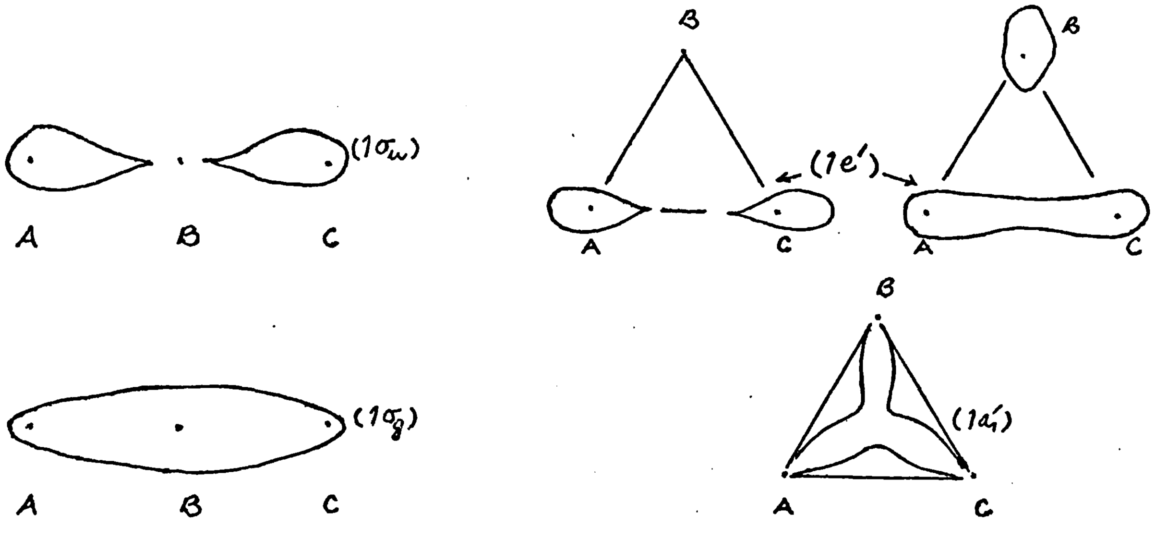
Of the above functions, Φ_1 , Φ_6 and Φ_9 are hereafter referred to as Heitler-London type functions.

It is possible to form linear combinations of the above functions which are eigenfunctions of the total spin-operator and which belong to some irreducible representation of the point group for the configuration (Chapter III). In particular, the symmetry-adapted functions formed from the Heitler-London type functions are:

$$\begin{array}{ll}
{}^2\Sigma_g^+ , & (\Phi_1 - \Phi_6) \\
{}^2\Sigma_u^+ , & (\Phi_1 + \Phi_6 + 2\,\Phi_9)
\end{array} \qquad \text{........(VII.3)}$$

Expressions for the energy of the ${}^2\Sigma_u^+$-state are given later.

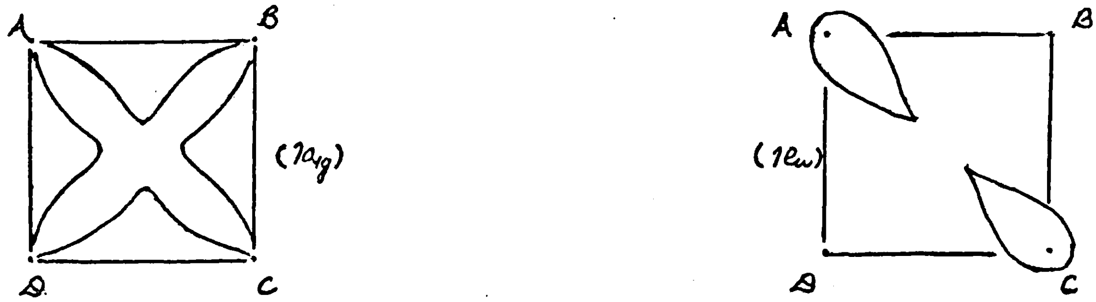
Figure (VII.1)



(i) (ii)

Schematic representations of the charge distribution arising from each of the occupied molecular orbitals for the linear (i) and equilateral triangular (ii) configurations for the Triatomic System.

Figure (VII.2)



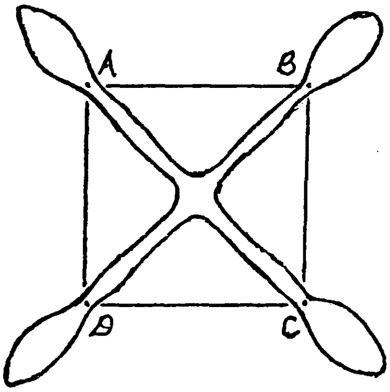
Pictorial descriptions of the charge distributions in the occupied a_{1g}- and e_u- states for the Square. The charge distribution of the second member of the doubly-degenerate e_u-level is similar to the one shown but oriented along other diagonal.

Irred. Repr^n.	Symmetry Operations. 1	2	3	4	5	6	7	8	9	10	11	12
A_1'	1	1	1	1	1	1	1	1	1	1	1	1
A_1''	1	1	1	−1	−1	−1	−1	1	1	1	−1	−1
A_2'	1	1	1	−1	−1	−1	1	−1	−1	−1	1	1
A_2''	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1
E'	2	−1	−1	0	0	0	2	0	0	0	−1	−1
E''	2	−1	−1	0	0	0	−2	0	0	0	1	1

The Character Table For The D_{3h}- Point Group.

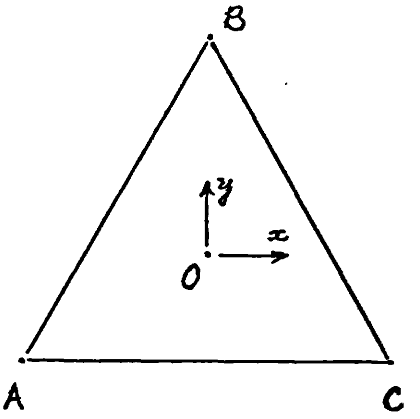
Table (VII.2).

Figure (VII.3)



A schematic representation of the charge distribution in the excited a_{1g}- orbital.

The Trimer: Equilateral Triangular Configuration.



In this case, the configuration belongs to the $\mathcal{D}_{3h}$ -point group. The twelve symmetry operations of this group are as follows:

1. Identity operation.

2 and 3. Rotations of $2\pi/3$ and $4\pi/3$ about the principal axis.

4, 5 and 6. Reflections in the three σ_v -planes.

7. Reflection in the σ_h -plane.

8, 9 and 10. Rotations about the three two-fold axes.

11 and 12. Rotations of $2\pi/3$ and $4\pi/3$ about the principal axis, each followed by a reflection in the σ_h -plane.

The Character Table for the group is given in Table (VII.2).

Molecular Orbital Description.

The symmetry orbitals for the system are

A_1' : $(s_a + s_b + s_c), (\sqrt{3}\, x_a + y_a - 2y_b - \sqrt{3}\, x_c + y_c)$

A_2' : $(x_a - \sqrt{3}\, y_a - 2x_b + x_c + \sqrt{3}\, y_c)$

A_2'' : $(z_a + z_b + z_c)$

E' : $(s_a - s_c)/(s_a - 2s_b + s_c), (x_a + x_b + x_c)/$
$(y_a + y_b + y_c), (x_a + \sqrt{3}\, y_a - 2x_b + x_c - \sqrt{3}\, y_c)/$
$(\sqrt{3}\, x_a - y_a + 2y_b - \sqrt{3}\, x_c - y_c)$

E'': $(z_a - z_c)/(z_a - 2z_b + z_c)$ ....(VII.4)

A qualitative analysis of the relative energies of the molecular orbitals of the system and the subsequent use of the aufbau prinzip indicates that the ground state is given mainly by the electronic configuration $(1a_1')^2(1e')^1$ and, therefore, has symmetry $^2E'$. According to a general theorem of Jahn and Teller (Chapter II), this state is unstable with respect to the doubly-degenerate E'-type distortions which remove its orbital degeneracy. Further discussion of the Jahn-Teller instability is given in Chapter VIII.

Valence Bond Description.

Using the Heitler-London type functions of equation (VII.2), the symmetry-adapted functions for the system are

$$^4A_2':\quad \Phi_1 + \Phi_6 - \Phi_9$$
$$^2E':\quad (\Phi_1 + \Phi_6 + 2\Phi_9)/(\Phi_1 - \Phi_6) \qquad \text{....(VII.5)}$$

From equations (VII.3) and (VII.5), the energies of the ground states of the linear symmetric and equilateral triangular systems are given by

Heitler-London Approximation:

$$\begin{aligned} E_{elec.}(^2\Sigma_u^+(linear)) = \;& (1 + S_{ab}^2 - S_{ac}^2 - S_{ab}^2S_{ac})^{-1}((2 + S_{ab}^2)< s_a| h_m| s_a> + 2< s_as_a \mid s_bs_b > \\ & + 2S_{ab}(1 - S_{ac})< s_a| h_m| s_b > - (S_{ab}^2 + 2S_{ac})< s_a| h_m| s_c > \\ & + (1 - S_{ac}^2)< s_b| h_m| s_b > + < s_as_a \mid s_cs_c > + < s_as_b \mid s_as_b > \\ & + 2S_{ab}< s_as_a \mid s_bs_c > - 2S_{ab}< s_as_b \mid s_as_c > - < s_as_c \mid s_as_c > \\ & - S_{ac}< s_as_b \mid s_bs_c > - 2S_{ac}< s_as_c \mid s_bs_b >) \end{aligned}$$

$$\begin{aligned} E_{elec.}(^2E'(triangular)) = \;& 3(1 - S_{ab}^3)^{-1}(< s_a| h_m| s_a > - S_{ab}^2< s_a| h_m| s_b > \\ & + < s_as_a \mid s_bs_b > - S_{ab}< s_as_b \mid s_as_c >) \end{aligned} \qquad \text{........(VII.6)}$$

Diatomics-In-Molecules Approximation:

$$\begin{aligned} E_{elec.}(^2\Sigma_u^+(linear)) = \;& 0.5(E_{elec.}(^3\Sigma_u^+; R_{ab}) + 2\,E_{elec.}(^3\Sigma_u^+; 2R_{ab}) \\ & + 3\,E_{elec.}(^1\Sigma_g^+; R_{ab}) - 6\,E_{at.}) \end{aligned}$$

$$E_{elec.}({}^2E'(\text{triangular})) = 0.5(\,3\,E_{elec.}({}^3\Sigma_u^+;R_{ab}) + 3\,E_{elec.}({}^1\Sigma_g^+;R_{ab}) - 6\,\varepsilon_{at.}) \quad \text{........(VII.7)}$$

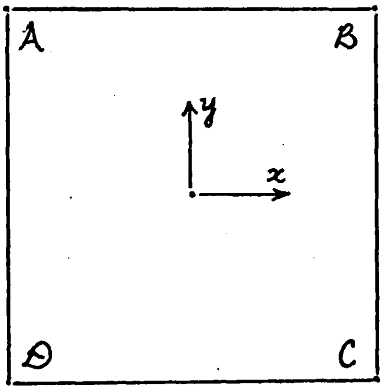
where $E_{elec.}({}^1\Sigma_g^+;R_{ab})$ and $E_{elec.}({}^3\Sigma_u^+;R_{ab})$ are, respectively, the energies, in the Valence Bond Description, of the valence electrons in the ground and first triplet states of the dimer, measured as a function of the internuclear separation, R_{ab}. $\varepsilon_{at.}$ is the valence electron energy in an isolated atom (equation (VI.26)).

The energy expressions of equation (VII.6) are derived in the appendix following this chapter.

Finally, from equation (VII.7), it is expected that the linear structure will be the more stable form for the trimer.

The Quadramer: Square Configuration.

In this section, the square configuration for the tetra-atomic cluster is investigated.



This structure belongs to the D_{4h}-point group. The sixteen operations have already been discussed during the study of the linear form for the triatomic system and the Character Table is given in Table (VII.1).

Molecular Orbital Description.

The symmetry orbitals for the aggregate are as follows:

A_{1g}: $(\, s_a + s_b + s_c + s_d \,)$, $(\, x_a - y_a - x_b - y_b - x_c + y_c + x_d + y_d \,)$

$$\begin{aligned}
A_{2u}&: \ (z_a + z_b + z_c + z_d) \\
A_{2g}&: \ (x_a + y_a + x_b - y_b - x_c - y_c - x_d + y_d) \\
B_{1g}&: \ (s_a - s_b + s_c - s_d),\ (x_a - y_a + x_b + y_b - x_c + y_c - x_d - y_d) \\
B_{1u}&: \ (z_a - z_b + z_c - z_d) \\
B_{2g}&: \ (x_a + y_a - x_b + y_b - x_c - y_c + x_d - y_d) \\
E_g&: \ (z_a - z_b - z_c + z_d) / (z_a + z_b - z_c - z_d) \\
E_u&: \ (s_a - s_b - s_c + s_d) / (s_a + s_b - s_c - s_d), \\
&\quad (x_a + x_b + x_c + x_d) / (y_a + y_b + y_c + y_d), \\
&\quad (y_a - y_b + y_c - y_d) / (x_a - x_b + x_c - x_d)
\end{aligned} \qquad \text{........(VII.8)}$$

Using the above basis set, therefore, all the one-electron states of the system, except those of a_{1u}- and b_{2u}-symmetry, may be studied. However, in the Minimal Basis calculation, only those with a_{1g}-, b_{1g}- and e_u-symmetry can be investigated.

A qualitative analysis of the charge distribution in each of the molecular orbitals of the system, formed as usual by suitable linear combinations of the above symmetry orbitals, suggests the following one-electron energy level scheme:

$$1a_{1g} < 1e_{\mu} < 1b_{1g} \lesssim 2a_{1g} < \text{........}$$

This scheme was derived by using the following qualitative argument:

a_{1g}-orbitals: There are two orbitals of this symmetry type. The most stable one will be composed mainly of s-type atomic functions. It will correspond to a build-up of electronic charge in the region between the nuclei where the potential energy is lowest (Figure (VII.2)). Furthermore, its relatively smooth spatial variation, as compared to the other molecular orbitals, indicates a lower kinetic energy and, hence, a lower orbital energy.

On the other hand, the second a_{1g}-orbital will have a large p-type component and correspond essentially to four hybrid lone-pairs situated on each atom as shown schematically in Figure (VII.3). This orbital will therefore be expected to have an orbital energy which is rather close to, but slightly less than, that of the p-level in the free atom.

e_{μ}-orbitals: The most stable orbitals of this symmetry type will again be composed mainly of s-type atomic functions, but, in addition, each will possess one nodal plane (Figure (VII.2)). The degeneracy of this state permits two distinct, but equally valid, descriptions of the nodal plane in each orbital. It may either coincide with a diagonal of the square or perpendicularly bisect a pair of parallel sides.

The presence of the nodal planes results in these orbitals having an increased kinetic energy relative to the first a_{1g}-orbital as well as less charge in the low-potential regions. However, they will be more stable than the second a_{1g}-orbital because of their larger component of s-type functions and greater concentration of charge in the internuclear regions.

The above arguments were repeated to determine the relative energies of some of the other orbitals.

The usual aufbau prinzip then indicates that the ground state of the system has ${}^3A_{2g}$-symmetry and is, therefore, paramagnetic. It is also very weakly Jahn-Teller active owing to its spin-degeneracy.

Valence Bond Description.

Employing one s-type function centred on each nucleus of the tetra-atomic system, it is possible to construct six Heitler-London type functions. These are

$$\Phi_1 = 24^{-1/2}(s_a^+ s_b^+ s_c^- s_d^-) \qquad \Phi_2 = 24^{-1/2}(s_a^+ s_c^+ s_b^- s_d^-) \qquad \Phi_3 = 24^{-1/2}(s_a^+ s_d^+ s_b^- s_c^-)$$

$$\Phi_4 = 24^{-1/2}(s_b^+ s_c^+ s_a^- s_d^-) \qquad \Phi_5 = 24^{-1/2}(s_b^+ s_d^+ s_a^- s_c^-) \qquad \Phi_6 = 24^{-1/2}(s_c^+ s_d^+ s_a^- s_b^-).$$

........(VII.9)

From these it is then possible to determine the symmetry-adapted determinantal functions for the square. These are as follows:

$$\begin{aligned}
&{}^5B_{2g}:\ (\Phi_1 - \Phi_2 + \Phi_3 + \Phi_4 - \Phi_5 + \Phi_6)\\
&{}^3A_{2g}:\ (\Phi_2 - \Phi_5)\\
&{}^3E_u:\ (\Phi_3 - \Phi_4)/(\Phi_1 - \Phi_6)\\
&{}^1A_{1g}:\ (\Phi_1 - \Phi_3 - \Phi_4 + \Phi_6)\\
&{}^1B_{2g}:\ (\Phi_1 + 2\Phi_2 + \Phi_3 + \Phi_4 + 2\Phi_5 + \Phi_6)
\end{aligned}$$

........(VII.10)

The energy of the ground state is then given by

Heitler-London Approximation:

$$\begin{aligned}
E_{elec.}({}^3A_{2g}) = {}&\\
&(1 - S_{ac}^2)^{-2}\big(4(1 - S_{ac}^2)(< s_a| h_m| s_a > - S_{ac}< s_a| h_m| s_c >)\\
&+ 4(< s_a s_a \mid s_b s_b > - S_{ab}^2 < s_a s_b \mid s_a s_b >) - 8S_{ac} < s_a s_a \mid s_b s_d >\\
&+ 2(1 - S_{ac}^2)(< s_a s_a \mid s_c s_c > - < s_a s_c \mid s_a s_c >) + 8S_{ab}^2 < s_a s_b \mid s_a s_d >\\
&- 4S_{ab}^2 < s_a s_b \mid s_c s_d > + 4S_{ac}^2 < s_a s_c \mid s_b s_d > \big)
\end{aligned}$$

........(VII.11)

Diatomics-In-Molecules Approximation:

$$\begin{aligned}
E_{elec.}({}^3A_{2g}) = {}& 2\, E_{elec.}({}^1\Sigma_g^+; R_{ab}) + 2\, E_{elec.}({}^3\Sigma_u^+; R_{ab})\\
&+ 2\, E_{elec.}({}^3\Sigma_u^+; \sqrt{2}R_{ab}) - 8\, \varepsilon_{at.}
\end{aligned}$$

........(VII.12)

All quantities are as defined previously during the study of the trimer or are explained in the appendix where the derivation of equation (VII.12) is also given.

It is interesting to note that, in the Diatomics-In-Molecules theory, the symmetry of the ground state for the square is ${}^1B_{2g}$, with energy given by (cf. equation (VII.12))

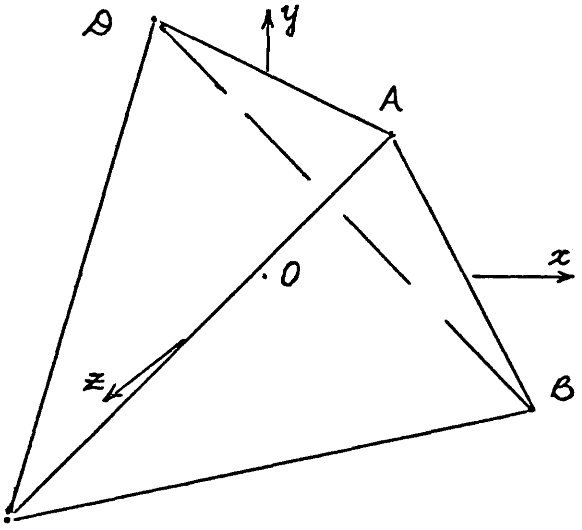
$$\begin{aligned}
E_{elec.}({}^1B_{2g}) = {}& 3\, E_{elec.}({}^1\Sigma_g^+; R_{ab}) + E_{elec.}({}^3\Sigma_u^+; R_{ab})\\
&+ 2\, E_{elec.}({}^3\Sigma_u^+; \sqrt{2}R_{ab}) - 8\, \varepsilon_{at.}
\end{aligned}$$

In the simple Molecular Orbital theory, the ${}^1B_{2g}$- and ${}^3A_{2g}$-states have the same orbital configuration:

${}^1B_{2g}$, $(1a_{1g})^2(1e_u)^2$, antiparallel spins in unfilled degenerate level;

$^3A_{2g}$, $(1a_{1g})^2(1e_{u})^2$, parallel spins in unfilled degenerate level. Their relative stability depends solely upon the nature of the exchange interaction in the half-filled degenerate state. Results of calculations performed using a Minimal Basis set confirm that the $^3A_{2g}$-state is the more stable. Moreover, this is in accord with experience and suggests that the present conclusions of the DIM theory are erroneous.

The Quadramer: Tetrahedral Configuration.



Such a structure belongs to the T_d-point group. The twenty-four symmetry operations are

1. Identity operation.

2,3 and 4. Rotations of π about the x-, y- and z-axes.

5, ... 8. Rotations of $2\pi/3$ in a positive direction about the axes OA, OB, OC and OD. <u>OA</u>, <u>OB</u>, etc., denote positive directions.

9, ... 12. Rotations of $4\pi/3$ in the same sense about the same four three-fold axes.

13,14, .. 18. Rotations of $\pi/2$ and $3\pi/2$ about the x-, y- and z-axes, each followed by an inversion in the origin.

19,20, .. 24. Reflections in the six σ_d-planes:
$x = \pm y$, $x = \pm z$, and $y = \pm z$.

Molecular Orbital Description.

Using the projection operator techniques discussed earlier in Chapter III and the Character Table for the T_d -point group (Jaffé and Orchin (1965)), the symmetry orbitals for the system are as follows:

$$\begin{aligned}
A_1 :&\quad (s_a + s_b + s_c + s_d), \\
&\quad (x_a + y_a + z_a + x_b - y_b - z_b - x_c - y_c + z_c - x_d + y_d - z_d) \\
E :&\quad (2x_a - y_a - z_a + 2x_b + y_b + z_b - 2x_c + y_c - z_c - 2x_d - y_d + z_d)/ \\
&\quad (y_a - z_a - y_b + z_b - y_c - z_c + y_d + z_d) \\
T_1 :&\quad (- y_a + z_a + y_b - z_b - y_c - z_c + y_d + z_d)/ \\
&\quad (x_a - z_a - x_b - z_b + x_c + z_c - x_d + z_d)/ \\
&\quad (- x_a + y_a + x_b + y_b + x_c - y_c - x_d - y_d) \\
T_2 :&\quad (s_a + s_b - s_c - s_d)/(s_a - s_b - s_c + s_d)/(s_a - s_b + s_c - s_d), \\
&\quad (x_a + x_b + x_c + x_d)/(y_a + y_b + y_c + y_d)/(z_a + z_b + z_c + z_d), \\
&\quad (y_a + z_a - y_b - z_b + y_c - z_c - y_d + z_d)/ \\
&\quad (x_a + z_a - x_b + z_b + x_c - z_c - x_d - z_d)/ \\
&\quad (x_a + y_a - x_b + y_b - x_c - y_c + x_d - y_d)
\end{aligned} \qquad \text{........(VII.13)}$$

In this approximation, therefore, all the one-electron states of the system, except those of a_2 -symmetry, may be investigated. Furthermore, the molecular orbitals of e - and t_1 -symmetry type are determined uniquely by symmetry.

A qualitative analysis, similar to that described earlier when studying the square configuration, indicates that the one-electron energy level scheme will be

$$1a_1 < 1t_2 < \;........$$

Thus, the most stable molecular state will have $^3T_1$ -symmetry and will, therefore, be unstable with respect to the degenerate E - and T_2 -type distortions. The cause of this instability is related to the charge distribution in the partially filled triply-degenerate $1t_2$ -level (Figure (VII.4)), as explained later in Chapter VIII.

Valence Bond Description.

Using the Slater determinants defined earlier in equation (VII.9), the symmetry-adapted functions for the tetrahedral system are

$$
\begin{aligned}
&{}^5A_2, \quad (\Phi_1 - \Phi_2 + \Phi_3 + \Phi_4 - \Phi_5 + \Phi_6) \\
&{}^1E, \quad (\Phi_2 + \Phi_3 + \Phi_4 + \Phi_5)/(2\Phi_1 + \Phi_2 - \Phi_3 - \Phi_4 + \Phi_5 + 2\Phi_6) \\
&{}^3T_1, \quad (\Phi_1 - \Phi_6)/(\Phi_3 - \Phi_4)/(\Phi_2 - \Phi_5)
\end{aligned}
\qquad \text{........(VII.14)}
$$

The energy of the ground state is then given by

Heitler-London Approximation:

$$
\begin{aligned}
E_{elec.}({}^3T_1) = \\
&(1 - S_{ab}^2)^{-2}(\,4(1 - S_{ab}^2)(< s_a|\, h_m \,|\, s_a > - S_{ab} < s_a|\, h_m \,|\, s_b >) \\
&\quad + 2(3 - S_{ab}^2) < s_a s_a \mid s_b s_b > - 8S_{ab} < s_a s_a \mid s_b s_c > \\
&\quad - 2(1 + S_{ab}^2) < s_a s_b \mid s_a s_b > + 8S_{ab}^2 < s_a s_b \mid s_a s_c > \,)
\end{aligned}
\qquad \text{........(VII.15)}
$$

Diatomics-In-Molecules Approximation:

$$
E_{elec.}({}^3T_1) = 2\,E_{elec.}({}^1\Sigma_g^+; R_{ab}) + 4\,E_{elec.}({}^3\Sigma_u^+; R_{ab}) - 8\,\varepsilon_{at.} \qquad \text{........(VII.16)}
$$

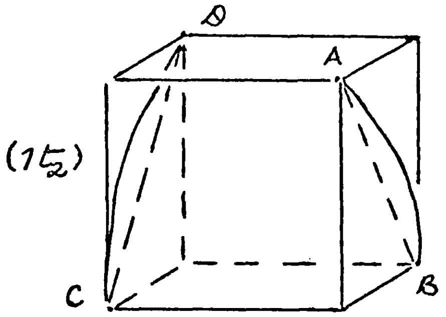
The conclusions of the Diatomics-In-Molecules theory are again in conflict with those of the simple Molecular Orbital theory. The DIM theory suggests that the symmetry of the ground state will be ${}^1E$, with the energy given by

$$
E_{elec}({}^1E) = 3\,E_{elec.}({}^1\Sigma_g^+; R_{ab}) + 3\,E_{elec.}({}^3\Sigma_u^+; R_{ab}) - 8\,\varepsilon_{at.}
$$

As mentioned before, however, it is most likely that the conclusions of the latter theory are erroneous.

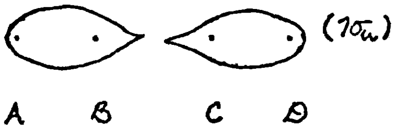
Finally, comparison of equation (VII.16) for the tetrahedron with equation (VII.12) for the square suggests that the latter is a more stable form for the tetra-atomic cluster.

Figure (VII.4)



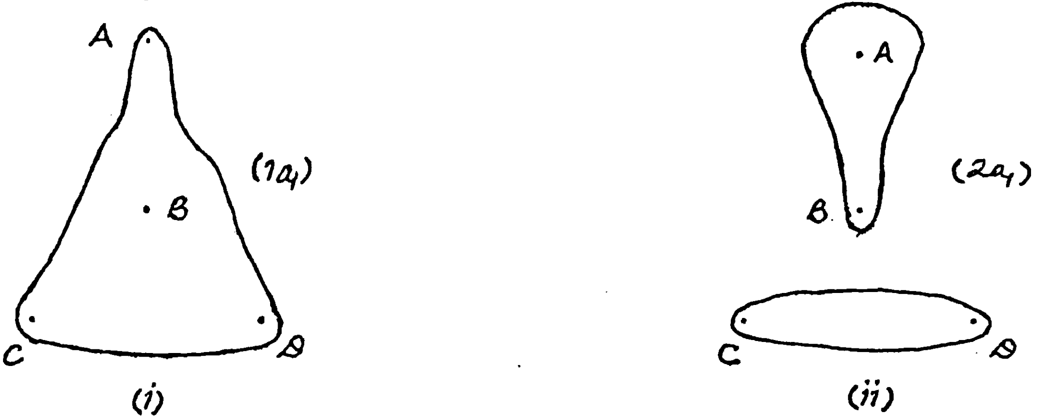
Schematic representation of the "banana"-type charge distribution in one orbital belonging to the triply-degenerate t_2-level for the tetrahedron. The charge distributions for the second and third members are similar but occur in regions AD and BC, and AC and BD, respectively.

Figure (VII.5)



Schematic representation of the charge distribution in the highest occupied molecular orbital for the linear isomer.

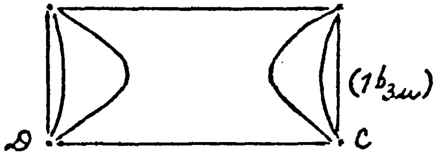
Figure (VII.6)



(i) (ii)

Pictorial descriptions arising from the lowest-energy (i) and the first-excited (ii) orbital states of the T- (or Y-) shaped structure for the tetra-atomic cluster.

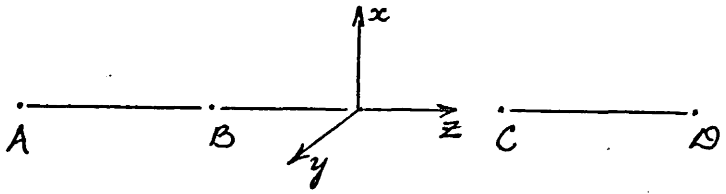
Figure (VII.7)



Pictorial description of the charge distributions for the highest occupied orbital for the rectangular configurations.

The Quadramer: Linear Configuration.

As was the case for the linear triatomic system, the above configuration belongs to the $\mathcal{D}_{\infty h}$-point group but only the $\mathcal{D}_{4h}$-subgroup of symmetry operations need be considered here.



Molecular Orbital Description.

The symmetry orbitals of the system are

Σ_g^+, $(s_a + s_d)$, $(s_b + s_c)$, $(z_a - z_d)$, $(z_b - z_c)$

Σ_u^+, $(s_a - s_d)$, $(s_b - s_c)$, $(z_a + z_d)$, $(z_b + z_c)$

Π_g : $(x_a - x_d)/(y_a - y_d)$, $(x_b - x_c)/(y_b - y_c)$

Π_u : $(x_a + x_d)/(y_a + y_d)$, $(x_b + x_c)/(y_b + y_c)$

........(VII.17)

In this case, therefore, the self-consistent field procedure outlined in Chapter IV must be used to determine all the molecular orbitals of the system.

Qualitative arguments indicate that, when the system is in its ground state, the first σ_g - and σ_u-molecular orbitals will each be doubly-occupied. The σ_g-orbital is the more stable of the two since it permits a greater build-up of charge in the low potential, internuclear regions (cf. Figure (VII.1(i))). As shown in Figure (VII.5), the σ_u-orbital allows charge build-up only in the regions AB and CD and, furthermore, the presence of the nodal plane indicates that an electron in this orbital will have a higher kinetic energy than one in the σ_g-orbital.

The above considerations suggest that the symmetry of the ground state will be ${}^1\Sigma_g^+$ and, also, that the most stable form of the linear structure will be such that $R_{ab} = R_{cd} \lesssim R_{bc}$.

Valence Bond Description.

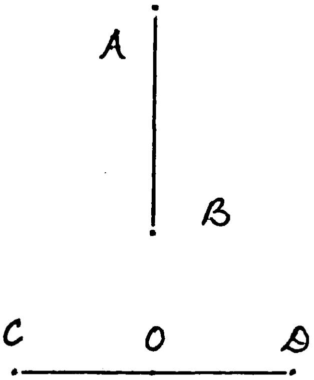
It is possible to determine linear combinations of the Slater determinants defined in equation (VII.9), which have $^1\Sigma_g^+$-symmetry. These are as follows:

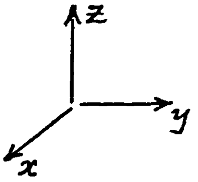
$$^1\Sigma_g^+, \quad (\Phi_2 + \Phi_3 + \Phi_4 + \Phi_5), \; (\Phi_1 - \Phi_3 - \Phi_4 + \Phi_6) \qquad \text{........(VII.18)}$$

In the language of Valence Bond theory, the first function represents electron-pair bonds between atoms A and B (A-B) and C and D (C-D), whereas the latter represents the bonds (A-C) and (B-D).

An approximate expression for the energy of the ground ($^1\Sigma_g^+$-) state is given later.

The Quadramer: T-(or Y -) Shaped Configuration.





This structure, which is shown in the above diagram, belongs to the C_{2v}-point group. The four symmetry operations of the group are

1. Identity operation.
2. Rotation of π about the principal axis.

3 and 4. Reflections in the two σ_v-planes: x = 0 and y = 0.

These operations form an Abelian group for which there is, therefore, four unidimensional irreducible representations. The Character Table may be found in the book by Jaffé and Orchin (loc. cit.).

Molecular Orbital Description.

The symmetry orbitals for the system are

$$
\begin{aligned}
A_1 &: \quad s_a,\ s_b,\ (s_c + s_d),\ (y_c - y_d),\ z_a,\ z_b,\ (z_c + z_d) \\
A_2 &: \quad (x_c - x_d) \\
B_1 &: \quad x_a,\ x_b,\ (x_c + x_d) \\
B_2 &, \quad (s_c - s_d),\ y_a,\ y_b,\ (y_c + y_d),\ (z_c - z_d)
\end{aligned}
$$

........(VII.19)

The usual qualitative arguments then indicate that the two most stable molecular orbitals will both have a_1 -symmetry properties. Their charge distributions are expected to be as shown schematically in Figure (VII.6).

It may also be concluded that the separation OB will be the result of the cancellation of the ' inter-dimeric ' repulsion forces by the ' cementation ' produced by the charge distribution of the nodeless $1a_1$ -orbital. The above repulsion arises from the nuclear forces as well as from the presence of the nodal surface of the highest occupied orbital.

Valence Bond Description.

From the Heitler-London type functions of equation (VII.9), the ground state of the system is represented by

$$ {}^1A_1 , \quad (\Phi_2 + \Phi_3 + \Phi_4 + \Phi_5) \qquad \text{........(VII.20)} $$

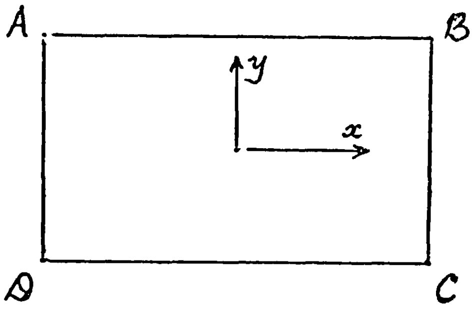
Its energy, in the Diatomics-In-Molecules theory, is then given by

$$
\begin{aligned}
E_{elec.}({}^1A_1) = 0.5(& 2E_{elec.}({}^1\Sigma_g^+; R_{ab}) + 3E_{elec.}({}^3\Sigma_u^+; R_{ac}) \\
& + E_{elec.}({}^1\Sigma_g^+; R_{ac}) + 3E_{elec.}({}^3\Sigma_u^+; R_{bc}) \\
& + E_{elec.}({}^1\Sigma_g^+; R_{bc}) + 2E_{elec.}({}^1\Sigma_g^+; R_{cd}) - 8E_{at.})
\end{aligned}
$$

........(VII.21)

The Quadramer: Rectangular Configuration.

This configuration, shown in the diagram below, belongs to the D_{2h}-point group.



The eight symmetry operations of the group are as follows:

1. Identity operation.

2. Rotation of π about the z-axis.

3 and 4. Reflections in the xz- and yz-planes.

5. Reflection in the xy-plane.

6. Reflection in the centre of symmetry.

7 and 8. Rotations of π about the x- and y-axes.

Molecular Orbital Description.

The symmetry orbitals for the system are

A_g: $(s_a + s_b + s_c + s_d)$, $(x_a - x_b - x_c + x_d)$, $(y_a + y_b - y_c - y_d)$
A_u: $(z_a - z_b + z_c - z_d)$
B_{1g}: $(s_a - s_b + s_c - s_d)$, $(x_a + x_b - x_c - x_d)$, $(y_a - y_b - y_c + y_d)$
B_{1u}: $(z_a + z_b + z_c + z_d)$
B_{2g}: $(z_a - z_b - z_c + z_d)$
B_{2u}: $(s_a + s_b - s_c - s_d)$, $(x_a - x_b + x_c - x_d)$, $(y_a + y_b + y_c + y_d)$
B_{3g}: $(z_a + z_b - z_c - z_d)$
B_{3u}: $(s_a - s_b - s_c + s_d)$, $(x_a + x_b + x_c + x_d)$, $(y_a - y_b + y_c - y_d)$

........(VII.22)

Qualitative analysis of the molecular orbitals then suggests that the orbital configuration and symmetry of the ground state will be $(1a_g)^2(1b_{3u})^2$ and ^1A_g, respectively. A schematic representation of the expected charge distribution in the $1b_{3u}$-orbital is given in Figure (VII.7).

In this, and many other cases, it has not been necessary to give pictorial descriptions of the charge distributions for all occupied states of the system being investigated. Those which have not been given may easily be deduced by comparison with previous examples. Thus, for example, the distribution in the $1a_g$-orbital is expected to correspond to a charge build-up along the diagonals of the rectangle.

Valence Bond Description.

Using the basis defined in equation (VII.9), the functions possessing the predicted symmetry properties of the ground state of the above system are

$$ {}^1A_g, \quad (\Phi_2 + \Phi_3 + \Phi_4 + \Phi_5), (\Phi_1 - \Phi_3 - \Phi_4 + \Phi_6) \qquad \text{........(VII.23)} $$

Employing the approximate Diatomics-In-Molecules theory and neglecting the atomic overlap integrals (Chapter V), the energy expressions for the ground states of the linear and rectangular systems are as follows:

$$ E_{elec.}({}^1\chi) = (A + \sqrt{B})/6 - 8\,\varepsilon_{at.} $$

For the linear configuration, $\chi = \Sigma_g^+$;

$$ \begin{aligned} A = {} & 6(E_{elec.}({}^1\Sigma_g^+; R_{ab}) + E_{elec.}({}^3\Sigma_u^+; R_{ab}) + E_{elec.}({}^1\Sigma_g^+; R_{ac}) \\ & + E_{elec.}({}^1\Sigma_g^+; R_{ac})) + 3(E_{elec.}({}^1\Sigma_g^+; R_{ad}) + E_{elec.}({}^3\Sigma_u^+; R_{ad}) \\ & + E_{elec.}({}^1\Sigma_g^+; R_{bc}) + E_{elec.}({}^3\Sigma_u^+; R_{bc})); \end{aligned} $$

$$ \begin{aligned} B = {} & 27(E_{elec.}({}^1\Sigma_g^+; R_{ab}) - E_{elec.}({}^3\Sigma_u^+; R_{ab}) - E_{elec.}({}^1\Sigma_g^+; R_{ac}) \\ & + E_{elec.}({}^3\Sigma_u^+; R_{ac}))^2 + 9(E_{elec.}({}^1\Sigma_g^+; R_{ab}) - E_{elec.}({}^3\Sigma_u^+; R_{ab}) \\ & + E_{elec.}({}^1\Sigma_g^+; R_{ac}) - E_{elec.}({}^3\Sigma_u^+; R_{ac}) - E_{elec.}({}^1\Sigma_g^+; R_{ad}) \\ & + E_{elec.}({}^3\Sigma_u^+; R_{ad}) - E_{elec.}({}^1\Sigma_g^+; R_{bc}) + E_{elec.}({}^3\Sigma_u^+; R_{bc}))^2 . \end{aligned} $$

........(VII.24)

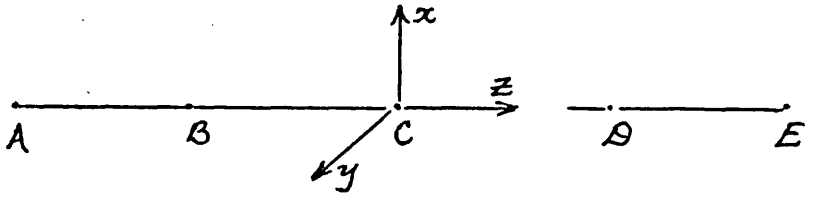
For the rectangular configuration, $\chi = A_g$;

$$A = 6(E_{elec.}(^1\Sigma_g^+; R_{ab}) + E_{elec.}(^3\Sigma_u^+; R_{ab}) + E_{elec.}(^1\Sigma_g^+; R_{ac}) + E_{elec.}(^3\Sigma_u^+; R_{ac}) + E_{elec.}(^1\Sigma_g^+; R_{ad}) + E_{elec.}(^3\Sigma_u^+; R_{ad}));$$

$$\begin{aligned} B = {} & 27(E_{elec.}(^1\Sigma_g^+; R_{ac}) - E_{elec.}(^3\Sigma_u^+; R_{ac}) - E_{elec.}(^1\Sigma_g^+; R_{ad}) + E_{elec.}(^3\Sigma_u^+; R_{ad}))^2 + 9(2 E_{elec.}(^1\Sigma_g^+; R_{ab}) - 2 E_{elec.}(^3\Sigma_u^+; R_{ab}) \\ & - E_{elec.}(^1\Sigma_g^+; R_{ac}) + E_{elec.}(^3\Sigma_u^+; R_{ac}) - E_{elec.}(^1\Sigma_g^+; R_{ad}) + E_{elec.}(^3\Sigma_u^+; R_{ad}))^2. \end{aligned}$$

........(VII.25)

The Pentamer: Linear Configuration.



The analysis of this structure is very similar to that for the linear triatomic system investigated earlier.

Molecular Orbital Description.

The symmetry orbitals for the system are as follows:

Σ_g^+, $(s_a + s_e), (s_b + s_d), s_c , (z_a - z_e), (z_b - z_d)$

Σ_u^+, $(s_a - s_e), (s_b - s_d), (z_a + z_e), (z_b + z_d), z_c$

Π_g : $(x_a - x_e)/(y_a - y_e), (x_b - x_d)/(y_b - y_d)$

Π_u : $(x_a + x_e)/(y_a + y_e), (x_b + x_d)/(y_b + y_d), x_c/y_c$

........(VII.26)

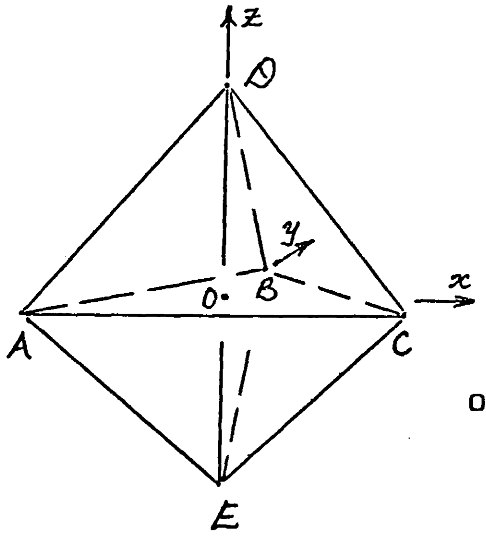
Qualitative arguments then indicate that the one-electron energy level scheme will be

$$1\sigma_g < 1\sigma_u < 2\sigma_g < \ldots\ldots ,$$

with the charge distributions in the $1\sigma_g$ - and $1\sigma_u$-orbitals being analogous to those (Figure (VII.1(i))) for the trimer. The $2\sigma_g$ - orbital possesses a nodal surface of σ_g -symmetry and is expected to correspond to the distribution shown schematically in Figure (VII.8).

The symmetry and orbital configuration of the ground state of this system are, therefore, expected to be $^2\Sigma_g^+$ and $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^1$, respectively. Also, the most stable form of the above structure will be such that $R_{ab} = R_{de} \lessgtr R_{bc} = R_{cd}$.

The Pentamer: Trigonal Bipyramid.



$OD = OE$

$\neq$ OA, etc., in general.

This configuration belongs to the D_{3h}-point group. Its twelve symmetry operations have already been discussed during the investigation of the equilateral triangular form for the trimer.

Molecular Orbital Description.

In addition to those given in equation (VII.4), the symmetry orbitals for the system are

A_1' : $(s_d + s_e), (z_d - z_e)$

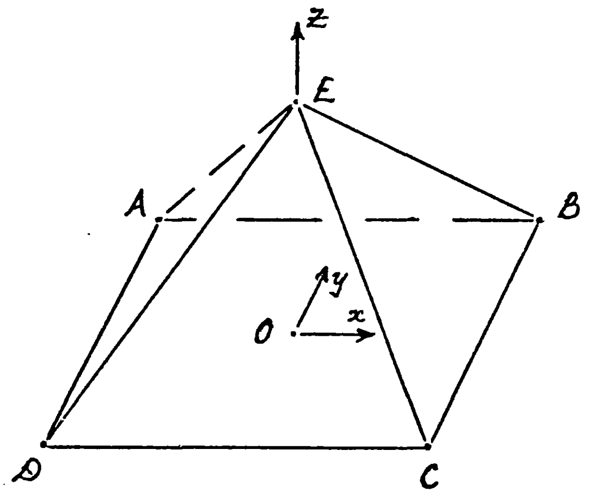
A_2'' : $(s_d - s_e), (z_d + z_e)$

E' : $(x_d + x_e)/(y_d + y_e)$

E'' : $(x_d - x_e)/(y_d - y_e)$ ....(VII.27)

Analysis of the relative stability of the molecular orbitals for the system indicates that the orbital configuration and symmetry of the ground state will be $(1a_1')^2(1e')^3$, or $(1a_1')^2(1a_2'')^2(1e')^1$, and $^2E'$, respectively. However, the expected near-degeneracy of the abovementioned orbital configurations suggests that the simple Molecular Orbital description will be inadequate and that the ground state may be better described mathematically by some combination of both configurations. In any case, the ground state will be unstable with respect to an E'-symmetry distortion.

The Pentamer: Square Pyramid.



This configuration belongs to the C_{4v}-point group. The eight symmetry operations consist of

1. Identity operation.

2 and 3. Rotations of $\pi/2$ and $3\pi/2$ about the principal axis.

4. Rotation of π about the principal axis.

5, .. 8. Reflections in the planes: x = 0, y = 0, x = ± y.

Molecular Orbital Description.

The symmetry orbitals for the system include

A_1, $(s_a + s_b + s_c + s_d)$, s_e, $(x_a - y_a - x_b - y_b - x_c + y_c + x_d + y_d)$,
$(z_a + z_b + z_c + z_d)$, z_e

A_2: $(x_a + y_a + x_b - y_b - x_c - y_c - x_d + y_d)$

B_1, $(s_a - s_b + s_c - s_d)$, $(x_a - y_a + x_b + y_b - x_c + y_c - x_d - y_d)$,
$(z_a - z_b + z_c - z_d)$

$\mathcal{B}_2$: $(x_a + y_a - x_b + y_b - x_c - y_c + x_d - y_d)$

$\mathcal{E}$: $(s_a - s_b - s_c + s_d)/(s_a + s_b - s_c - s_d)$,

$(x_a + x_b + x_c + x_d)/(y_a + y_b + y_c + y_d)$, x_e/y_e ,

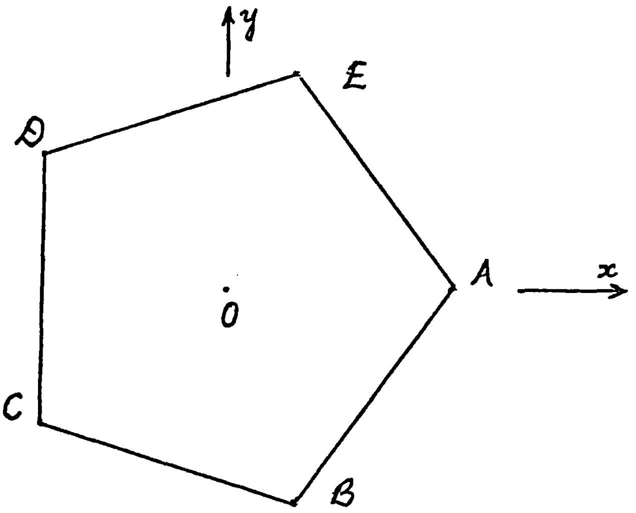
$(y_a - y_b + y_c - y_d)/(x_a - x_b + x_c - x_d)$,

$(z_a - z_b - z_c + z_d)/(z_a + z_b - z_c - z_d)$

........(VII.28)

By the usual analysis, the orbital configuration and symmetry of the ground state are expected to be $(1a_1)^2(1e)^3$ and $^2\mathcal{E}$, respectively. This state will therefore be Jahn-Teller active, being unstable with respect to the $\mathcal{B}_1$ - and $\mathcal{B}_2$ -symmetry distortions.

<u>The Pentamer:</u> Pentagonal Configuration.



This structure, shown in the above diagram, belongs to the $\mathcal{D}_{5h}$ -point group. Its twenty symmetry operations include

1. Identity operation.

2 and 3. Rotations of $2\pi/5$ and $8\pi/5$ about the principal axis.

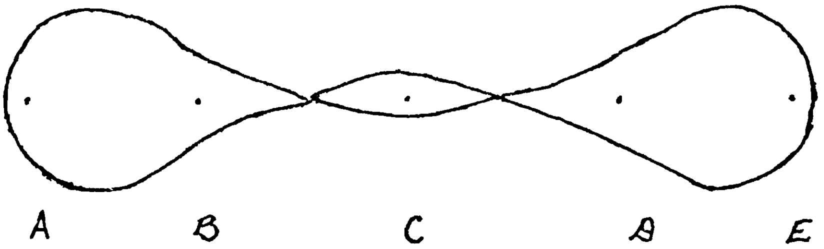
4 and 5. Rotations of $4\pi/5$ and $6\pi/5$ about the principal axis.

6, .. 10. Rotations of π about the five two-fold axes which are perpendicular to the principal axis.

11. Reflection in the σ_h-plane.

12, .. 16. Reflections in the five σ_v -planes.

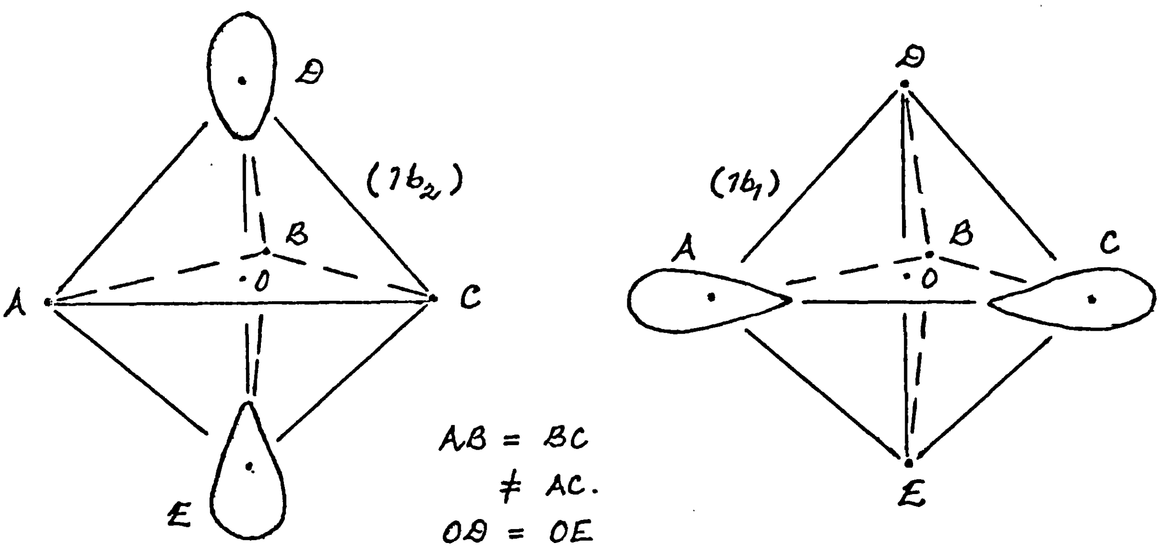
17 and 18. Rotations of $2\pi/5$ and $8\pi/5$ about the principal axis,



Charge distribution in first excited σ_g-orbital.

Figure (VII.8)

Figure (VII.9)



$AB = BC$
$\neq AC.$
$OD = OE$
$\neq OA$, etc.,
in general.

Schematic representations of the charge distributions expected in the lowest-energy b_2- and b_1- molecular orbitals. The relative stability of these orbitals depends upon the separations AC and DE. Assuming that AC is smaller than DE, the b_2-orbital is the stabler of the two.

each followed by a reflection in the σ_h-plane.

19 and 20. Rotations of $4\pi/5$ and $6\pi/5$ about the principal axis, each followed by a reflection in the σ_h-plane.

Molecular Orbital Description.

The symmetry orbitals for the system are as follows:

A_1': $(s_a + s_b + s_c + s_d + s_e)$,

$(x_a + [x_b + x_e]\cos\theta + [x_c + x_d]\cos 2\theta - [y_b - y_e]\sin\theta - [y_c - y_d]\sin 2\theta)$

A_2': $([x_b - x_e]\sin\theta + [x_c - x_d]\sin 2\theta + y_a + [y_b + y_e]\cos\theta$

$+ [y_c + y_d]\cos 2\theta)$

A_2'': $(z_a + z_b + z_c + z_d + z_e)$

E_1': $(s_a + [s_b + s_e]\cos\theta + [s_c + s_d]\cos 2\theta)/$

$([-s_b + s_e]\sin\theta + [-s_c + s_d]\sin 2\theta$

$(x_a + [x_b + x_e]\cos 2\theta + [x_c + x_d]\cos\theta - [y_b - y_e]\sin 2\theta + [y_c - y_d]\sin\theta)/$

$([x_b - x_e]\sin 2\theta - [x_c - x_d]\sin\theta + y_a + [y_b + y_e]\cos 2\theta + [y_c + y_d]\cos\theta)$,

$(x_a + x_b + x_c + x_d + x_e)/(y_a + y_b + y_c + y_d + y_e)$

E_1'': $([z_b - z_e]\sin\theta + [z_c - z_d]\sin 2\theta)/$

$(z_a + [z_b + z_e]\cos\theta + [z_c + z_d]\cos 2\theta)$

E_2': $(s_a + [s_b + s_e]\cos 2\theta + [s_c + s_d]\cos\theta)/$

$([-s_b + s_e]\sin 2\theta + [s_c - s_d]\sin\theta)$,

$(x_a + [x_b + x_e]\cos\theta + [x_c + x_d]\cos 2\theta + [y_b - y_e]\sin\theta + [y_c - y_d]\sin 2\theta)/$

$(-[x_b - x_e]\sin\theta - [x_c - x_d]\sin 2\theta + y_a + [y_b + y_e]\cos\theta + [y_c + y_d]\cos 2\theta)$,

$(x_a + [x_b + x_e]\cos 2\theta + [x_c + x_d]\cos\theta + [y_b - y_e]\sin 2\theta - [y_c - y_d]\sin\theta)/$

$(-[x_b - x_e]\sin 2\theta + [x_c - x_d]\sin\theta + y_a + [y_b + y_e]\cos 2\theta + [y_c + y_d]\cos\theta)$

E_2'': $([z_b - z_e]\sin 2\theta + [-z_c + z_d]\sin\theta)/$

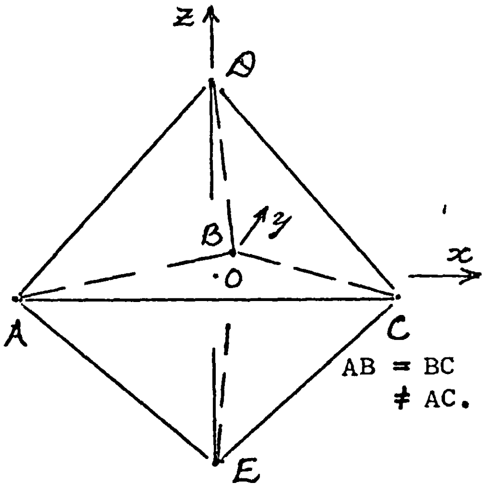
$(z_a + [z_b + z_e]\cos 2\theta + [z_c + z_d]\cos\theta$

where $\theta = 2\pi/5$. ....(VII.29)

The usual qualitative analysis then indicates that the ground state has ${}^2E'$-symmetry properties, with orbital configuration $(1a_1')^2(1e_1')^3$, and is, therefore, unstable with respect to the E_1'- and E_2'-symmetry distortions.

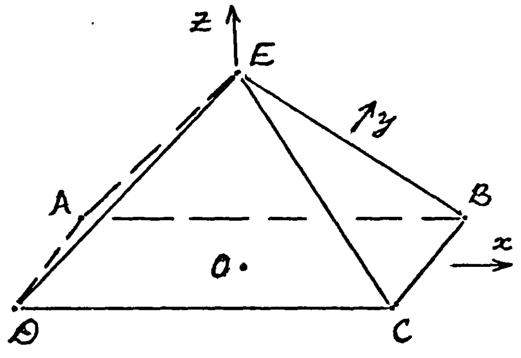
The Pentamer: Triangular Bipyramid and Rectangular Pyramid.

These structures, shown in the diagram below, are obtained by an E'-symmetry distortion of the trigonal bipyramid and a B_2-symmetry distortion of the square pyramid, respectively. It may be recalled that the ground states of the trigonal bipyramid and square pyramid were found to be unstable with respect to these distortions.



AB = BC
≠ AC.

OD = OE
≠ OA, etc., in general.



Both of the above configurations belong to the C_{2v}-point group and have the following symmetry operations:

1. Identity operation.
2. Rotation of π about the principal axis.
3. and 4. Reflections in the σ_v-planes:

$x = 0$ and $z = 0$ for the triangular bipyramid.

$x = 0$ and $y = 0$ for the rectangular pyramid.

Molecular Orbital Description.

The symmetry orbitals for these systems are as follows:

Triangular Bipyramid

A_1: $(s_a + s_c)$, s_b, $(s_d + s_e)$, $(x_a - x_c)$, y_b, $(y_a + y_c)$, $(y_d + y_e)$, $(z_d - z_e)$

A_2: $(z_a - z_c)$, $(x_d - x_e)$

B_1: $(s_a - s_c)$, $(x_a + x_c)$, $(x_d + x_e)$, x_b, $(y_a - y_c)$

B_2: $(s_d - s_e)$, $(y_d - y_e)$, $(z_a + z_c)$, z_b, $(z_d + z_e)$

........(VII.30)

Rectangular Pyramid

$$A_1: \quad (s_a + s_b + s_c + s_d),\ s_e ,\ (x_a - x_b - x_c + x_d),$$
$$(y_a + y_b - y_c - y_d),\ (z_a + z_b + z_c + z_d),\ z_e$$
$$A_2: \quad (s_a - s_b + s_c - s_d),\ (x_a + x_b - x_c - x_d),$$
$$(y_a - y_b - y_c + y_d),\ (z_a - z_b + z_c - z_d)$$
$$B_1: \quad (s_a - s_b - s_c + s_d),\ (x_a + x_b + x_c + x_d),\ x_e ,$$
$$(y_a - y_b + y_c - y_d),\ (z_a - z_b - z_c + z_d)$$
$$B_2: \quad (s_a + s_b - s_c - s_d),\ (x_a - x_b + x_c - x_d),$$
$$(y_a + y_b + y_c + y_d),\ y_e ,\ (z_a + z_b - z_c - z_d)$$

........(VII.31)

Qualitative analysis of the relative stability of the molecular orbitals indicates that the ground states of the above systems will be as follows:

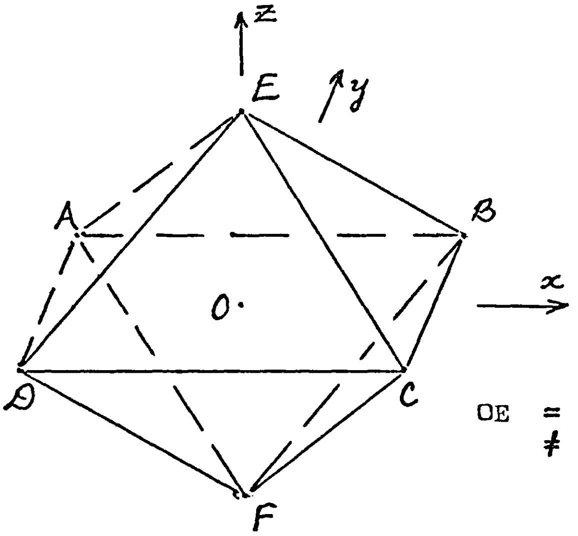
Triangular Bipyramid	$(1a_1)^2 (1b_2)^2 (1b_1)^1$;	$^2B_1$ -symmetry.
Rectangular Pyramid	$(1a_1)^2 (1b_1)^2 (1b_2)^1$;	$^2B_2$ -symmetry.

Schematic representations of the charge distributions expected for the b_1- and b_2-states of the triangular bipyramidal system are given in Figure (VII.9). The distributions for the corresponding states of the rectangular pyramid are expected to be analogous to that (Figure (VII.7)) for the b_{3u}-level of the rectangle.

The Hexamer: Octahedron.

The usual qualitative analysis suggests that the ground state of this system will be triply-degenerate. In the simple Molecular Orbital description, it is specified by the following orbital configuration: $(1a_{1g})^2 (1t_{1u})^4$; $^3T_{2g}$-symmetry. As described later during the analysis of the cube, each of the t_{1u}-orbitals possesses a nodal plane which may be chosen to coincide with one of the coordinate planes. Furthermore, the partial occupation of this level results in the intrinsic instability of the ground state (Chapter VIII).

The Hexamer: Square Bipyramid.



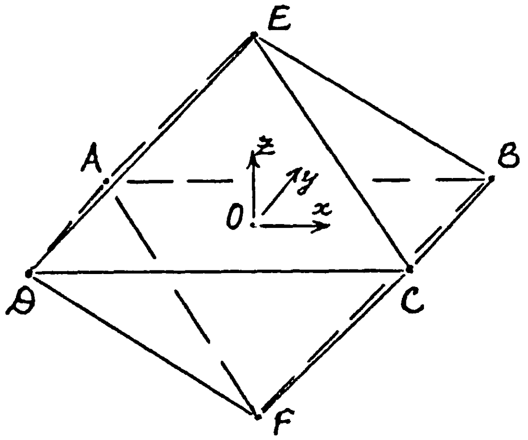
OE = OF
≠ OA, etc., in general.

The analysis of this structure is similar to that performed on the square configuration for the quadramer. In addition to those given in equation (VII.8), the symmetry orbitals for the system include

$$
\begin{aligned}
A_{1g}&: \quad (s_e + s_f),\ (z_e - z_f) \\
A_{2u}&: \quad (s_e - s_f),\ (z_e + z_f) \\
E_g&: \quad (x_e - x_f)/(y_e - y_f) \\
E_u&: \quad (x_e + x_f)/(y_e + y_f) \qquad \text{........(VII.32)}
\end{aligned}
$$

The symmetry and orbital configuration of the ground state are expected to be $^1A_{1g}$ and $(1a_{1g})^2(1e_u)^4$, respectively. The charge distributions in the occupied states will be analogous to those shown for the square.

The Hexamer: Rectangular Bipyramid.



In addition to the functions given in equation (VII.22) for the rectangular complex, the symmetry orbitals for this system are

$$\begin{array}{ll} A_g: & (s_e + s_f),\ (z_e - z_f) \\ B_{1u}: & (s_e - s_f),\ (z_e + z_f) \\ B_{2g}: & (x_e - x_f) \\ B_{2u}: & (y_e + y_f) \\ B_{3g}: & (y_e - y_f) \\ B_{3u}: & (x_e + x_f) \end{array} \qquad \text{........(VII.33)}$$

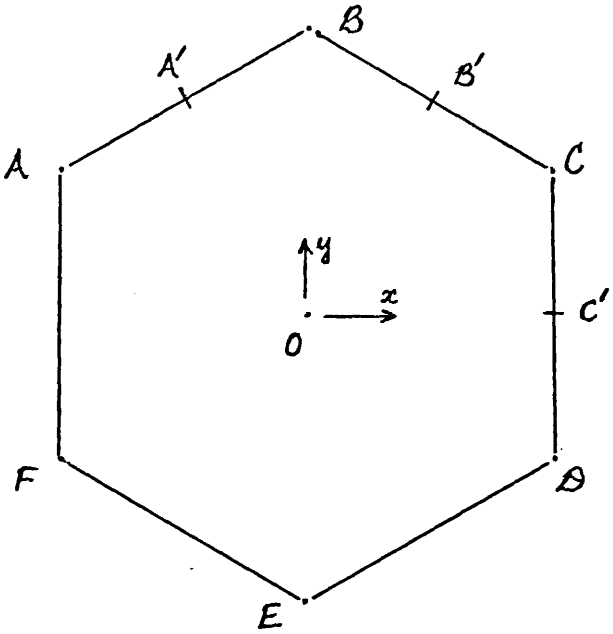
The simple Molecular Orbital description then indicates that the orbital configuration and symmetry of the ground state will be $(1a_g)^2(1b_{3u})^2(1b_{2u})^2$ and ^1A_g, respectively. The charge distributions in the occupied states will be analogous to those for the rectangle.

The Hexamer: Linear Configuration.

There is a straightforward connection between the study of this system and that of the linear form of the tetra-atomic cluster. In particular, the corresponding Molecular Orbital description suggests that the orbital configuration and symmetry of its ground state will be $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2$ and $^1\Sigma_g^+$, respectively. The charge distributions in the $1\sigma_g$ - and $1\sigma_u$-orbitals will be similar to those in the corresponding states for the linear tetra-atomic system and that in the $2\sigma_g$ -orbital will be analogous to the representation (Figure (VII.8)) for the corresponding state of the linear penta-atomic complex.

The Hexamer: Hexagonal Structure.

This configuration, shown in the diagram below, belongs to the



D_{6h}-point group and its twenty-four symmetry operations are as follows:

1. Identity operation.

2. Rotation of π about the principal axis.

3 and 4. Rotations of $2\pi/3$ and $4\pi/3$ about the same axis.

5 and 6. Rotations of $\pi/3$ and $5\pi/3$ about the same axis.

7, ... 9. Rotations of π about the three two-fold axes, OA, OB and OC.

10, .. 12. Rotations of π about the three two-fold axes, OA′, OB′ and OC′.

13. Inversion in the centre of symmetry.

14. Reflection in the xy-plane.

15, .. 18. Rotations of $\pi/3$, $5\pi/3$, $2\pi/3$ and $4\pi/3$ about the principal axis, each followed by a reflection in the xy-plane.

19, .. 21. Reflections in the planes through OA′, OB′ and OC′.

22, .. 24. Reflections in the planes through OA, OB and OC.

Molecular Orbital Description.

The symmetry orbitals for the system include

A_{1g}: $(s_a + s_b + s_c + s_d + s_e + s_f)$,

$(\sqrt{3}x_a - y_a - 2y_b - \sqrt{3}x_c - y_c - \sqrt{3}x_d + y_d + 2y_e + \sqrt{3}x_f + y_f)$

A_{2g}: $(x_a + \sqrt{3}y_a + 2x_b + x_c - \sqrt{3}y_c - x_d - \sqrt{3}y_d - 2x_e - x_f + \sqrt{3}y_f)$

A_{2u}: $(z_a + z_b + z_c + z_d + z_e + z_f)$

B_{1u}: $(s_a - s_b + s_c - s_d + s_e - s_f),$

$(\sqrt{3}x_a - y_a + 2y_b - \sqrt{3}x_c - y_c + \sqrt{3}x_d - y_d + 2y_e - \sqrt{3}x_f - y_f)$

B_{2g}: $(z_a - z_b + z_c - z_d + z_e - z_f)$

B_{2u}: $(x_a + \sqrt{3}y_a - 2x_b + x_c - \sqrt{3}y_c + x_d + \sqrt{3}y_d - 2x_e + x_f - \sqrt{3}y_f)$

E_{1u}: $(s_a - s_c - s_d + s_f) / (s_a + 2s_b + s_c - s_d - 2s_e - s_f),$

$(x_a + x_b + x_c + x_d + x_e + x_f) / (y_a + y_b + y_c + y_d + y_e + y_f),$

$(\sqrt{3}x_a - y_a + \sqrt{3}x_c + y_c + \sqrt{3}x_d - y_d + \sqrt{3}x_f + y_f) /$

$(\sqrt{3}x_a - y_a - 4y_b - \sqrt{3}x_c - y_c + \sqrt{3}x_d - y_d - 4y_e - \sqrt{3}x_f - y_f)$

E_{1g}: $(z_a + 2z_b + z_c - z_d - 2z_e - z_f) / (z_a - z_c - z_d + z_f)$

E_{2g}: $(s_a - 2s_b + s_c + s_d - 2s_e + s_f) / (s_a - s_c + s_d - s_f),$

$(x_a - \sqrt{3}y_a + 2\sqrt{3}y_b - x_c - \sqrt{3}y_c - x_d + \sqrt{3}y_d - 2\sqrt{3}y_e + x_f + \sqrt{3}y_f) /$

$(5x_a - \sqrt{3}y_a - 2x_b + 5x_c + \sqrt{3}y_c - 5x_d + \sqrt{3}y_d + 2x_e - 5x_f - \sqrt{3}y_f),$

$(\sqrt{3}x_a + y_a + 2y_b - \sqrt{3}x_c + y_c - \sqrt{3}x_d - y_d - 2y_e + \sqrt{3}x_f - y_f) /$

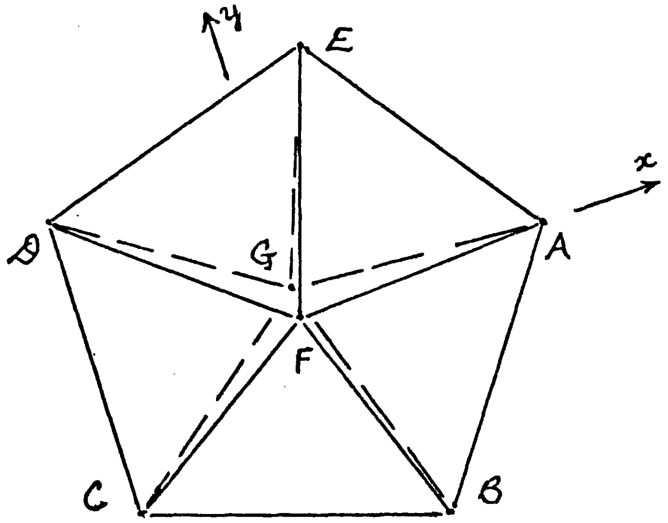
$(x_a - \sqrt{3}y_a + 2x_b + x_c + \sqrt{3}y_c - x_d + \sqrt{3}y_d - 2x_e - x_f - \sqrt{3}y_f)$

E_{2u}: $(z_a - z_c + z_d - z_f) / (z_a - 2z_b + z_c + z_d - 2z_e + z_f)$

........(VII.34)

Qualitative analysis of the relative stability of the molecular orbitals and the subsequent use of the aufbau prinzip then indicates that the symmetry of the ground state will be $^1A_{1g}$, with orbital configuration $(1a_{1g})^2 (1e_{1u})^4$.

The Septamer: Pentagonal Bipyramid.



This configuration belongs to the $\mathcal{D}_{5h}$-point group. Its twenty symmetry operations have already been discussed during the investigation of the pentagonal structure for the pentamer.

Molecular Orbital Description.

In addition to the functions of equation (VII.29), the symmetry orbitals for the system are

A_1': $(s_f + s_g)$, $(z_f - z_g)$
A_2'': $(s_f - s_g)$, $(z_f + z_g)$
E_1': $(x_f + x_g)/(y_f + y_g)$
E_1'': $(x_f - x_g)/(y_f - y_g)$ ....(VII.35)

Qualitative Molecular Orbital theory then suggests that the symmetry and orbital configuration of the ground state will be $^2A_1'$ and $(1a_1')^2(1e_1')^4(2a_1')^1$, respectively.

The Septamer: Linear Configuration.

The analysis of this system is similar to the previous investigations of the same structure for the trimer and pentamer.

Qualitative considerations indicate that the one-electron energy level scheme will be either

(i) $1\sigma_g < 1\sigma_\mu < 2\sigma_g < 2\sigma_\mu < \dots$
or (ii) $1\sigma_g < 1\sigma_\mu < 2\sigma_g < 1\pi_\mu < \dots$,

with the charge distributions in the $2\sigma_\mu$- and $1\pi_\mu$-orbitals analogous to those shown in Figure (VII.10).

For clusters composed of hydrogen and lithium, the first scheme is expected to be the correct one. For the heavier atoms, however, the alternative scheme is quite probable. In this case, the uncertainty can only be resolved by quantitative study.

The symmetry and orbital configuration of the ground state will then be either (i) $^2\Sigma_\mu^+$: $(1\sigma_g)^2(1\sigma_\mu)^2(2\sigma_g)^2(2\sigma_\mu)^1$ or

(ii) $^{2}\Pi_{\mu}$: $(1\sigma_g)^2(1\sigma_\mu)^2(2\sigma_g)^2(1\pi_\mu)^1$, respectively.

The Octamer: Linear Configuration.

The uncertainty, described in the previous section, in the energy-level ordering also results in two possible orbital configurations for the ground state of this system. These are

(i) $^{1}\Sigma_g^{+}$: $(1\sigma_g)^2(1\sigma_\mu)^2(2\sigma_g)^2(2\sigma_\mu)^2$, and

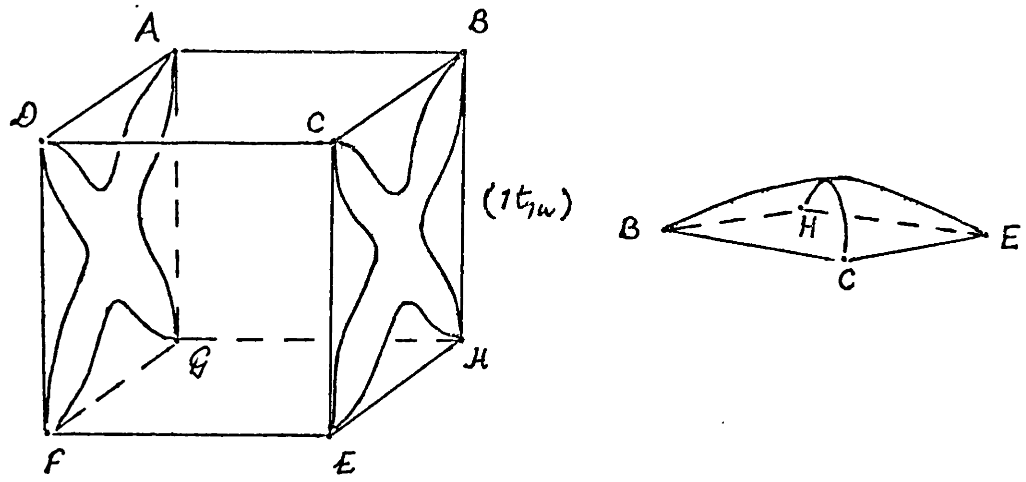
(ii) $^{3}\Sigma_g^{-}$: $(1\sigma_g)^2(1\sigma_\mu)^2(2\sigma_g)^2(1\pi_\mu)^2$.

Schematic representations of the charge distributions expected in the $2\sigma_g$ - and $1\pi_\mu$-orbitals are given in Figure (VII.10).

The above orbital designation represents a single Slater determinant of one-electron spin-orbitals (Chapter IV). However, the actual electronic motion is too complicated to be described by such a wave-function (Chapter II) and, therefore, the simple Molecular Orbital, or Hartree-Fock-Slater, theory can only explain the gross features of these systems.

It has proved possible to overcome some of the inadequacies inherent in the Hartree-Fock-Slater formalism by requiring, wherever possible, that the antisymmetry property be satisfied by the spatial portion of the one-electron functions. This tends to reduce the probability of close approach of any two electrons of the system being considered, thereby simulating the effect produced by the interelectronic Coulomb repulsion. A consequence of this is that the actual energy level scheme that results in the best simple Molecular Orbital description of a many-electron system may differ from that obtained when assuming a set of noninteracting single-particle states.

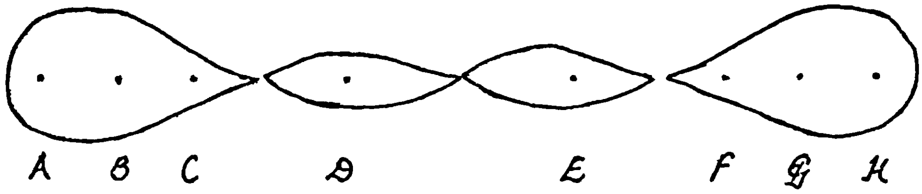
In view of these considerations, it appears to be also necessary to study the following orbital configurations for the ground states of the Septamer and Octamer in their linear forms:



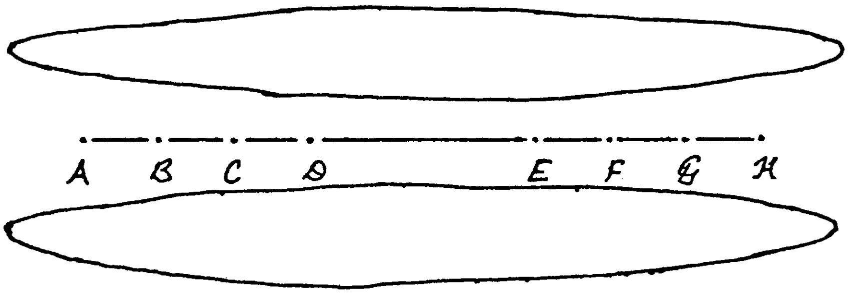
A schematic representation of the charge distribution expected from one of the occupied t_{1u}-orbitals. The distribution forms "caps" on a pair of parallel surfaces of the cube.

Figure (VII.11)

Figure (VII.10)



Charge distribution in first-excited σ_u-orbital.



Charge distribution in lowest-energy π_u-molecular orbital.

Septamer $^4\Pi_g$: $(1\sigma_g)^2(1\sigma_\mu)^2(2\sigma_g)^1(2\sigma_\mu)^1(1\pi_\mu)^1$

$^4\Sigma_g^-$: $(1\sigma_g)^2(1\sigma_\mu)^2(2\sigma_g)^1(1\pi_\mu)^2$.

Octamer $^1\Sigma_g^+$: $(1\sigma_g)^2(1\sigma_\mu)^2(1\pi_\mu)^4$

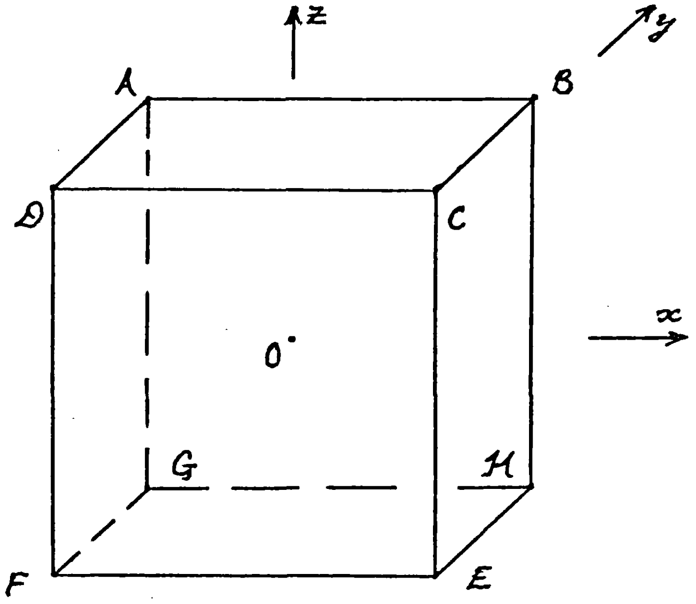
$^3\Pi_\mu$: $(1\sigma_g)^2(1\sigma_\mu)^2(2\sigma_g)^1(1\pi_\mu)^3$

$^3\Pi_g$: $(1\sigma_g)^2(1\sigma_\mu)^2(2\sigma_g)^2(2\sigma_\mu)^1(1\pi_\mu)^1$

$^5\Sigma_\mu^-$: $(1\sigma_g)^2(1\sigma_\mu)^2(2\sigma_g)^1(2\sigma_\mu)^1(1\pi_\mu)^2$.

As mentioned before, quantitative analysis is needed in order to resolve these uncertainties.

<u>The Octamer:</u> Cubic Configuration.



This configuration, shown in the diagram above, belongs to the full cubic group, O_h, of symmetry operations. The forty-eight operations of the group include

1. Identity operation.
2, ... 9. Rotations of $2\pi/3$ and $4\pi/3$ about the four diagonals of the cube.
10, ... 15. Rotations of π about the six two-fold axes.
16, ... 21. Rotations of $\pi/4$ and $3\pi/4$ about the x-, y- and z-axes.
22, ... 24. Rotations of π about the x-, y- and z-axes.

25, ... 48. These operations are formed by combining each of the above twenty-four operations with a reflection in the centre of symmetry.

Molecular Orbital Description.

The symmetry orbitals for the system are as follows:

A_{1g}: $(s_a + s_b + s_c + s_d + s_e + s_f + s_g + s_h)$,

$$(x_a - y_a - z_a - x_b - y_b - z_b - x_c + y_c - z_c + x_d + y_d - z_d - x_e + y_e + z_e + x_f + y_f + z_f + x_g - y_g + z_g - x_h - y_h + z_h)$$

A_{2u}: $(s_a - s_b + s_c - s_d - s_e + s_f - s_g + s_h)$,

$$(x_a - y_a - z_a + x_b + y_b + z_b - x_c + y_c - z_c - x_d - y_d + z_d + x_e - y_e - z_e + x_f + y_f + z_f - x_g + y_g - z_g - x_h - y_h + z_h)$$

$E_{g,u}$: $$[(2x_a + y_a + z_a - 2x_c - y_c + z_c + 2x_f - y_f - z_f - 2x_h + y_h - z_h) \mp (2x_b - y_b - z_b - 2x_d + y_d - z_d + 2x_e + y_e + z_e - 2x_g - y_g + z_g)] /$$

$$[(x_b + y_b - 2z_b - x_d - y_d - 2z_d + x_e - y_e + 2z_e - x_g + y_g + 2z_g) \mp (x_a - y_a + 2z_a - x_c + y_c + 2z_c + x_f + y_f - 2z_f - x_h - y_h - 2z_h)]$$

T_{1g}:

$$(x_a + y_a + x_b - y_b - x_c - y_c - x_d + y_d - x_e - y_e - x_f + y_f + x_g + y_g + x_h - y_h)$$

$$/(-x_a - z_a - x_b + z_b - x_c + z_c - x_d - z_d + x_e + z_e + x_f - z_f + x_g - z_g + x_h + z_h)$$

$$/(-y_a + z_a - y_b + z_b - y_c - z_c - y_d - z_d + y_e - z_e + y_f - z_f + y_g + z_g + y_h + z_h)$$

T_{1u}: $(s_a + s_b + s_c + s_d - s_e - s_f - s_g - s_h)/$

$(s_a + s_b - s_c - s_d - s_e - s_f + s_g + s_h)/$

$(s_a - s_b - s_c + s_d - s_e + s_f + s_g - s_h)$,

$(z_a + z_b + z_c + z_d + z_e + z_f + z_g + z_h)/$

$(y_a + y_b + y_c + y_d + y_e + y_f + y_g + y_h)/$

$(x_a + x_b + x_c + x_d + x_e + x_f + x_g + x_h)$,

$$(x_a - y_a - x_b - y_b - x_c + y_c + x_d + y_d + x_e - y_e - x_f - y_f - x_g + y_g + x_h + y_h)$$

$$/(x_a - z_a - x_b - z_b + x_c + z_c - x_d + z_d + x_e - z_e - x_f - z_f + x_g + z_g - x_h + z_h)$$

$$/(-y_a - z_a + y_b + z_b - y_c + z_c + y_d - z_d - y_e - z_e + y_f + z_f - y_g + z_g + y_h - z_h)$$

T_{2g}: $(s_a - s_b + s_c - s_d + s_e - s_f + s_g - s_h)/$

$(s_a - s_b - s_c + s_d + s_e - s_f - s_g + s_h)/$

$(s_a + s_b - s_c - s_d + s_e + s_f - s_g - s_h)$,

$$\mathcal{T}_{2g}: \quad (z_a - z_b + z_c - z_d - z_e + z_f - z_g + z_h)/$$

$$(y_a - y_b + y_c - y_d - y_e + y_f - y_g + y_h)/$$

$$(x_a - x_b + x_c - x_d - x_e + x_f - x_g + x_h),$$

$$(x_a - y_a + x_b + y_b - x_c + y_c - x_d - y_d - x_e + y_e - x_f - y_f + x_g - y_g + x_h + y_h)$$

$$/(x_a - z_a + x_b + z_b + x_c + z_c + x_d - z_d - x_e + z_e - x_f - z_f - x_g - z_g - x_h + z_h)$$

$$/(-y_a - z_a - y_b - z_b - y_c + z_c - y_d + z_d + y_e + z_e + y_f + z_f + y_g - z_g + y_h - z_h)$$

$$\mathcal{T}_{2u}:$$

$$(x_a + y_a - x_b + y_b - x_c - y_c + x_d - y_d + x_e + y_e - x_f + y_f - x_g - y_g + x_h - y_h)$$

$$/(-x_a - z_a + x_b - z_b - x_c + z_c + x_d + z_d - x_e - z_e + x_f - z_f - x_g + z_g + x_h + z_h)$$

$$/(-y_a + z_a + y_b - z_b - y_c - z_c + y_d + z_d - y_e + z_e + y_f - z_f - y_g - z_g + y_h + z_h)$$

........(VII.36)

Qualitative analysis of the charge distribution expected in each of the molecular orbitals of the system indicates that the symmetry and orbital configuration of the ground state will be $^1A_{1g}$ and $(1a_{1g})^2(1t_{1u})^6$, respectively. The charge distribution arising from one of the occupied t_{1u}-orbitals is expected to be as shown schematically in Figure (VII.11).

The Nonamer: Body-Centred Cubic Structure.

This configuration has the same symmetry properties as discussed in the previous section for the cube. The symmetry orbitals for the system are given by

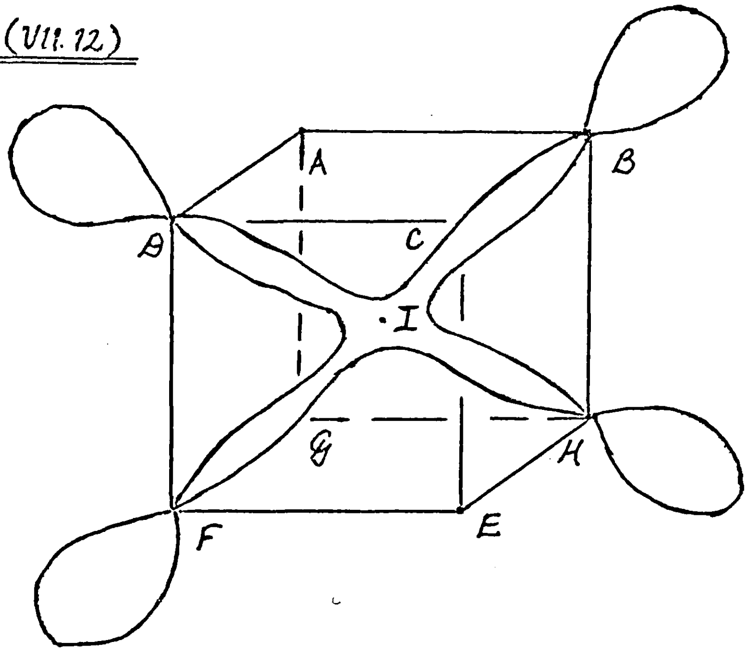
$$A_{1g}: \quad s_i$$

$$\mathcal{T}_{1u}: \quad z_i / y_i / x_i \qquad \text{........(VII.37)}$$

and those already defined in equation (VII.36).

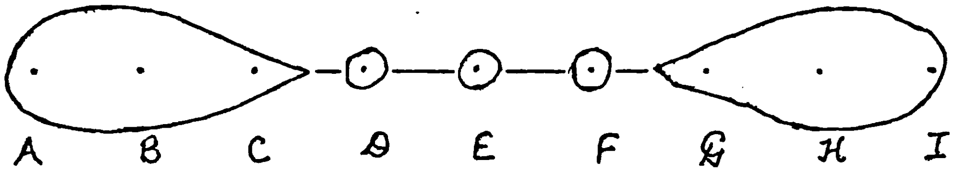
Qualitative Molecular Orbital theory then indicates that the symmetry and orbital configuration of the ground state will be $^2A_{1g}$ and $(1a_{1g})^2(1t_{1u})^6(2a_{1g})^1$, respectively. Figure (VII.12) is a pictorial description of the charge distribution expected to arise from the $2a_{1g}$-orbital; the distribution arising from the $1t_{1u}$-state is similar to that (Figure (VII.11)) described in the previous section for the cube.

Figure (VII.12)



A pictorial description of a cross-section through the charge distribution in the first-excited a_{1g}-orbital for the body-centred-cubic structure.

Figure (VII.13)



Charge distibution in second excited σ_g-orbital.

The Nonamer: Linear Configuration.

In this case, there are three possible energy-level schemes to consider. These are

(i) $1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 3\sigma_g < \ldots.$

(ii) $1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 1\pi_u < \ldots.$

(iii) $1\sigma_g < 1\sigma_u < 2\sigma_g < 1\pi_u < \ldots.$.

The charge distribution arising from the occupation of the $3\sigma_g$-orbital is expected to be as indicated schematically in Figure (VII.13).

Use of the aufbau prinzip then suggests that the symmetry of the ground state will be either (i) ${}^2\Sigma_g^+$ or (ii) and (iii) ${}^2\Pi_u$. However, as mentioned during the analysis of the octamer, the above conclusions may also not be in agreement with those of experimental or more elaborate quantitative investigations, owing to the inherent shortcomings of the simple Molecular Orbital theory.

Results Of Model Calculation.

The following is a brief discussion of the results obtained from the investigation of some SODIUM clusters using the model Hamiltonian of Chapter VI. The results are given in Tables (VII.3) to (VII.7). (It was originally hoped that a much more exhaustive study of at least the trimer and quadramer systems, including investigation of several isomeric forms, be performed. However, owing to several difficulties which arose at the outset of the project, this plan had to be abandoned through lack of time.)

In order to examine the suitability of the chosen model for investigating larger systems, fairly extensive calculations were first performed on the dimer. It was then observed that, in order to obtain a reasonable potential energy curve for the ground state of this system, it was necessary to determine the ' near optimal ' basis function exponent as a function of the internuclear separation; the values used are still quite far from being truly optimum and this may explain the spurious results (for $R = 7.40$ a. u.) in the potential energy curves for the trimer and quadramer.

An interesting by-product of the above optimization procedure is the indication that the variation of the optimal basis function exponent with decreasing internuclear separation may be quite similar to that described by Slater (1963) for the hydrogen molecule. However, the initial decrease of the exponent appears larger and may be a consequence of the weaker binding of the valence electron to its parent nucleus; the decrease in the exponent may be considered as a measure of the degree to which the valence electron is perturbed by the presence of the ion-core of a foreign atom.

As a result of the rather large equilibrium bond distances involved, it is expected that the Valence Bond method will be more suitable for determining the binding energies of the various clusters. This is supported by the numerical results which show that the energies as determined using the Valence Bond description are always lower than those of the Molecular Orbital formalism. Indeed, quite promising results have been obtained using this method. Thus, the equilibrium bond distance and ionization potential are in fair agreement with experimental findings and the accuracy of the computed binding energy is about the same as that obtained from more exhaustive calculations on simpler systems. Experience has shown that improper treatment of correlation effects causes a correlation error of approximately 0.5 e.v. per electron-pair bond.

The lack of any binding in the Minimal Basis Molecular Orbital description of the dimer was an unexpected result which may be due primarily to the poor description of the Hartree-Fock orbitals of the system by the chosen Slater basis (Szasz and McGinn (1968)). This hypothesis is further supported by the disappointing results obtained from a reference calculation which explicitly considered all the electrons of the system.

R(a.u.)		5.00	5.33	5.60	5.80
$\alpha_{opt.}$		0.9431	0.8863	0.8500	0.8259
$\tilde{W}_{Tot.}(^1\Sigma_g^+)$	Valence Bond Description	-0.380599	-0.383608	-0.383844	-0.383049
	Minimal Basis Molecular Orbital Formalism	-0.367599	-0.371243	-0.371665	-0.370939
	plus Configuration Interaction	-0.380953	-0.383917	-0.384113	-0.383289
	Extended Basis Molecular Orbital Formalism	-0.370135	-0.374924	-0.376302	-0.376266
	plus Configuration Interaction	-0.383812	-0.387323	-0.388099	-0.387746
	Reference Calculation		-0.34801		

Potential Energy (a.u.) Curve for the ground ($^1\Sigma_g^+$) state of the Sodium Dimer.

Table (VII. 3).

(see also page 217.)

	R (a.u.)	5.00	5.33	5.60	5.80
	$\alpha_{opt.}$	0.9431	0.8863	0.8500	0.8259
Minimal Basis Molecular Orbital Formation	$\tilde{W}_{Tot.}({}^2\Sigma_g^+)$	−0.194864	−0.196149	−0.196449	−0.196200
	$\tilde{W}_{Tot.}({}^1\Sigma_u^+)$	−0.234858	−0.247305	−0.254323	−0.258206
	$\tilde{W}_{Tot.}({}^3\Sigma_u^+)$	−0.340296	−0.346451	−0.349655	−0.351040
Extended Basis Molecular Orbital Formation	$\tilde{W}_{Tot.}({}^2\Sigma_g^+)$	−0.207326	−0.204330	−0.205959	−0.206630
plus Configuration Interaction		−0.209268	−0.212566	−0.214387	−0.215165
	$\tilde{W}_{Tot.}({}^3\Sigma_u^+)$	−0.340731	−0.347527	−0.350599	−0.351776
plus Configuration Interaction		−0.342958	−0.349655	−0.352962	−0.354430

Potential Energy (a.u.) Curves for the ${}^1\Sigma_u^+$- and ${}^3\Sigma_u^+$- States of the dimer and for the ${}^2\Sigma_g^+$- State of the ionized system.

Table (VII.4).

(see also page 217.)

Tables (VII.3) and (VII.4) continued: Comments.

The main conclusions to be drawn from the results displayed in Tables (VII.3) and (VII.4) include:

1. The model gives the correct ordering of the lowest energy levels for the dimer, with reasonable potential energy curves for each. However, the level separations are poorly described; for example,

   ΔE_1 (first electronic transition energy) $\sim$ 3 e.v.

   Experimental value = 1.82 e.v.

2. The Valence Bond formalism gives a better initial approximation for investigating the system. In fact, binding is poorly described in the Molecular Orbital framework even when a limited Configuration Interaction (Chapter II) is used in the Extended Basis calculation. A disappointing result is also obtained from the reference calculation in which all the electrons of the system are explicitly considered. Hereafter, the discussion is concerned with the results obtained by using the Valence Bond method.

3. The values obtained for the equilibrium geometry and the ionization potential are in quite good agreement with those determined by experimental and similar theoretical analysis. Also, the binding energy is of the order of magnitude expected when it is remembered that correlation between the valence electrons is improperly accounted for.

The following is a comparison of theoretical and experimental results obtained for the abovementioned properties of the dimer:

Ionization Potential = 4.90 e.v. (experimental; Table (VIII.1))
= 4.94 e.v. (Pickup and Byers Brown (1972))
= 5.10 e.v. (present work)

Equilibrium Internuclear Separation
= 5.50 a.u. (present work and Pickup et. al. (1972))
= 5.80 a.u. (experimental)
= 6.18, 6.85 a.u. (Szasz and McGinn (1968))

Tables (VII.3) and (VII.4) continued: Comments.

Dissociation Energy = 0.196, 0.229 e.v. (Szasz et. al. (1968))
= 0.259 e.v. (present work)
= 0.386 e.v. (Pickup et. al. (1972))
= 0.740 e.v. (experimental)

(Experimental data for the equilibrium geometry and dissociation energy is taken from Herzberg G. (1950) ' Molecular Spectra and Molecular Structure ', Vol. I (Spectra of Diatomic Molecules) 2nd. ed., Van Nostrand, New York.)

Tables (VII.5) to (VII.7): Comments.

The potential energy curves for the ground states of the equilateral triangular, tetrahedral and square systems are shown in Tables (VII.5) to (VII.7). The spurious results obtained for R = 7.40 a.u. is most certainly due to the incomplete optimization, as explained in the text.

The results displayed in Tables (VII.6) and (VII.7) confirm that the square configuration is more stable than the tetrahedral. The square itself is, however, unstable with respect to two noninteracting dimers.

Once again, the Valence Bond formalism provides the better initial approximation for investigating binding energies, as can be seen clearly from the data of Table (VII.7).

Finally, the ionization potential and equilibrium nearest-neighbour separation for the square are estimated to be 4.2 e.v. and 6.9 a.u., respectively.

Table (VII.5). (see also page 218)

Triatomic Molecule: Equilateral Triangular Configuration.

R (a.u.)	5.00	5.80	6.60	7.40	∞
$\alpha_{opt.}$	0.9437	0.8259	0.9089	0.9100	0.9000
$\tilde{W}_{Tot.}(^2E')$	-0.511993	-0.533670	-0.566894	-0.561175	-0.567471

Potential Energy (a.u.) Curve for ground state of the Equilateral system, using the Valence Bond Formalism.

Table (VII.6). (see also page 219)

Tetra-Atomic Molecule: Tetrahedral Configuration.

R (a.u.)	5.00	5.40	5.80	6.60	7.40	∞
$\alpha_{opt.}$	0.9431	0.8728	0.8559	0.9089	0.9100	0.9000
$\tilde{W}_{Tot.}(^3T_2)$	-0.619531	-0.645219	-0.667332	-0.751298	-0.739505	-0.748628

Potential Energy (a.u.) Curve for the ground state of the tetrahedral system, using the Valence Bond Scheme.

Table (VII.7). (see also page 219)

Tetra-Atomic Molecule: Square Configuration.

R (a.u.)		5.00	5.40	5.80	6.60	7.40	∞
$\alpha_{opt.}$		0.9431	0.8728	0.8359	0.9089	0.9100	0.9000
$\tilde{W}_{Tot.}(^3A_{2g})$	1.	−0.699929	−0.717472	−0.729988	−0.753986	−0.751520	
	2.		−0.729030				−0.748628
	3.	−0.692251	−0.710537	−0.722046	−0.735156	−0.723179	
$\tilde{W}_{Tot.}(^2E_g)^*$	1.	−0.529789	−0.542134	−0.550436	−0.579556	−0.573312	−0.561471

Energy (a.u.) variations for the $^3A_{2g}$- and ^2E_g- States of the Square configuration with nearest-neighbour separation. Calculations were performed within (1) The Valence Bond, (2) The Extended Basis Molecular Orbital and (3) The Minimal Basis Molecular Orbital Formalisms.

* Ground State for Ionized System.

The excited states of the dimer are also rather poorly described. This may be due in part to the improper choice of basis function exponent as well as to the inadequacies of the Slater basis set.

As yet, there is little published work with which the results for the trimer and quadramer may be compared. However, the calculations suggest that the square is more stable than the tetrahedron and that none of the structures considered for the trimer or quadramer are stable with respect to the ' dimer plus monomer ' and ' dimer plus dimer ' complexes, respectively.

The above conclusions may be compared with those of Taylor et. al. (1933) and Pickup and Byers Brown (1972). A model calculation by Pickup et. al. indicated that the linear configuration is the most stable form for the triatomic cluster. However, this equilibrium geometry appeared to represent a saddle-point on the potential energy surface, with the non-interacting dimer plus monomer complex being energetically more favourable. Besides corroborating these findings on the triatomic system, the semi-empirical analysis of Taylor et. al. also concluded that, of all the structures considered, the square configuration was indeed the most stable form for a system of four sodium atoms and, furthermore, that this aggregate was slightly more stable than two non-interacting sodium molecules.

APPENDIX.

The Trimer: Linear Symmetric and Equilateral Triangular Systems.

In this section, expressions are derived for the energies of the ground states of these systems. For either configuration, the energy of the ground state is given, in the ' Heitler-London ' approximation, by

$$E_{elec.}\left({}^2\Sigma_u^+(\text{linear});\ {}^2E'(\text{triangular})\right) = \langle \Phi | \mathcal{H}_{model} | \Phi \rangle / \langle \Phi | \Phi \rangle$$

where ....(VII.38)

$$\mathcal{H}_{model} = \sum_i \left[h_m(i) + \sum_{j(\neq i)} (2r_{ij})^{-1} \right] .$$ (equation (VI.5)),

$$\Phi = \Phi_1 + \Phi_6 + 2\,\Phi_9 ,$$

$$\Phi_1 = 6^{-1/2}(s_a^+ s_b^+ s_c^-) , \quad \Phi_6 = 6^{-1/2}(s_b^+ s_c^+ s_a^-) \text{ and } \Phi_9 = 6^{-1/2}(s_a^+ s_c^+ s_b^-).$$

To determine the above matrix elements, it is convenient to define the following Overlap determinants (equations (III.47) to (III.49)):

$$\det | S_{ij}^{1,1} | = \det | S_{ij}^{6,6} | = \begin{vmatrix} 1 & S_{ab} & 0 \\ S_{ab} & 1 & 0 \\ 0 & 0 & 0 \end{vmatrix} ,$$

$$\det | S_{ij}^{1,9} | = \det | S_{ij}^{6,9} | = \begin{vmatrix} 1 & S_{ac} & 0 \\ S_{ab} & S_{ab} & 0 \\ 0 & 0 & S_{ab} \end{vmatrix} ,$$

$$\det | S_{ij}^{1,6} | = \begin{vmatrix} S_{ab} & S_{ac} & 0 \\ 1 & S_{ab} & 0 \\ 0 & 0 & S_{ac} \end{vmatrix} \quad \text{and} \quad \det | S_{ij}^{9,9} | = \begin{vmatrix} 1 & S_{ac} & 0 \\ S_{ac} & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} .$$

The Overlap matrices are then given by

$$\langle \Phi_1 | \Phi_1 \rangle = (1 - S_{ab}^2); \qquad \langle \Phi_6 | \Phi_6 \rangle = (1 - S_{ab}^2);$$

$$\langle \Phi_1 | \Phi_6 \rangle = (S_{ab}^2 S_{ac} - S_{ac}^2); \qquad \langle \Phi_6 | \Phi_9 \rangle = (1 - S_{ac})S_{ab}^2;$$

$$\langle \Phi_1 | \Phi_9 \rangle = (1 - S_{ac})S_{ab}^2; \text{ and } \langle \Phi_9 | \Phi_9 \rangle = (1 - S_{ac}^2)$$

........(VII.39)

The one-electron parts of the Hamiltonian matrix are

$$\langle \Phi_1 | \sum_i h_m(i) | \Phi_1 \rangle = \langle s_a | h_m | s_a \rangle - 2S_{ab}\langle s_a | h_m | s_b \rangle$$

$$+ \langle s_b | h_m | s_b \rangle + (1 - S_{ab}^2)\langle s_c | h_m | s_c \rangle$$

$$< \Phi_1 | \sum_i h_m(i) | \Phi_6 > = S_{ab}S_{ac} < s_a | h_m | s_b > - S_{ac}^2 < s_b | h_m | s_b >$$
$$+ (S_{ab}^2 - 2S_{ac}) < s_a | h_m | s_c > + S_{ab}S_{ac} < s_b | h_m | s_c >$$

$$< \Phi_1 | \sum_i h_m(i) | \Phi_9 > = S_{ab}^2 (< s_a | h_m | s_a > - < s_a | h_m | s_c >)$$
$$- S_{ab}S_{ac} (< s_a | h_m | s_b > + < s_b | h_m | s_c >)$$
$$+ 2S_{ab} < s_b | h_m | s_c >$$

$$< \Phi_6 | \sum_i h_m(i) | \Phi_6 > = (1 - S_{ab}^2) < s_a | h_m | s_a > + < s_b | h_m | s_b >$$
$$+ < s_c | h_m | s_c > - 2S_{ab} < s_b | h_m | s_c >$$

$$< \Phi_6 | \sum_i h_m(i) | \Phi_9 > = (2S_{ab} - S_{ab}S_{ac}) < s_a | h_m | s_b > - S_{ab}^2 < s_a | h_m | s_c >$$
$$- S_{ab}S_{ac} < s_b | h_m | s_c > + S_{ab}^2 < s_c | h_m | s_c >$$

$$< \Phi_9 | \sum_i h_m(i) | \Phi_9 > = < s_a | h_m | s_a > + (1 - S_{ac}^2) < s_b | h_m | s_b >$$
$$- 2S_{ac} < s_a | h_m | s_c > + < s_c | h_m | s_c > .$$
$$\text{........(VII.40)}$$

Similarly, the two-electron parts of the Hamiltonian matrix are

$$< \Phi_1 | \sum_{i<j} r_{ij}^{-1} | \Phi_1 > = < s_a s_a | s_b s_b > + < s_a s_a | s_c s_c > + < s_b s_b | s_c s_c >$$
$$-2S_{ab} < s_a s_b | s_c s_c > - < s_a s_b | s_a s_b >$$

$$< \Phi_1 | \sum_{i<j} r_{ij}^{-1} | \Phi_6 > = S_{ac} (< s_a s_b | s_b s_c > - 2 < s_a s_c | s_b s_b >)$$
$$+ S_{ab} (< s_a s_b | s_a s_c > + < s_a s_c | s_b s_c >) - < s_a s_c | s_a s_c$$

$$< \Phi_1 | \sum_{i<j} r_{ij}^{-1} | \Phi_9 > = < s_b s_c | s_b s_c > - S_{ac} < s_a s_b | s_b s_c >$$
$$+ S_{ab} (2 < s_a s_a | s_b s_c > - < s_a s_b | s_a s_c > - < s_a s_c | s_c s_b$$

$$< \Phi_6 | \sum_{i<j} r_{ij}^{-1} | \Phi_6 > = < s_a s_a | s_b s_b > + < s_a s_a | s_c s_c > + < s_b s_b | s_c s_c >$$
$$-2S_{ab} < s_a s_a | s_b s_c > - < s_b s_c | s_b s_c >$$

$$< \Phi_6 | \sum_{i<j} r_{ij}^{-1} | \Phi_9 > = < s_a s_b | s_a s_b > - S_{ac} < s_a s_b | s_b s_c >$$
$$+ S_{ab} (2 < s_a s_b | s_c s_c > - < s_a s_b | s_a s_c > - < s_a s_c | s_b s_c >$$

$$< \Phi_9 | \sum_{i<j} r_{ij}^{-1} | \Phi_9 > = < s_a s_a | s_b s_b > + < s_a s_a | s_c s_c > + < s_b s_b | s_c s_c >$$
$$-2S_{ac} < s_a s_c | s_b s_b > - < s_a s_c | s_a s_c > .$$
$$\text{........(VII.41)}$$

Finally, substituting equations (VII.39) to (VII.41) into equation (VII.38) determines the energies of the ground states of the systems.

The Quadramer: Square Configuration.

In the Diatomics-In-Molecules theory (Chapter V), the ground state energy for the square configuration is given by

$$\mathcal{E}_{elec.}({}^3A_{2g}) = \langle \Phi | H_{model} | \Phi \rangle / \langle \Phi | \Phi \rangle \qquad \text{........(VII.42)}$$

where
$$\mathcal{H}_{model} = 4\,\mathcal{H}^{AB}_{model} + 2\,\mathcal{H}^{AC}_{model} - 8\,\mathcal{H}^{A}_{model}$$
(cf. equation (V.23))

$$\Phi = \Phi_2 - \Phi_5 ,$$

$$\Phi_2 = 24^{-1/2}(s_a^+ s_c^+ s_b^- s_d^-) ; \qquad \Phi_5 = 24^{-1/2}(s_b^+ s_d^+ s_a^- s_c^-).$$

In the Heitler-London formalism, the lowest two states of the dimer, AB, are represented by the following functions:

$${}^3\Sigma_u^+ : \quad \tilde{\Phi}_1^{AB} = | s_a^+ s_b^+ | = A_{AB}[s_a^+ s_b^+]$$

$$\tilde{\Phi}_2^{AB} = A_{AB}[s_a^+ s_b^-] - A_{AB}[s_b^+ s_a^-]$$

$$\tilde{\Phi}_3^{AB} = | s_a^- s_b^- | = A_{AB}[s_a^- s_b^-]$$

$${}^1\Sigma_g^+ \quad \tilde{\Phi}_4^{AB} = A_{AB}[s_a^+ s_b^-] + A_{AB}[s_b^+ s_a^-] \qquad \text{....(VII.43)}$$

Analogous expressions hold for the corresponding states of the diatomic, AC.

Now

$$\langle \Phi | \mathcal{H}_{model} | \Phi \rangle = 4 \langle \Phi | \mathcal{H}^{AB}_{model} | \Phi \rangle + 2 \langle \Phi | \mathcal{H}^{AC}_{model} | \Phi \rangle - 8 \langle \Phi | \mathcal{H}^{A}_{model} | \Phi \rangle \qquad \text{........(VII.44)}$$

where

$$\langle \Phi | \mathcal{H}^{AB}_{model} | \Phi \rangle = \int \Phi^* A^{(AB)}_{AB}\, \mathcal{H}^{AB}_{model}\, A_{AB}\, A_{(AB)}[\phi]\, d\underline{x} ,$$

Writing $[\phi] = s_a^+ s_c^+ s_b^- s_d^- - s_b^+ s_d^+ s_a^- s_c^-$, then

$$A_{AB}\, A_{(AB)}[\phi] = | s_a^+ s_b^- || s_c^+ s_d^- | - | s_b^+ s_a^- || s_d^+ s_c^- | .$$

From equation (VII.43), it is easily shown that

$$A_{AB}\,A_{(AB)}[\,\phi\,] \;=\; 0.5(\,\tilde{\Phi}_2^{AB} + \tilde{\Phi}_4^{AB})|\,s_c^+ s_d^-\,| \;+\; 0.5(\,\tilde{\Phi}_2^{AB} - \tilde{\Phi}_4^{AB})|\,s_d^+ s_c^-\,| \;.$$

Thus,

$$\begin{aligned}\mathcal{H}^{AB}_{model}\,A_{AB}\,A_{(AB)}[\,\phi\,] \;=\;& 0.5\;\mathcal{E}_{elec.}(^3\Sigma_u^+;R_{ab})\;\tilde{\Phi}_2^{AB}\,|\,s_c^+ s_d^-\,| \\ &+ 0.5\;\mathcal{E}_{elec.}(^1\Sigma_g^+;R_{ab})\;\tilde{\Phi}_4^{AB}\,|\,s_c^+ s_d^-\,| \\ &+ 0.5\;\mathcal{E}_{elec.}(^3\Sigma_u^+;R_{ab})\;\tilde{\Phi}_2^{AB}\,|\,s_d^+ s_c^-\,| \\ &- 0.5\;\mathcal{E}_{elec.}(^1\Sigma_g^+;R_{ab})\;\tilde{\Phi}_4^{AB}\,|\,s_d^+ s_c^-\,|\end{aligned}$$

........(VII.45)

where $\mathcal{E}_{elec.}(^1\Sigma_g^+;R_{ab})$ and $\mathcal{E}_{elec.}(^3\Sigma_u^+;R_{ab})$ are the ground singlet and excited triplet eigenvalues for the dimer, AB, at the internuclear distance corresponding to the separation, R_{ab}, in the square.

Using equation (VII.43) again, equation (VII.45) becomes

$$\begin{aligned}&\mathcal{H}^{AB}_{model}\;A_{AB}\,A_{(AB)}[\,\phi\,] \\ &= 0.5\,\mathcal{E}_{elec.}(^3\Sigma_u^+;R_{ab})\;(\;|\,s_a^+ s_b^-\,||\,s_c^+ s_d^-\,| - |\,s_b^+ s_a^-\,||\,s_c^+ s_d^-\,| \\ &\qquad\qquad + |\,s_a^+ s_b^-\,||\,s_d^+ s_c^-\,| - |\,s_b^+ s_a^-\,||\,s_d^+ s_c^-\,|\;) \\ &\quad + 0.5\,\mathcal{E}_{elec.}(^1\Sigma_g^+;R_{ab})\;(\;|\,s_a^+ s_b^-\,||\,s_c^+ s_d^-\,| + |\,s_b^+ s_a^-\,||\,s_c^+ s_d^-\,| \\ &\qquad\qquad - |\,s_a^+ s_b^-\,||\,s_d^+ s_c^-\,| - |\,s_b^+ s_a^-\,||\,s_d^+ s_c^-\,|\;)\end{aligned}$$

and

$$\begin{aligned}&A^{(AB)}_{AB}\,\mathcal{H}^{AB}_{model}\;A_{AB}\,A_{(AB)}[\,\phi\,] \\ &\quad= 0.5\,\mathcal{E}_{elec.}(^3\Sigma_u^+;R_{ab})\;(\,(\,\Phi_2 - \Phi_5\,) + (\,\Phi_3 - \Phi_4\,)\,) \\ &\quad\;+ 0.5\,\mathcal{E}_{elec.}(^1\Sigma_g^+;R_{ab})\;(\,(\,\Phi_2 - \Phi_5\,) - (\,\Phi_3 - \Phi_4\,)\,)\end{aligned}$$

........(VII.46)

$(\,\Phi_3 - \Phi_4\,)$ is as defined by equations (VII.9) and (VII.10). Finally, therefore,

$$\begin{aligned}&<\Phi\,|\mathcal{H}^{AB}_{model}|\,\Phi> \\ &\quad= 0.5(\,\mathcal{E}_{elec.}(^3\Sigma_u^+;R_{ab}) + \mathcal{E}_{elec.}(^1\Sigma_g^+;R_{ab})\,)<\Phi\,|\,\Phi>\end{aligned}$$

........(VII.47)

since $(\,\Phi_2 - \Phi_5\,)$ and $(\,\Phi_3 - \Phi_4\,)$ are orthogonal by symmetry.

Similarly,

$$<\Phi\,|\mathcal{H}^{AC}_{model}|\,\Phi> \;=\; \mathcal{E}_{elec.}(^3\Sigma_u^+;R_{ac})<\Phi\,|\,\Phi>$$

and

$$<\Phi\,|\mathcal{H}^{A}_{model}|\,\Phi> \;=\; \mathcal{E}_{at.}<\Phi\,|\,\Phi> \qquad ....(VII.48)$$

where $\mathcal{E}_{at.}$ is the valence state eigenvalue for the free atom.

By combining equations (VII.42), (VII.44), (VII.47) and (VII.48), the ground state energy for the square configuration is then represented by

$$E_{elec.}({}^3A_{2g}) = 2\,E_{elec.}({}^3\Sigma_u^+; R_{ab}) + 2\,E_{elec.}({}^1\Sigma_g^+; R_{ab}) + 2\,E_{elec.}({}^3\Sigma_u^+; R_{ac}) - 8\,\mathcal{E}_{at.} \qquad \text{........(VII.49)}$$

It is noted that, in this case, there is no need for the additional assumption of neglecting the atomic overlap integrals.

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CHAPTER VIII.

DISCUSSION.

Binding Energy.

The electrostatic theorem of Hellmann (1937) and Feynman (1939) provides a most convenient formulation for the discussion of the structural properties of possible configurations for aggregates of univalent atoms. According to this theorem, the classical force acting on the μ-th nucleus of the structure is given by

$$\mathcal{F}_\mu = -\langle \Psi | (\partial H / \partial \underline{R}_\mu) | \Psi \rangle$$

$$= Z_\mu \left\{ \int \rho_1(\underline{r}_1 | \underline{r}_1)\, \underline{r}_{\mu 1}\, dv_1 / r_{\mu 1}^3 - \sum_{\nu(\neq\mu)} Z_\nu \underline{R}_{\mu\nu} / R_{\mu\nu}^3 \right\}$$

........(VIII.1)

where the Hamiltonian operator, H , is defined by

$$H = \sum_i^N \left(-\nabla_i^2/2 - \sum_\mu Z_\mu / r_{\mu i} \right) + \sum_{i<j}^N r_{ij}^{-1} + \sum_{\mu<\nu} Z_\mu Z_\nu R_{\mu\nu}^{-1}.$$

Ψ is the electronic wavefunction for the state of the system being investigated and for which, it is assumed, the Hellmann-Feynman theorem holds (Deb (1973)). All other quantities are as defined previously.

An immediate consequence of equation (VIII.1) is that the formation of a stable polyatomic structure is accompanied by a build-up of electronic charge in specific regions or directions in order to counterbalance the internuclear forces. In particular, for a cluster of given size, the most stable isomeric form will be one in which the above cementatory force is largest.

In the single-determinant independent-particle model, it is possible to rewrite equation (VIII.1) in the form

$$\mathcal{F}_\mu = Z_\mu \left[\sum_i m_i \underline{f}_{\mu i} - \sum_{\nu(\neq\mu)} Z_\nu \underline{R}_{\mu\nu} / R_{\mu\nu}^3 \right]$$

........(VIII.2)

where $\underline{f}_{\mu i} = \langle \psi_i | (\underline{r}_\mu / r_\mu^3) | \psi_i \rangle$

and the first summation is over the set of molecular orbitals defining the single-determinantal function, Ψ ; m_i(m_i= 1, 2) is the occupation number of the i-th orbital of the set.

Equation (VIII.2) shows that, in this model, the electronic binding force is a sum of orbital contributions. Furthermore, it provides a pictorial understanding of the cementation of the nuclei by the electron-nuclear attractive forces arising from the charge distribution in each occupied molecular orbital. This equation also forms the mathematical basis of the following qualitative discussion of the relative stability of the various structures considered in the previous chapter.

The Trimer.

There are two possible shapes for this system: linear and bent. Using the LCAO-MO formalism, it was possible to obtain pictorial descriptions of the occupied molecular orbitals for the linear and equilateral triangular isomers. Figure (VII.1) shows the charge distributions arising from these states.

For the linear isomer, the lowest energy orbital is the nodeless $1\sigma_g$. The highest occupied orbital is the $1\sigma_u$ which has a nodal plane perpendicular to the nuclear plane and passing through the central nucleus. Symmetry considerations then indicate that the internuclear forces and the binding forces arising from the electronic distribution in each occupied orbital are both directed along the molecular axis and, therefore, an equilibrium is possible.

For the equilateral system, there is one doubly-occupied nodeless a_1'-orbital and one singly-occupied doubly-degenerate e'-orbital. It is immediately seen that the charge distribution in the e'-orbital does not effectively counterbalance the internuclear forces which, by symmetry, are directed along the three two-fold symmetry axes. This suggests that this system and, indeed, all triangular structures will be less stable than the linear form.

However, there is a more profound reason for the instability of the equilateral configuration. This arises from the non-symmetrical nature of the e'-charge distribution which, in turn, implies a non-equivalent electronic environment for the three spatially equivalent nuclei (Clinton et. al. (1959)). Thus, if the forces on the nuclei A and C are zero, those on the nucleus B will be finite since the internuclear forces are symmetric.

The above predictions are in agreement with the results of ab initio calculations reported to date (Pickup et. al. (1972); Liu (1973)).

The Quadramer.

There are many possible structures for the quadramer. Of these, only five have been investigated in this research. They are shown in Figures (VII.2) to (VII.7), along with pictorial descriptions of the charge distributions arising from the corresponding sets of occupied orbitals.

For the square configuration, there is one doubly-occupied nodeless a_{1g}-orbital and one doubly-occupied, doubly-degenerate e_u-level; each member of the degenerate pair has a nodal plane and is assumed to be singly-occupied. The symmetry of the e_u-orbitals prohibits a build-up of electronic charge along the diagonals of the square (Figure (VII.2)) and thus the corresponding binding force will not be large.

For the tetrahedron, there will be one doubly-occupied a_1-orbital and two singly-occupied orbitals from the triply-degenerate t_2-level. The latter do not permit charge build-up in the directions (along the diagonals of the circumscribing cube) to counterbalance the internuclear forces. This result, in conjunction with the larger value of the nuclear repulsion forces, suggests that the tetrahedral structure will be less stable than the square. Moreover, as explained in the case of the equilateral triangular structure, the partial occupancy of the t_2-level results in an asymmetric charge distribution and the intrinsic instability of the tetrahedral isomer.

For the linear structure, each of the most stable σ_g- and σ_u-orbitals will be doubly-occupied. The smaller internuclear forces and the symmetry of the charge distribution in each of these orbitals indicate that the binding forces will be larger than for the square and the tetrahedron. Hence, the linear is expected to be the most stable of the three.

For the T - (or Y -) shaped configuration, it is expected that each of the lowest two a_1-orbitals will be doubly-occupied; their charge distributions are shown schematically in Figure (VII.6). The total binding force will be slightly smaller than for the linear structure owing to the slightly less efficient counterbalancing of the internuclear repulsions.

A lengthening of two opposite sides of the square removes the degeneracy of the e_u-level and produces a rectangular structure. In the ground state, the lowest a_g- and b_{3u}-orbitals are each expected to be doubly-occupied. Their charge distributions, shown schematically in Figure (VII.7), are expected to compensate for the decreased nuclear interactions in a more efficient manner and result, therefore, in the increased stability of this structure relative to the square.

The above qualitative discussion indicates the following order of increasing energy for the structures investigated:

linear < T - shaped < rectangular < square < tetrahedral.

It is to be expected that the various structures will have different equilibrium internuclear separations; the weaker the binding force, the larger will the separation be. These differences will most certainly influence the relative energies of the various isomers but not the overall conclusions arrived at earlier. Thus far, these conclusions have indeed been corroborated by quantitative investigations on hydrogen (Gimarc (1970)) and on sodium (Chapter VII).

Larger Clusters.

Application of the above qualitative theory to some possible isomeric forms for larger clusters leads to the following conclusions concerning their relative stability:

Pentamer: linear < pentagon (Jahn-Teller active)
< rectangular pyramid < square pyramid (J-T active)
< triangular bipyramid < trigonal bipyramid (J-T active)

Hexamer: linear < hexagon < rectangular bipyramid
< square bipyramid < octahedron (Jahn-Teller active)

Septamer: linear < pentagonal bipyramid

Octamer: linear < cube

Nonamer: linear < body-centred cubic

The above predictions may, at first sight, appear rather strange. Indeed, they are in complete opposition to the classical concepts of bonding and emphasize an important difference between classical and quantal systems. Thus, for example, the predicted instability of the cubic and body-centred cubic structures relative to the corresponding linear forms may be traced to the fact that electrons obey the Pauli exclusion principle. This principle may be stated in the following form (Slater (1939)): for a given range of momenta, there is a maximum possible density of electrons in coordinate space. The net effect of this is that the majority of the valence charge lies outside the volumes enclosed by the cubic and body-centred cubic structures (Figures (VII.11) and (VII.12)). Consequently, the charge distributions are not effective in counterbalancing the large nuclear repulsion forces inherent in such configurations.

Experimental and all available theoretical evidence, however, indicates that, with the exception of the dimer, the abovementioned clusters will, at best, have small binding energies and may readily dissociate into smaller and more stable species. This, in turn, indicates the necessity of including some description of the distortion and polarization effects within such systems, when attempting to determine the relative stability of various isomeric forms and, more important, the relative stability of clusters of different sizes. Thus, it is expected that the inclusion of p-type orbitals in the Extended Basis calculation, or any similar improvements upon the Minimal Basis formalism (Chapter VI), will be necessary in any quantitative description of these small systems.

Using the insight gained from the above qualitative analysis, it appears possible to suggest a definite trend in the relative stability of some of the possible isomeric forms for clusters consisting of larger numbers of atoms. The number of possible isomers increases very rapidly with the size of the agglomerate but there is not, as yet, any established method for predicting its value. In spite of this, experience does indicate that three-dimensional structures will gradually become the most stable and important of all possible isomers as the number of atoms in the aggregate increases.

It is impossible at this stage to give a definite answer as to why and when this transition does occur. It is hoped, however, that the following argument will provide a useful framework within which the answers to these questions may be sought.

As the size of the cluster increases, structures can be formed in which additional atoms (surface atoms) will be distributed peripherally around an inner core of interior atoms. Thus, for example, a body-centred cubic configuration consisting of thirty-five atoms can be considered to have twenty-six surface and nine interior atoms. The nuclear repulsion forces for such configurations will be much greater than those for the corresponding linear or two-dimensional isomers. Simultaneously, the occupied orbitals for the more symmetrical systems are expected to permit an increasingly larger proportion of the valence charge to be distributed inside the volumes enclosed by the structures, owing to the large number of degenerate states and the much lower nuclear potential fields associated with such complexes. In particular, a low potential field counters the ' dispersive ' influence of the Pauli exclusion principle. Consequently, it seems reasonable to expect that the electronic binding forces in the more symmetrical, three-dimensional structures will increase very rapidly. This increase, being much larger than that in other isomers, will tend to make these configurations the most stable for large aggregates.

It is also expected that the abovementioned behaviour of the enthalpy of dissociation will be reflected in the variation of other conformational properties with cluster size. Thus, there is expected to be a gradual decrease of the interatomic separation and increase of the high-frequency limit, arising from the breathing or stretching vibrational modes, accompanying the increasing stability of the three-dimensional structures. Corresponding variations for the other configurations will more quickly approach their limiting values, which are expected to be respectively larger and smaller than the values for the bulk material.

The recent interest shown in the structure of small groups of hydrogen and alkali-metal atoms has again spotlighted the rather unique properties of hydrogen systems. It is hoped that investigation of such systems may, for example, give some physical insight into ' Why should an agglomerate of sodium atoms have metallic properties, while an agglomerate of hydrogen atoms has not ? ' Wigner and Huntington (1935) have investigated the conditions under which a metallic form of hydrogen would exist and concluded that it was possible at room temperature under a sufficiently high pressure.

Recently Roach and Baybutt (1970) have shown that the presence of the core electrons in alkali-metal systems is directly responsible for the decrease in ionization potential (Table (VIII.1)) on going from the monomer to dimer. There is an increase for the corresponding

Table (VIII.1).

H : 13.60[1]	Li : 5.39	Na , 5.14		K : 4.34	Cs , 3.89
H_2 : 15.50[2]	Li_2 : 5.15	Na_2 : 4.90	NaK : 4.50	K_2 : 4.00	Cs_2 : 3.80
H_3 : 10.10[2]	Li_3 :	Na_3 : 3.90	NaK_2 : 3.40	K_3 : 3.40	Cs_3 : 3.20
			Na_2K : 3.60		
		Na_4 : 4.20	Na_2K_2 : 4.10	K_4 : 3.60	Cs_4 . 3.20

Ionization Potential (e.V.) of Clustered Monovalent Atoms.

[Data taken from Foster P.J., Leckenby R.E. and Robbins E.J. (1969) J. Phys. B2, 478
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	Dissociation Energy (e.V.)	Bond Lengths (Angstroms)
H_2	4.45	0.75
Li_2	1.74	2.67
Na_2 (1)	0.73	3.08
K_2	0.51	3.91
NaK (1)	0.62	

Dissociation Energies and Bond Lengths of Monovalent Atoms Dimers.

[Data taken from Slater J.C. (1939) Introduction To Chemical Physics, p.132, McGraw-Hill, New York and (1) Roach A.C. and Baybutt P. (1970) Chem. Phys. Lett. 7, 7.]

Table (VIII.2).

hydrogen series. Moreover, bonding in alkali-metal dimers is substantially weaker than in the hydrogen molecule, as indicated by the results given in Table (VIII.2).

The only reported investigation on alkali-triatomics by Pickup et. al. (loc. cit.) suggests that they, like the corresponding hydrogen system, are unstable with respect to the dimer plus monomer complex. However, their classical activation energies are much smaller than that for the hydrogen system:

$$W_{Tot.}(H_2+H) - W_{Tot.}(H_3) = -9.8 \text{ kcal. mole}^{-1}$$

$$W_{Tot}(Na_2+Na) - W_{Tot.}(Na_3) = -1.2 \text{ kcal. mole}^{-1}$$

$$W_{Tot.}(K_2+K) - W_{Tot.}(K_3) = -0.8 \text{ kcal. mole}^{-1} \qquad \text{........(VIII.3)}$$

(The results for sodium and potassium clusters are deduced from the data given by Pickup B. T. and Byers Brown W. (1972) Mol. Phys. 23, 1189. Data for the hydrogen system is taken from the article by Liu B. (1973) J. Chem. Phys. 58, 1925.)

Although the above results on the alkali systems can only be accepted with some reservations (the model employed was found to fail when applied to lithium, rubidium and caesium systems and, furthermore, neglected all polarization and correlation effects), the assumption, made by Leckenby et. al. (1968), that the large reduction in the ionization potential of the trimer implies a fairly strong bond between the monomer and dimer appears to be somewhat inaccurate. This can be seen quite clearly by considering the following equation:

$$I(M_2) - I(M_3) = W_{Tot.}(M_2^+) - W_{Tot.}(M_2) - W_{Tot.}(M_3^+) + W_{Tot.}(M_3)$$

or

$$I(M_2) - I(M_3) = -\left[W_{Tot.}(M_2) + W_{Tot.}(M) - W_{Tot.}(M_3)\right] + \left[W_{Tot.}(M_2^+) + W_{Tot.}(M) - W_{Tot.}(M_3^+)\right] \qquad \text{........(VIII.4)}$$

In this equation, the bracketed expressions respectively measure the bond energies of the systems M-M_2 (equation (VIII.3)) and M-M_2^+ (linear symmetric configuration). The bond energies for the latter are given by

$$W_{Tot.}(H_2 + H^+) - W_{Tot.}(H_3^+) = 104.1 \text{ kcal. mole}^{-1}$$

$$W_{Tot.}(Na_2^+ + Na) - W_{Tot.}(Na_3^+) = 15.5 \text{ kcal. mole}^{-1}$$

$$W_{Tot.}(K_2^+ + K) - W_{Tot.}(K_3^+) = 11.9 \text{ kcal. mole}^{-1} \quad \text{........(VIII.5)}$$

(Data for hydrogen is deduced from the article by Poshusta R. D. and Zetik D. F. (1973) J. Chem. Phys. 58, 118.)

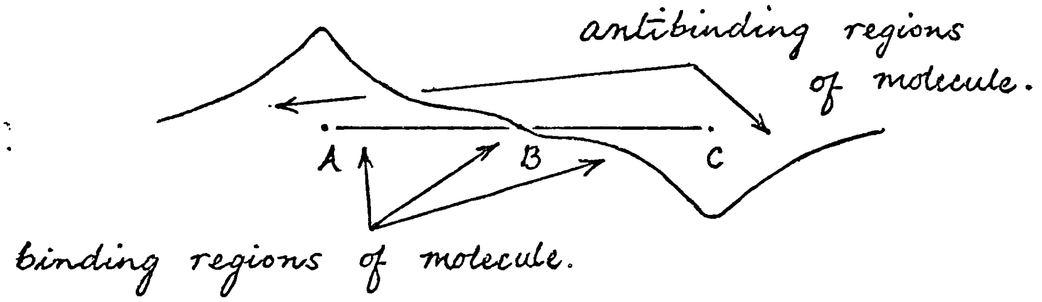
Thus, it is seen from equation (VIII.4) that the difference in the ionization potentials of the dimer and trimer cannot be used to make any definite statement about the strength of the M-M_2 bond without prior knowledge of the M-M_2^+ system.

As a result of the experimental and theoretical investigations performed thus far on clusters of univalent atoms, it may be concluded that

1. the electrons of the hydrogen systems move in lower potential fields, due to the absence of any core electrons, than those of the corresponding metal systems. This is consistent with the results of equation (VIII.5) and Table (VIII.2).
2. The classical activation energy for the monomer-dimer-trimer complex is much smaller for the alkali than for the hydrogen systems (Equation (VIII.3)). Also, progression from the dimer to the trimer is accompanied by a reduction in ionization potential owing to the build-up of charge in the antibinding regions (Figure (VIII.1)) of the structure (Table (VIII.1)); this change appears to be greatest for the hydrogen series. The lower binding energy per atom of the trimer is also due primarily to the instability of the highest occupied orbital.

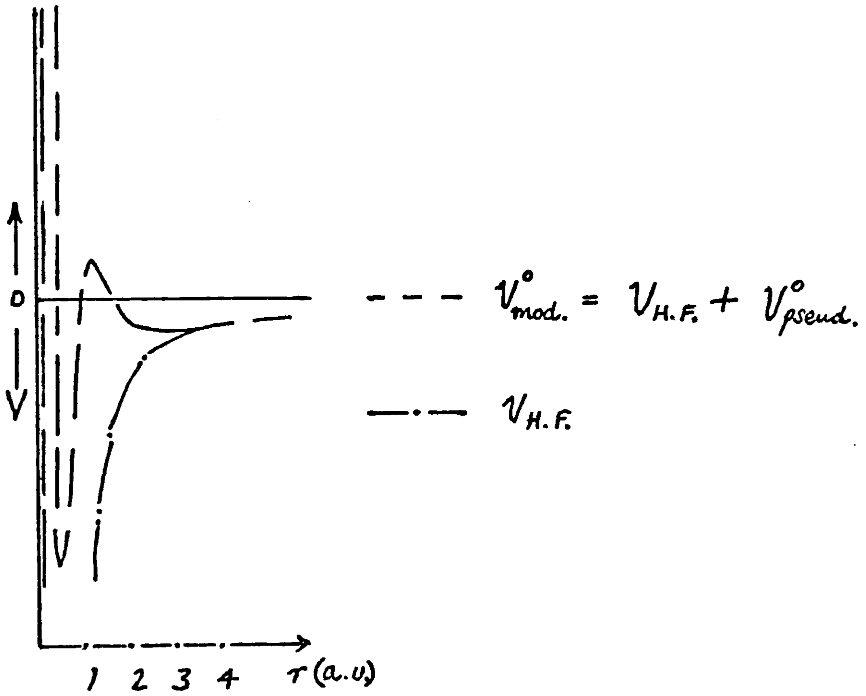
Thus far, the presence of the core electrons has been shown to be the main cause of the decreased stability of the valence states of the alkali-metal monomer and dimer relative to those for hydrogen. Their presence also appears to indirectly reduce the destabilizing effect of

Figure (VIII. 1).



Schematic Representation Of The Highest Occupied Orbital For The Trimer, Along the Molecular Axis.

Figure (VIII. 2).



Schematic Reproduction Of An Accurate Plot given by L. Szasz and G. McGinn (J. Chem. Phys. 47, 3495 (1967)) showing the Effect Of the Core-Electrons On the Valence 3S-State in Sodium, assuming Phillips-Kleinman formalism.

the antibonding orbital mentioned in the previous paragraph, thereby accounting for the smaller reductions in ionization potentials for, and the smaller activation energies of, the metal systems.

As shown in Figure (VIII.2), the size and spatial variation of the nuclear (or core) potential field are greatest in the regions near the nuclei. In the interatomic regions of an aggregate, their magnitudes will depend on the atomic separations but are generally smaller than in the core regions. In this connection, a major difference between hydrogen and other univalent atoms is immediately apparent. The presence of the core electrons forces the valence charge to be predominantly in regions where the potential energy is low (in absolute value) and slowly varying. This exclusion effect arises on account of the Pauli exclusion principle and is evidenced by the occurrence of large potential barriers in Figure (VIII.2). Consequently, the separation in orbital energy of two states which differ mainly in their charge distributions will be much smaller for the alkali-metals than for hydrogen.

These considerations, besides providing some physical understanding of the abovementioned results of quantitative analysis on trimer systems, also explains the ability of alkali atoms to form lattice structures whereas hydrogen forms a molecular solid. The rather strongly localized nature of the occupied states and the very large energy gap between these and the more delocalized, excited states indicate that, under normal conditions, a molecular solid composed of hydrogen atoms will be an insulator. A decrease in the size and spatial variation of the interatomic potential field by application of an external pressure will result in a rapid decrease in orbital-energy separation and a movement towards a metallic form of hydrogen, as discussed by Wigner and Huntington (loc. cit.).

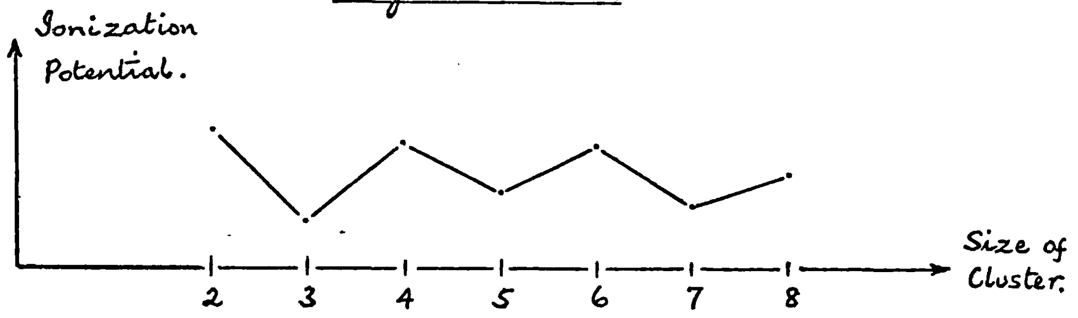
The above interpretation of the metallic bond may be compared with the unsynchronized ionic-covalent resonance concept used by Pauling (1960) and Slater (1951).

Electronic Energy Levels.

In the Molecular Orbital formalism, some indication concerning the chemical behaviour which will be exhibited by a cluster of given size and isomeric form may be obtained from an analysis of the molecular orbitals and associated energy levels of the system. Experience gained from quite exhaustive investigations performed on atomic, molecular and solid bulk systems further suggests that this behaviour will be governed mainly by the properties of the highest occupied and lowest unoccupied orbitals. The following is a brief discussion of some of the important chemical properties of the small clusters studied earlier.

By tracing the changing properties of the highest occupied orbital as the size of the cluster increases, it is possible to determine qualitatively the variation of the Fermi level and ionization potential with cluster size. This is shown schematically in Figure (VIII.3) below for linear structures.

Figure (VIII. 3)



The variation of Ionization Potential with Size for linear clusters.

The schematic representations, shown in Figure (VIII.4), of the charge distribution in each of the occupied orbital states for linear chains of N-atom clusters ($2 \leqslant N \leqslant 9$) forms the basis for the arguments used in deriving the above variation. It is assumed that the energy level scheme is (see Chapter VII): $1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 3\sigma_g$.

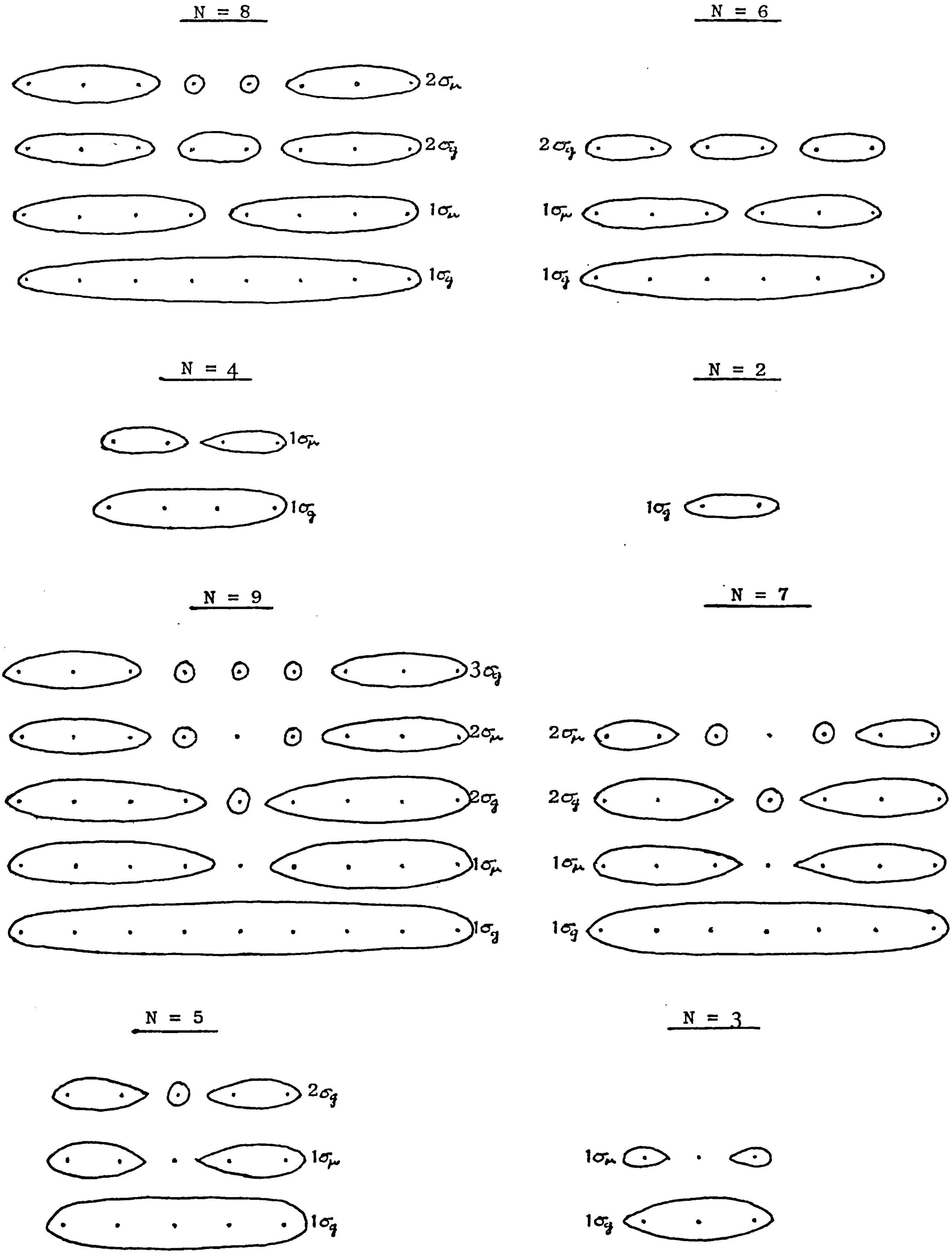


Figure (VIII. 4)

Orbital charge density distributions for linear clusters.

As shown above, qualitative analysis indicates a decreasing trend in ionization potential with cluster size; this results from the occupancy of increasingly less stable orbital states. Superimposed upon this trend is an oscillatory variation, depending upon whether the clusters consist of even or odd numbers of atoms. The former systems tend to have higher ionization potentials because of the relatively smoother spatial variation (lower kinetic energy) of their highest occupied orbitals.

As the size of the cluster increases, however, it is expected that this oscillation will become less pronounced and that the ionization potential will tend to some fixed limiting value coinciding with that for the polygonal isomers. The following argument appears to justify such expectations.

For very long linear clusters, electrons in the highest occupied or ' lowest unoccupied ' orbitals can be shown to have small probabilities of being near either end of the chain. Simultaneously, those atoms which are well away from the ends become spatially identical. Thus, it appears that the imposition of cyclic boundary conditions will not seriously affect the main properties of such chains (cf. Born-Von Karman treatment of perfect solids). Under such conditions, the linear chain may be considered as part of a larger aggregate having a polygonal structure.

As shown by Slater (1963), the spread in energy of the molecular orbitals for such a system is independent of the size of the cluster; in the Molecular Orbital formalism, it depends only upon the amount of overlapping of the atomic orbitals centred on the atoms constituting the ring. With increasing cluster size, the angles of the polygon will approach 180 degrees and, provided that the interatomic separation remains fixed, the spread in orbital energies will remain unchanged. There will therefore be a gradual decrease in the energy differences between orbital states. In particular, there is a decrease in the energy of separation between the highest occupied and lowest unoccupied molecular states. The energy of the highest occupied orbital state will also approach a definite limit.

This discussion so far has been concerned with linear chains for N-atom clusters. For the corresponding three-dimensional structures, it is expected that the spread in orbital energies will be larger than for the linear or polygonal isomers; the bonding orbitals will have lower energies mainly because of the lower potential fields due to the more symmetrical nuclear frameworks, whereas the antibonding states will be less stable mainly because of their higher kinetic energies. Also, as the size of the agglomerate becomes very large, the width of the energy level spectrum is expected to tend to some fixed value which depends solely upon the particular stable configuration. The energy of the highest occupied orbital for three-dimensional systems will depend very sensitively upon the symmetry of the structure. Thus, besides providing regions of low potential energy as mentioned above, highly symmetrical structures will permit larger numbers of the electrons of the system to occupy low energy states because of degeneracy. The variation of ionization potential with cluster size will, therefore, be much more erratic for these isomers than for the linear ones. Furthermore, its value is expected to be in general smaller, and to converge to a smaller limiting value, than that for the corresponding linear and polygonal forms.

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CHAPTER IX.

INTEGRAL EVALUATION.

In this and the following chapter, some of the computational and practical aspects of this research are briefly considered. The importance of such considerations need hardly be stressed for, although it may be theoretically possible to perform completely rigorous calculations on any conceivable system, definite restrictions are placed upon the accuracy of any investigation of this nature by the inherent computational and practical difficulties. Indeed, this is the reason for choosing some simplified model possessing, it is hoped, the essential physics of the infinitely more complicated system it represents.

This chapter is concerned mainly with the method of computation of the various integrals required. The practical aspect of the problem is considered in the following chapter.

One-Electron Integrals .

These are the Overlap, Kinetic and Potential Energy integrals over the chosen set of basis functions. They are defined by the following equations:

$$<\mu,i\ |\ \nu,j> = \int \chi_i^{\mu}(r_{\mu 1})\ \chi_j^{\nu}(r_{\nu 1})\ \underline{dr_1}\ ; \qquad \text{Overlap}$$

$$<\mu,i\ |(-\nabla_1^2/2)|\ \nu,j> = -0.5\int \chi_i^{\mu}(r_{\mu 1})\ \nabla_1^2\ \chi_j^{\nu}(r_{\nu 1})\,\underline{dr_1};\text{Kinetic Energy}$$

and

$$<\mu,i\ |(\sum_{\lambda} \rho_{core}^{\lambda}(r_{\lambda 1})/r_{\lambda 1})\ \ |\ \nu,j> = \int \chi_i^{\mu}(r_{\mu 1})(\sum_{\lambda} \rho_{core}^{\lambda}(r_{\lambda 1})/r_{\lambda 1})\,\chi_j^{\nu}(r_{\nu 1})\,\underline{dr_1}$$

Potential Energy

........(IX.1)

where

$\chi_i^{\mu}(r_{\mu 1})$ is a Slater orbital (Chapter VI) specified by the index, i , centred on the point, μ ;

$\rho_{core}^{\lambda}(r_{\lambda 1})/r_{\lambda 1}$ is the potential at any point due to the core electrons and nuclear charge on the centre at the point, λ ;

and $\sum_{\lambda}$ denotes a summation over all the centres of the molecular configuration.

An approximate expression for $\rho^{\lambda}_{core}(r_{\lambda 1})$ is derived in equations (IX.17) and (IX.20) of this chapter.

The particular method used for the evaluation of the above integrals depended upon the number of centres involved; that is, upon the positions of the points μ , ν and λ . In particular, all the Overlap, Kinetic and Potential integrals involving one centre only were evaluated using the following analytical expressions:

$$
\begin{aligned}
<\mu,i\,|\mu,j> &= \delta(s_i,s_j)\ \delta(m_i,m_j)\ \delta(l_i,l_j)\ S_{ij} \\
<\mu,i\,|(-\nabla_1^2/2)|\mu,j> &= \delta(s_i,s_j)\ \delta(m_i,m_j)\ \delta(l_i,l_j)\ T_{ij} \\
<\mu,i\,|(\rho^{\mu}_{core}(r_{\mu 1})/r_{\mu 1})|\mu,j> &= \delta(s_i,s_j)\ \delta(m_i,m_j)\ \delta(l_i,l_j)\ U_{ij}(\mu)
\end{aligned}
$$

........(IX.2)

where each Slater orbital, χ_i^{μ} , is specified by the parameters n_i , l_i , $|m_i|$, α_i and s_i (equation (VI.22)).

The quantities S_{ij}, T_{ij} and $U_{ij}(\mu)$ are defined by the equations:

$$
\begin{aligned}
S_{ij} &= \int_0^{\infty} R_{n_i}(r)\ R_{n_j}(r)\ r^2\ dr \quad ; \\
T_{ij} &= \int_0^{\infty} r^2\ R_{n_i}(r)\ [-1/2\ d^2/dr^2 - 1/r\ d/dr + l_j(l_j+1)/2r^2]\ R_{n_j}(r)\ dr\ ; \\
U_{ij}(\mu) &= \int_0^{\infty} R_{n_i}(x)\ \rho^{\mu}_{core}(x)\ R_{n_j}(x)\ x\ dx \quad ,
\end{aligned}
$$

where

$$
\begin{aligned}
\rho^{\nu}_{core}(x) &= -Z_{\nu} + \sum_i^{(\nu)} \rho_i^{\nu}(x) \quad , \\
\rho_i^{\nu}(x) &= \omega_i^{\nu}\ [1 - \exp(-2\alpha_i^{\nu}x) \sum_{k=0}^{2n_i^{\nu}-1} (2\alpha_i^{\nu}x)^k (1 - k/2n_i^{\nu})/k!\ ]
\end{aligned}
$$

........(IX.3)

Z_{ν} is the nuclear charge on centre, ν ; ω_i^{ν} is the occupation number of the i-th core shell on the centre, ν , and $\sum_i^{(\nu)}$ denotes summation over the core shells on the centre, ν (see section at the end of chapter).

Expressions for S_{ij} and T_{ij} are given in the article by Roothaan and Bagus (1963). Similar analysis gives

$$v_{ij}(\mu) = -\left[V_{2n_i}(\alpha_i)\,V_{2n_j}(\alpha_j)\right]^{-1/2}\Big[\; Z^{eff}_{\mu}\, V_{n_i+n_j-1}(\alpha_i+\alpha_j)$$

$$+ \sum_{p}^{(\mu)} \omega^{\mu}_{p} \sum_{k=0}^{2n^{\mu}_{p}-1} \frac{(2\alpha^{\mu}_{p})^{k}(1-k/2n^{\mu}_{p})\,V_{n_i+n_j+k-1}(2\alpha^{\mu}_{p}+\alpha_i+\alpha_j)}{k!}\Big]$$

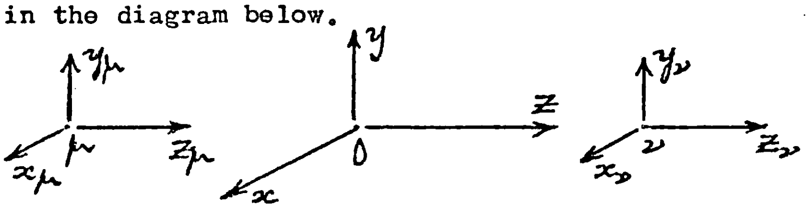
where $V_i(x) = i!\,x^{-i-1}$; z^{eff}_{μ} is the net charge of the core electrons and nuclear charge on the centre at the point, μ .

All the other many-centre integrals were evaluated numerically by Gauss-Legendre or Gauss-Laguerre quadrature. The Kinetic Energy integrals were determined indirectly by relating them to certain Overlap integrals. Thus, following Harris and Michels (1967),

$$\begin{aligned} <\mu;\, n_i, l_i, \alpha_i|(-\nabla^2/2)|\nu;\, n_j, l_j, \alpha_j> = \\ -0.5(n_j(n_j - 1) - l_j(l_j + 1)) <\mu;\, n_i, l_i, \alpha_i|\nu;\, (n_j - 2), l_j, \alpha_j> \\ + n_j\alpha_j <\mu;\, n_i, l_i, \alpha_i|\nu;\, (n_j - 1), l_j, \alpha_j> \\ -0.5\,\alpha_j^2 <\mu;\, n_i, l_i, \alpha_i|\nu;\, n_j, l_j, \alpha_j> \end{aligned} \qquad \text{........(IX.4)}$$

The coordinate system used in determining the many-centred integrals depended upon whether the points, μ and ν , the origins of the basis functions, coincided or not. In the former case, the many-centred Potential Energy integrals were evaluated using spherical polar coordinates*, defined relative to the system of cartesian axes at the common orbital centre.

When the points, μ and ν , were distinct, all the Overlap and Potential Energy integrals were computed using ellipsoidal coordinates. This system was defined with the points, μ and ν , as foci and with the set of cartesian axes at each focus being mutually parallel, as in the diagram below.



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* This coordinate system was chosen in preference to an ellipsoidal one in order to avoid the problem of redefining the axes for each point, λ (equation (IX.1)), as would have been necessary if the latter system had been used.

It was implicitly assumed that each of the local cartesian coordinate systems, for example, the system (x_μ, y_μ, z_μ) at the point, μ, was originally chosen to be parallel to that (the global cartesian coordinate system) in which the molecular configuration was defined. In general, therefore, it was necessary to rotate each of the local systems at μ and ν to obtain the situation depicted in the above diagram.

Two-Electron Integrals.

These are defined most generally by the equation

$$< ij \mid kl > = \iint \chi_i^{\mu}(r_{\mu 1})\, \chi_j^{\nu}(r_{\nu 1})\, r_{12}^{-1}\, \chi_k^{\lambda}(r_{\lambda 2})\, \chi_l^{\sigma}(r_{\sigma 2})\, d\tau_1\, d\tau_2 \qquad \text{........(IX.5)}$$

The above integrals may be divided into two broad categories:

1.) one-centre, and

2.) many-centre two-electron integrals.

Each category of integrals was evaluated differently, as explained below.

1.) One-Centre Integrals.

These were computed directly over Slater orbitals using the analytical expression:

$$\begin{aligned} < ij \mid kl > = {} & \sum_{p=0}^{\infty} R^p(ijkl)\, \omega_p^0(l_i,m_i;\, l_j,m_j)\, \omega_p^0(l_k,m_k;\, l_l,m_l) \\ & \qquad \delta(m_i,m_j)\, \delta(m_k,m_l)\, \delta(s_i,s_j)\, \delta(s_k,s_l) \\ & + 2 \sum_{p=1}^{\infty} R^p(ijkl) \sum_{q=1}^{p} \omega_p^q(l_i,m_i;\, l_j,m_j)\, \omega_p^q(l_k,m_k;\, l_l,m_l) \\ & \times \big[C_q(|m_i|,s_i;\, |m_j|,s_j)\, C_q(|m_k|,s_k;\, |m_l|,s_l) \\ & \qquad + S_q(|m_i|,s_i;\, |m_j|,s_j)\, S_q(|m_k|,s_k;\, |m_l|,s_l) \big] \end{aligned} \qquad \text{........(IX.6)}$$

with

$$R^p(ijkl) = \int_0^{\infty} dr_1\, r_1^{-p+1} \int_0^{r_1} dr_2\, r_2^{p+2}\, (1+P(1,2))\, R_{n_i}(r_1) R_{n_j}(r_1) \times R_{n_k}(r_2) R_{n_l}(r_2)$$

where P(1,2) permutes the subscripts, 1 and 2 ;

$$\omega_p^q(l,m;r,s) = \sqrt{\frac{(p-|q|)!}{(p+|q|)!}(2l+1)\frac{(l-|m|)!}{(l+|m|)!}(2r+1)\frac{(r-|s|)!}{(r+|s|)!}}$$

$$\times (1/2)\int_{-1}^{1} P_l^{|m|}(x)\, P_p^{|q|}(x)\, P_r^{|s|}(x)\ dx \quad ;$$

$$C_q(|m|,s;|m|,t) = \pi^{-1}\int_0^{2\pi} f(s,|m|\phi)\cos|q|\phi\, f(t,|m|\phi)\ d\phi ,$$

$$S_q(|m|,s;|m|,t) = \pi^{-1}\int_0^{2\pi} f(s,|m|\phi)\sin|q|\phi\, f(t,|m|\phi)\ d\phi ,$$

and $f(s, |m|\phi) = 1, \cos|m|\phi , \sin|m|\phi$

if $s = 0, 1$ and 2 respectively (Chapter VI).

........(IX.7)

R^p(ijkl) was determined using the formula of Roothaan and Bagus (loc. cit.) and ω_p^q(l,m;r,s) by the method quoted by Slater (1960).

2.) Many-Centre Integrals.

Although Slater type orbitals have become the natural basis functions for use in molecular calculations, considerable difficulty occurs in the evaluation of the general many-centre integrals met during the investigation of polyatomic systems. Boys (1950) has pointed out the considerable simplification which can be made if such integrals were evaluated instead over a certain class of Gaussian functions. The above simplification arises mainly because the product of any two of these Gaussian orbitals centred upon distinct points can be expressed as a third Gaussian centred upon a third point (Taketa et. al. (1966)).

However, in the description of molecules, a Gaussian function has two serious defects as compared to a Slater orbital. These are

1.) failure to describe the electron density at the nucleus upon which it is centred; and

2.) failure to describe the electron density at large distances from its ' parent ' nucleus.

In molecular calculations, the above inadequacies of the Gaussian functions have been overcome in one of two ways:

1.) A basis set consisting of a very large number of Gaussian orbitals with very large and very small exponents was used. This had the disadvantage that, although it was relatively simple to evaluate all the necessary integrals, the number of unique integrals was greatly increased. In particular, the number of two-electron integrals to be processed in each cycle of the self-consistent field procedure (Chapters IV and X) was very large.

2.) A basis set consisting of a number of ' contracted ' functions, defined as linear combinations of Gaussian orbitals, was used. Each contracted function may be chosen to represent as closely as possible a much more physically appealing function; for example, a Slater type orbital. In such a contracted basis set, the number of basis functions is smaller and consequently the number of integrals will be fewer. However, the disadvantage of the contraction method is the resultant loss in flexibility of the basis set since, for the same number of Gaussian orbitals as originally employed, there are now fewer variationally determined coefficients. More explicitly, using a basis set of m contracted functions formed from N ($N > m$) Gaussian orbitals, there are only m linear coefficients to be determined for each molecular orbital by the self-consistent field procedure as compared to the original number, N , of the previous scheme. However, the number of two-electron integrals ($\sim m^4$) required for the variational procedure is much smaller than the original number ($\sim N^4$).

As mentioned earlier, a contracted function is usually formed to represent some other function (Huzinaga (1965); Allen (1962)). There are two main methods of obtaining such representations. These are:

1.) Variational Method (McWeeny (1953)).

The contracted function is chosen to be an approximate eigenfunction of some Hamiltonian. Thus, for example, the normalized

Slater orbital, defined by

$$\chi^{S}_{n_s l m}(r) = R^{S}_{n_s}(r) Y_{l,m}(\theta,\phi) \quad ,$$

where

$$R^{S}_{n_s}(r) = [(2n_s)!]^{-1/2} (2Z/n_s)^{n_s+1/2} \, r^{n_s-1} \, e^{-Zr/n_s}$$

and $Y_{l,m}(\theta,\phi)$ are the normalized spherical harmonics, satisfy the following equations for any value of Z :

$$H_S \chi^{S}_{n_s l m} = E_S \chi^{S}_{n_s l m} \quad ,$$

where

$$H_S = -\nabla^2/2 - Z/r - [l(l+1) - n_s(n_s-1)]/2r^2$$

$$E_S = -0.5\,(Z/n_s)^2 \qquad \text{........(IX.8)}$$

A linear combination of Gaussian type orbitals, defined by

$$\chi^{G}_{i,nlm}(r) = R^{G}_{i,n}(r) Y_{l,m}(\theta,\phi),$$

$$R^{G}_{i,n}(r) = 2^{n+1} [(2n-1)!!]^{-1/2} (2\pi)^{-1/4} \alpha_i^{(2n+1)/4} \, r^{n-1} \, e^{-\alpha_i r^2} \qquad \text{........(IX.9)}$$

where $(2n-1)!! = (2n-1)(2n-3).......5.3.1$,

and (n - 1) is an ODD number (n > 1)*, is then chosen to satisfy the variational theorem (Chapter II) for the operator, H_S , defined above.

The main disadvantage of this method is that the inadequate form of the Gaussian orbitals is emphasized since the largest contribution to the energy functional of the variational equation comes from an ' intermediate ' region in space (McWeeny (loc. cit.)). The best fit of the Slater orbital by the contracted function therefore occurs in such a region instead of over all space.

---

* This latter restriction is imposed in order to select only those Gaussian orbitals over which the many-centred integrals may be easily performed.

2.) Least Square Method (Taketa et. al. (loc. cit.)).

The Gaussian expansion for a Slater orbital is given by

$$\chi^{S}_{nlm}(\eta, r) \doteq \sum_{i=1}^{N} c_i \, \chi^{g}_{i,nlm}(\alpha_i, r) ,$$

........(IX.10)

where N is the number of Gaussians in the expansion. It is noted that the orbitals on both sides of the above equation have the same angular dependence.

The present method varies from the former by the manner in which the expansion coefficients $\{c_i\}$ and exponent parameters $\{\alpha_i\}$ are determined; here they are found by a least-square fitting technique.

There is an important Scaling Theorem associated with the expansion of equation (IX.10). This theorem states that, if the series,

$$\sum_{i} c_i \, \chi^{g}_{i}(\alpha_i) ,$$

represents a Slater orbital with unit exponent parameter, then the expansion for the Slater orbital having an exponent parameter of arbitrary value, η , is

$$\sum_{i} c_i \, \chi^{g}_{i}(\eta^2 \alpha_i) .$$

The proof of this theorem is given in the relevant section at the end of this chapter.

The above theorem implies that it is sufficient to have the ' standard ' expansions of Slater orbitals with unit exponent parameters.

The essence of the least-square fitting procedure is to minimize the Error Function,

$$V(\eta; c_i, \alpha_i) = \int \left| \chi^{S}_{nlm}(\eta, r) - \chi(c_i, \alpha_i; r) \right|^2 d\underline{v}$$

$$+ \nu \left(1 - \int \chi^{*} \chi \, d\underline{v} \right) ,$$

where $\chi(c_i, \alpha_i; r) = \sum_{i} c_i \, \chi^{g}_{i,nlm}(\alpha_i, r)$; ..(IX.11)

ν is a Lagrangian Multiplier and the integration is performed over all space, with respect to the series parameters $\{\alpha_i, c_i\}$ (Stewart (1969, 1970)).

In evaluating the many-centred two-electron integrals, each Slater orbital was expanded in terms of four Gaussians. The expansion coefficients and orbital exponents were taken from the tables of Stewart (1970), where there are given for an orbital with unit exponent. The integral evaluation was then performed over Gaussians using the formulae given by Taketa et. al. (loc. cit.). The equation relating the integrals over Slater orbitals to those over Gaussians is

$$< ij \mid kl > (\text{Slater}) =$$

$$\sum_{r,s,t,u} C_{ir} C_{js} C_{kt} C_{lu} < rs \mid tu > (\text{Gaussian}) \qquad \ldots\ldots\ldots(\text{IX.12})$$

The necessity of performing many summations, as in equation (IX.12) above, may often offset the advantages accruing from the special properties of Gaussian orbitals for integral computation. The article of Huzinaga (1967) may be referred to for further discussions on this point as well as for a general review of molecular integral evaluation.

The above has been a brief discussion of some of the basic philosophy underlying the programmes developed by the Theoretical Chemistry Department of Sheffield University under Professor R. McWeeny and used in this research.

APPENDIX.

In the following sections, further consideration is given to the evaluation of the core potential of equation (IX.1) and the approximate representation of the inter-core effects. Also, the Least Square Method for constructing contracted Gaussian functions is discussed in somewhat greater detail.

In this section, the expression for the potential due to the i-th core shell, with occupation number, ω_i^ν , at a point, r_ν , from the centre, ν , is derived. This is given by

$$e_i^\nu(r_\nu)/r_\nu = 4\pi N_i^\nu \omega_i^\nu \, [\, (\int_0^{r_\nu} \chi_i^{\nu *}(x) \, \chi_i^\nu(x) \, x^2 \, dx \,)/r_\nu + \int_{r_\nu}^{\infty} \chi_i^{\nu *}(x) \, \chi_i^\nu(x) \, x \, dx \,]$$

........(IX.13)

where χ_i^ν is the radial function of the i-th core shell on centre, ν .

To represent the above radial function, an s-type Slater orbital is chosen. Thus,

$$\chi_i^\nu(r_\nu) = r_\nu^{\,n_i^\nu - 1} \exp(-\alpha_i^\nu r_\nu)$$

........(IX.14)

and the normalization constant, $(N_i^\nu)^{1/2}$, is given by

$$N_i^\nu = (2\alpha_i^\nu)^{2n_i^\nu + 1} / \, 4\pi (2n_i^\nu)!$$

........(IX.15)

Equations (IX.13) and (IX.14) then give

$$e_i^\nu(r_\nu)/r_\nu = 4\pi N_i^\nu \omega_i^\nu \, [\, r_\nu^{-1} \int_0^{r_\nu} x^{2n_i^\nu} e^{-2\alpha_i^\nu x} \, dx + \int_{r_\nu}^{\infty} x^{2n_i^\nu - 1} e^{-2\alpha_i^\nu x} \, dx \,]$$

$$= 4\pi N_i^\nu \omega_i^\nu \, [\, r_\nu^{-1} ((2n_i^\nu)!/(2\alpha_i^\nu)^{2n_i^\nu + 1} - e^{-2\alpha_i^\nu r_\nu} \sum_{p=0}^{2n_i^\nu} \frac{(2n_i^\nu)!\,(2\alpha_i^\nu r_\nu)^{2n_i^\nu - p}}{(2\alpha_i^\nu)^{2n_i^\nu + 1}\,(2n_i^\nu - p)!} + e^{-2\alpha_i^\nu r_\nu} \sum_{p=0}^{(2n_i^\nu - 1)} \frac{(2n_i^\nu - 1)!\,(2\alpha_i^\nu r_\nu)^{2n_i^\nu - p}}{(2\alpha_i^\nu)^{2n_i^\nu + 1}\,(2n_i^\nu - p - 1)!}) \,]$$

where the formulae

$$\int_0^b x^n e^{-\alpha x}\,dx = n!/\alpha^{n+1} - \alpha^{-n-1} e^{-\alpha b} \sum_{r=0}^{n} n!\,(\alpha b)^{n-r}/(n-r)!$$

$$\int_b^{\infty} x^n e^{-\alpha x}\,dx = \alpha^{-n-1} e^{-\alpha b} \sum_{r=0}^{n} n!\,(\alpha b)^{n-r}/(n-r)!$$

........(IX.16)

have been used.

Therefore, by combining the terms in the summations,

$$\rho_i^\nu(r_\nu) = 4\pi N_i^\nu \omega_i^\nu (2n_i^\nu)!\,(2\alpha_i^\nu)^{-2n_i^\nu-1}$$

$$\times \left[1 - e^{-2\alpha_i^\nu r_\nu}\left(1 + \sum_{p=1}^{2n_i^\nu-1} \frac{(2\alpha_i^\nu r_\nu)^{2n_i^\nu-p}\,p}{2n_i^\nu(2n_i^\nu-p)!} \right) \right]$$

But $$4\pi N_i^\nu (2n_i^\nu)!\,(2\alpha_i^\nu)^{-2n_i^\nu-1} = 1$$

Therefore

$$\rho_i^\nu(r_\nu) = \omega_i^\nu \left[1 - e^{-2\alpha_i^\nu r_\nu} \sum_{p=1}^{2n_i^\nu} (2\alpha_i^\nu r_\nu)^{2n_i^\nu-p}\, p/2n_i^\nu(2n_i^\nu-p)! \right]$$

or

$$\rho_i^\nu(r_\nu) = \omega_i^\nu \left[1 - e^{-2\alpha_i^\nu r_\nu} \sum_{k=0}^{2n_i^\nu-1} (1-k/2n_i^\nu)(2\alpha_i^\nu r_\nu)^k/k! \right]$$

....(IX.17)

where equation (IX.15) has been used.

In the calculation of the total molecular energy of a polyatomic system, it is necessary to consider terms arising from the interaction of core electrons and nucleus on centre, λ , with the core electrons and nucleus on centre, ν . The interaction of the core electrons on any centre with themselves and with their parent nucleus is an additive atomic constant at all internuclear separations. Mathematically, the energy of the inter-core interactions is given by

$1s_A$	$2s_A$	$2p_A^x$	$2p_A^z$	$2p_A^y$	$1s_b$	$2s_b$	$2p_B^x$	$2p_B^z$	$2p_B^y$
1.000000	0.250761	0.000000	0.000000	0.000000	0.000000	0.000001	0.000000	-0.000007	0.000000
	1.000000	0.000000	0.000000	0.000000	0.000007	0.000164	0.000000	-0.000203	0.000000
		1.000000	0.000000	0.000000	0.000000	0.000000	0.000019	0.000000	0.000000
			1.000000	0.000000	0.000000	0.000203	0.000000	-0.000253	0.000000
				1.000000	0.000000	0.000000	0.000000	0.000000	0.000019
					1.000000	0.250761	0.000000	0.000000	0.000000
						1.000000	0.000000	0.000000	0.000000
							1.000000	0.000000	0.000000
								1.000000	0.000000
									1.000000

R_{ab} = 5.00 a.u.

Overlap Matrix For Core Orbitals on Centres A and B.

(Orbital Exponents as given by Clementi et. al. (1963))

Table (IX.1)

$$\mathcal{E}_{core-core} = \sum_{\lambda} \sum_{\nu(\neq\lambda)} \sum_{i}^{(\lambda)} \langle \chi_i^\lambda | -Z_\nu/r_\nu | \chi_i^\lambda \rangle$$

$$+ \sum_{\lambda>\nu} \sum_{i}^{(\lambda)} \sum_{j}^{(\nu)} \langle \chi_i^\lambda \chi_i^\lambda | \chi_j^\nu \chi_j^\nu \rangle$$

$$+ \sum_{\lambda>\nu} Z_\lambda Z_\nu / R_{\lambda\nu}$$

........(IX.18)

where $\sum_{i}^{(\lambda)}$ indicates summation over all core-electrons on centre, λ ; $\sum_{\nu}$ indicates a summation over all the centres of the system; $R_{\lambda\nu}$ is the separation between centres, λ and ν , and Z_ν is the nuclear charge on centre, ν .

In the above expression, the Exchange terms arising from the core-core interaction have been ignored since they are proportional roughly to the square of the overlap charge density between core-orbitals centred on different nuclei. These densities are expected to be negligibly small (Chapter VI and Table (IX.1)).

The summations over the core-electrons can be replaced by summations over the core shells and the use of the appropriate occupation number for each shell. Furthermore, the computation of the potential at any point arising from the core-electrons on any centre is greatly simplified by noting that each core shell has an exactly spherical charge distribution about its centre. This follows since the core states are assumed to be completely filled in accordance with the Pauli Exclusion Principle (Slater (1968)). Therefore, equation (IX.18) can be rewritten in the form

$$\mathcal{E}_{core-core} = \sum_{\lambda} \sum_{\nu(\neq\lambda)} \sum_{i}^{(\lambda)} \langle \chi_i^\lambda | \rho_{core}^{\nu}(r_\nu)/r_\nu | \chi_i^\lambda \rangle \, \omega_i^\lambda$$

$$+ \sum_{\lambda>\nu} Z_\lambda Z_\nu / R_{\lambda\nu}$$

........(IX.19)

where $\sum_{i}^{(\lambda)}$ now indicates summation over the core shells on centre, λ ; $e^{\nu}_{core}(r_\nu)/r_\nu$ is the potential at any point, distance r_ν from the centre, ν, arising from the core-electrons and the nucleus on this centre. It is given by the expression

$$e^{\nu}_{core}(r_\nu) = -Z_\nu + \sum_{i}^{(\nu)} e^{\nu}_{i}(r_\nu)$$

........(IX.20)

The expression for $e^{\nu}_{i}(r_\nu)$ is given in equation (IX.17).

Since the core-core interaction term consists of a series of two-centre integrals, its value may be computed most conveniently in ellipsoidal coordinates and the use of standard numerical integration techniques. Thus, consider any two centres, μ and ν. Assume that the potential energy of the i-th core shell of electrons on centre, μ, in the total field of the core-electrons and nucleus on centre, ν, is to be computed. Then, from equation (IX.19), this is given by

$$\mathcal{E}_{i}^{\mu\nu} = N_{i}^{\mu}\,\omega_{i}^{\mu} \int r_\mu^{2(n_i^\mu-1)}\, e^{-2\alpha_i^\mu r_\mu}\, e^{\nu}_{core}(r_\nu)/r_\nu \,\underline{dv}$$

........(IX.21)

Substituting $r_\nu = 0.5R_{\mu\nu}(\xi - \eta)$

$r_\mu = 0.5R_{\mu\nu}(\xi + \eta)$

$$\underline{dv} = (R_{\mu\nu}/2)^3(\xi^2-\eta^2)\,d\xi\,d\eta\,d\phi\ ,$$

where

$$1 \leqslant \xi \leqslant \infty\ ;\ -1 \leqslant \eta \leqslant 1\ ;\ 0 \leqslant \phi \leqslant 2\pi\ ,$$

into equation (IX.21) gives

$$\mathcal{E}_{i}^{\mu\nu} = N_i^\mu\,\omega_i^\mu\,(R_{\mu\nu}/2)^3\,(R_{\mu\nu}/2)^{2(n_i^\mu-1)}\,(R_{\mu\nu}/2)^{-1}$$
$$\times \int_0^{2\pi}\int_{-1}^{1}\int_{1}^{\infty}(\xi^2-\eta^2)(\xi+\eta)^{2(n_i^\mu-1)}(\xi-\eta)^{-1}$$
$$e^{-R_{\mu\nu}\alpha_i^\mu(\xi+\eta)}\,e^{\nu}_{core}\ d\xi\,d\eta\,d\phi$$

or

$$\mathcal{E}_i^{\mu\nu} = 2\pi\, N_i^{\mu}\, \omega_i^{\mu}\, (R_{\mu\nu}/2)^{2n_i^{\mu}} \times \int_{-1}^{1}\int_{1}^{\infty} (\zeta+\eta)^{2n_i^{\mu}-1}\, e^{-R_{\mu\nu}\alpha_i^{\mu}(\zeta+\eta)}\, \varrho_{core}^{\nu}\, d\zeta\, d\eta$$

with

$$\varrho_{core}^{\nu} \equiv \varrho_{core}^{\nu}\left(R_{\mu\nu}(\zeta-\eta)/2 \right) \qquad \text{........(IX.22)}$$

In order to bring the integral of equation (IX.22) into a form where Gaussian integration techniques may be employed in its evaluation, the transformation

$$x = R_{\mu\nu}\,\alpha_i^{\mu}(\zeta-1)$$ is made.

Then

$$\mathcal{E}_i^{\mu\nu} = C_i^{\mu\nu} \int_{-1}^{1}\int_{0}^{\infty} (\eta+1+x/R_{\mu\nu}\alpha_i^{\mu})^{2n_i^{\mu}-1}\, e^{-x}\, e^{-R_{\mu\nu}\alpha_i^{\mu}\eta}\, \varrho_{core}^{\nu}\, dx\, d\eta \qquad \text{....(IX.23)}$$

$$\approx C_i^{\mu\nu} \sum_{l,m} A_l(x)\, A_m(\eta)\, f(x_l,\eta_m) \qquad \text{........(IX.24)}$$

with

$$f(x,\eta) = (1+\eta+x/R_{\mu\nu}\alpha_i^{\mu})^{2n_i^{\mu}-1}\, \varrho_{core}^{\nu}(x,\eta)\, e^{-R_{\mu\nu}\alpha_i^{\mu}\eta} \quad ;$$

$$C_i^{\mu\nu} = \pi\, N_i^{\mu}\, \omega_i^{\mu}\, (R_{\mu\nu}/2)^{2n_i^{\mu}-1} / \alpha_i^{\mu}\, e^{R_{\mu\nu}\alpha_i^{\mu}} \quad ;$$

$$\varrho_{core}^{\nu}(x,\eta) = -Z_{\nu} + \sum_{j}^{(\nu)} \varrho_j^{\nu}(x,\eta) \quad ;$$

$$\varrho_j^{\nu}(x,\eta) = \omega_j^{\nu}\left[1 - e^{-y} \sum_{k=0}^{2n_j^{\nu}-1} (1-k/2n_j^{\nu})\, y^k/k! \right] \quad ;$$

and

$$y = \alpha_j^{\nu}\left(x/\alpha_i^{\mu} + R_{\mu\nu}(1-\eta) \right) .$$

$A_l(x)$ and x_l are respectively the weights and points for the Gauss-Laguerre integration formula; $A_m(\eta)$ and η_m are respectively the weights and points for the Gaussian-Legendre integration formula.

The total interaction energy for centres, μ and ν, is then

$$\mathcal{E}^{\mu\nu} = \sum_{i}^{(\mu)} \mathcal{E}_i^{\mu\nu} \qquad \text{........(IX.25)}$$

This quantity was evaluated as a function of the separation parameter, $R_{\mu\nu}$, for a system of two SODIUM cores. The exponents for the core orbitals were taken from the tables of Clementi and Raimondi (1963) (equation (VI.21)).

$R_{\mu\nu}$ (a.u.)	$\varepsilon^{\mu\nu}$ (a.u.)	$R_{\mu\nu}^{-1}$
0.8	-1.384	1.250
1.0	-2.241	1.000
1.2	-1.289	0.833
1.4	-0.423	0.714
1.6	0.079	0.625
2.0	0.396	0.500
3.0	0.382	0.333
4.0	0.250	0.250
5.0	0.200	0.200
6.0	0.167	0.167
7.0	0.143	0.143

Table (IX.2)

Interaction Energy for two Sodium Cores.

The results are shown in the above table and compared with the expression for $\varepsilon^{\mu\nu}$ ($= R_{\mu\nu}^{-1}$), if it is assumed that the cores interact as point charges. Thus, it is concluded that the core interactions are determined quite accurately by the equation

$$\varepsilon^{\mu\nu}_{1} = R_{\mu\nu}^{-1} \qquad \text{.......(IX.26)}$$

in the region ($5.0 \leqslant R_{\mu\nu} \leqslant 7.0$) of investigation in this research (cf. equation (VI.6)).

In this final section, further consideration is given to the Least Square Method of determining contracted functions for representing Slater orbitals.

Proof Of Scaling Theorem.

Consider the Error Function:

$$V(\eta; c_i, \alpha_i) = \int | \chi^{S}_{nlm}(\eta, r) - \chi(c_i, \alpha_i; r) |^2 \, dv + \nu \left(1 - \int \chi^{*} \chi \, dv\right) \quad \text{........(IX.11)}$$

where $\chi(c_i, \alpha_i; r) = \sum_{i}^{N} c_i \, \chi^{g}_{i,n'lm}(\alpha_i, r)$.

As both the Slater and Gaussian orbitals have the same angular dependence, the integration over the angular coordinates may be performed to give

$$V(\eta; c_i, \alpha_i) = 1 - 2 \sum_{i}^{N} c_i \, P_i(\eta, \alpha_i) + \nu + (1 - \nu) \sum_{i,j}^{N} c_i c_j \, S_{ij} \quad ,$$

where

$$P_i(\eta, \alpha_i) = \int_0^{\infty} R^{S}_{n}(\eta, r) \, R^{g}_{i,n'}(\alpha_i, r) \, r^2 \, dr$$

and

$$S_{ij} = \int_0^{\infty} R^{g}_{i,n'}(\alpha_i, r) \, R^{g}_{j,n'}(\alpha_j, r) \, r^2 \, dr \quad \text{....(IX.27)}$$

Employing the definitions (equations (IX.8) and (IX.9)) for $R^{S}_{n}(\eta, r)$ and $R^{g}_{i,n'}(\alpha_i, r)$, then

$$P_i(\eta, \alpha_i) = A(n, n') \, \eta^{n+1/2} \, \alpha_i^{(2n'+1)/4} \int_0^{\infty} r^{n+n'} \, e^{-(\eta r + \alpha_i r^2)} \, dr$$

where

$$A(n, n') = [(2n)!]^{-1/2} \, [(2n'-1)!!]^{-1/2} \; 2^{(n+n'+5/4)} \; \pi^{-1/4} \quad .$$

Substituting $x = \eta r$, it is easily seen that

$$P_i(\eta, \alpha_i) = P_i(1, \alpha_i/\eta^2) \quad .$$

Similarly, it can be shown that

$$S_{ij}(\alpha_i, \alpha_j) = S_{ij}(\alpha_i/\eta^2, \alpha_j/\eta^2)$$

and thus

$$V(\eta; c_i, \alpha_i) = V(1; c_i, \alpha_i/\eta^2) \quad \text{........(IX.28)}$$

As mentioned before, the essence of the Least Square fitting methods is to minimize the Error Function with respect to the series parameters $\{\alpha_i, c_i\}$. The necessary condition for a minimum is

$$\varepsilon_j' = \partial V/\partial x_j = 0 \quad ; \qquad j = 1, 2, \ldots\ldots (2N + 1)$$

$$\ldots\ldots\ldots(IX.29)$$

where x_j(j = 1, 2, ... 2N) are the Gaussian parameters

and $x_{2N+1} = \nu$, the Lagrangian multiplier.

Following the procedure outlined by Stewart (1970), ε_j' is now expanded about a set of approximate parameters $\{x_j^o\}$ as follows:

$$\varepsilon_j' = \varepsilon_j'(\underline{x}^o) + \sum_k^{2N+1} (\partial\varepsilon_j'/\partial x_k)_{\underline{x}^o} \; \Delta x_k$$

$$j = 1, 2, \ldots\ldots (2N + 1)$$

$$\ldots\ldots\ldots(IX.30)$$

where $\underline{x}^o \equiv \{x_k^o\}$, $\underline{x} \equiv \{x_k\}$,

$$(\partial\varepsilon_j'/\partial x_k)_{\underline{x}^o} = (\partial\varepsilon_j'(\underline{x})/\partial x_k)_{\underline{x} = \underline{x}^o} ,$$

and $\Delta x_k = x_k - x_k^o$.

Combining equations (IX.29) and (IX.30), the condition for minimum then becomes

$$(\partial V/\partial x_j)_{\underline{x}^o} = - \sum_k^{2N+1} (\partial^2 V/\partial x_j \partial x_k)_{\underline{x}^o} \; \Delta x_k$$

$$j = 1, 2, \ldots (2N + 1)$$

$$\ldots\ldots\ldots(IX.31)$$

or in matrix form $\underline{B} = \underline{W}\,\underline{A}$ ....(IX.32)

where $\underline{B}$ is a column vector with elements

$$b_j(j \neq 2N+1) = \left(\int [\chi_{nlm}^S(\eta,\underline{r}) + (\nu-1)\chi(\alpha_i,c_i;\underline{r})](\partial\chi/\partial x_j)\, d\underline{r} \right)_{\underline{x}^o}$$

$$b_{2N+1} = 0.5\left(1 - \int |\chi(\alpha_i,c_i;\underline{r})|^2 d\underline{r}\right)_{\underline{x}^o} \; ;$$

$\underline{W}$ is a symmetrical matrix possessing elements given by

$$w_{j,k}(j,k \neq 2N+1) = (1-x_{2N+1}^o)\left[\int \frac{\partial\chi}{\partial x_j}\frac{\partial\chi}{\partial x_k}\, d\underline{r} + \int \chi \frac{\partial^2\chi}{\partial x_j \partial x_k}\, d\underline{r}\right]_{\underline{x}^o}$$

$$- \left[\int \chi_{nlm}^S \frac{\partial^2\chi}{\partial x_j \partial x_k}\, d\underline{r}\right]_{\underline{x}^o} ,$$

$$w_{j,2N+1} = \left[\int \chi (\partial \chi / \partial x_j) \, d\underline{v} \right]_{\underline{x}^0} \quad (j \neq 2N+1) \; ,$$

and $$w_{2N+1,2N+1} = 0 \; ;$$

$\underline{A}$ is a column vector whose elements are Δx_k.

Equation (IX.32) was then solved iteratively until the residues, $\underline{A}$, were zero. Then, if $\underline{W}$ was non-singular, $\underline{B}$ was zero and the necessary condition of equation (IX.29) automatically satisfied. Stewart (1970) also investigated the final $\underline{W}$-matrix and determined it to be positive definite which, in conjunction with equation (IX.29), provides the necessary and sufficient conditions that the Error Function has a minimum value.

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CHAPTER X.

MISCELLANEOUS.

Integral File Handling.

Any calculation in molecular quantum mechanics requires the handling of vast amounts of data. This is an essential part of the computation and hence a brief consideration is given to the methods used in this research.

One-Electron Integrals.

For a basis set consisting of M functions, the number of one-electron integrals evaluated was $0.5M(M + 1)$. This number may be further decreased by utilizing the conditions imposed by the symmetry of the particular molecular configuration. The storage and manipulation of these integrals was quite a straightforward procedure.

Two-Electron Integrals.

These form the bulk of the data required for each complete calculation. A general two-electron integral (equation (IX.5)), if stored in a straightforward manner, would require six computer words; four to contain the labels i , j , k and l and two for the value of the integral.

A reduction in the storage requirement for each integral can be made by using a method developed by the POLYATOM team (Csizmadia et. al. (1966)). The labels i , j , k and l have maximum values of M , the size of the basis set. A typical value of M is 64 or less. However, the maximum number of an integer variable which can be stored in one computer word of sixteen bits is typically 2^{24} or 2^{32} . There is, therefore, too much space for storing the integer labels. The principle is thus to use one computer word for storing more than one integer label. In fact, the six integer labels i , j , k , l , m and n (m and n are used for storing more information about the integral, as described later) are stored in two computer words on the IBM 1130 machine used here, so that the first four integers can take positive values from 1 to 63 , requiring six least significant bits each, and the last two positive values from 1 to 15, requiring four least significant bits each. Thus, the six integer labels require a total of thirty-two bits, which is exactly two sixteen-bit computer words. These two words can then be considered as the storage allocated for a real number, A say, and consequently each integral can be characterized by the two real numbers, A and V, its actual value.

The array, A, containing all the labels of the two-electron integrals required for a particular calculation, is stored on disc together with the array, V, which contains the associated integral values in the same order. When the integrals are needed, they can be read from the disc in blocks of any size. The numbers, A, are decoded into the original six numbers i, j, k, l, m and n and the associated integral value, V, can be used.

An obvious reduction in the number of two-electron integrals to be computed and stored can be made if the basis functions are all real, as is generally the case. Then, for a particular choice of i, j, k and l, there may be as many as eight integrals with the same value as $\langle ij \mid kl \rangle$. These are formed by permutation of the labels:

$$\begin{aligned} &\langle ij \mid kl \rangle = \langle ij \mid lk \rangle = \langle ji \mid kl \rangle = \langle ji \mid lk \rangle \\ &= \langle kl \mid ij \rangle = \langle lk \mid ij \rangle = \langle kl \mid ji \rangle = \langle lk \mid ji \rangle \end{aligned} \qquad \text{........(X.1)}$$

In practice, therefore, it is only necessary to compute and store one of these integrals, since the others may be obtained when required by the use of the appropriate permutation symmetry. In this way, the number of integrals to be stored is reduced from M^4 to $(1/8)M(M + 1)(M^2 + M + 2)$.

In order to determine which one of the above integrals (equation (X.1)) to compute and store, one of two ordering conventions may be used:

$$i \geqslant j \; ; \quad k \geqslant l \; ; \quad (ij) \geqslant (kl) \qquad \text{........(X.2)}$$

$$i \leq j \; ; \quad k \leq l \; ; \quad (ij) \leq (kl) \qquad \text{........(X.3)}$$

where $\quad (ij) = 0.5(i - 1)i + j$.

In this research, the former convention was used.

Molecular symmetry may also be used to decrease the number of integrals to be computed. In general, the effect of a symmetry operation is to send a basis function into a linear combination of the whole set but this has proved too complex to program. Thus, the only type of symmetry operations taken into account here are those which permute the labels i , j , k and l . However, care must be taken to ensure that the set of operations considered forms a subgroup of the group of symmetry operations for the molecule.

Consequently, only the permutationwise distinct integrals which are non-zero by symmetry are stored on disc, and only the distinct, permutationwise and symmetrywise, ones are actually evaluated. A further extension of this idea has been given by Dacre (1970).

The method of dealing with the two-electron integrals is then as follows:

1.) Create a list of labels, corresponding to the integrals which are non-zero on symmetry grounds. This list is stored in the array, A , together with dummy values for the actual integrals in the array, V . The input into this routine is a row vector containing the centres about which each basis function is defined, along with a matrix containing the transformation properties of all the basis functions under the subgroup of operations mentioned above. The routine then forms all the possible combinations of the four labels i , j , k and l , subject to the ordering convention of equation (X.2). Each such combination undergoes all the operations of the subgroup and each new set of labels satisfying the ordering convention is written in the list, together with the integer number: $m = 0$, 1 or 2 .

$m = 0$ indicates that the integral is unique and has to be evaluated.

m = 1 indicates that the integral has the same value as the integral being operated on by the operations of the subgroup.

m = 2 indicates that the integral is minus the value of the integral being operated on by the operations of the subgroup.

Those integrals which are zero by symmetry are ignored, and no integral label is listed more than once.

The output from the transformation part of the routine is a file on disc containing all the non-zero integral labels, each being followed by a dummy value for the particular integral. The complete information specifying each unique integral is immediately followed by similar information for those integrals which are related to the unique one by some symmetry operation.

The unique two-electron integrals are computed by one of two methods, as described in the previous chapter. The integer label, n , gives such information about each integral on the file. All the one-centre two-electron integrals were denoted by $n = 0$, and the many-centre ones by $n = 2$.

2.) Compute the values of the unique integrals and fill in the values for those which are related to them by symmetry. The order in which this is done is dictated by the order in which the integrals are stored on the file.

Solutions Of Roothaan's Equations.

The most general method adopted for the solution of a matrix eigenvalue equation is due to Jacobi (Householder (1964); John (1966)). Unfortunately, the most frequently occurring form of Roothaan's equation (cf. equation (IV.52))

$$\underline{h}\,\underline{c} = \varepsilon\,\underline{S}\,\underline{c} \qquad \ldots\ldots\ldots(X.4)$$

is not very suitable for solution by the Jacobi method. However, it is possible, by making the transformations

$$\underline{\tilde{c}} = \underline{S}^{1/2}\,\underline{c}$$

and $$\underline{\tilde{h}} = \underline{S}^{-1/2}\,\underline{h}\,\underline{S}^{-1/2} \quad , \qquad \ldots\ldots\ldots(X.5)$$

where $\underline{S}$ is the overlap matrix defined by equation (IV.38), to bring the above equation (X.4) into the convenient form

$$\underline{\tilde{h}}\,\underline{\tilde{c}} = \varepsilon\,\underline{\tilde{c}} \qquad \ldots\ldots\ldots(X.6)$$

In practice, therefore, the Hartree-Fock matrix, for example, for the closed-shell case:

$$\underline{h}^{f} = \underline{h} + \underline{G}(\,2\underline{R}\,)\ , \qquad \ldots\ldots\ldots(X.7)$$

is constructed and then transformed according to equation (X.5). On diagonalization, the matrix of eigenvectors, $\underline{\tilde{U}}$, is obtained and $\underline{R}_{new}$ constructed:

$$\underline{\tilde{R}}_{new} = \underline{\tilde{T}}\,\underline{\tilde{T}}^{+}\ ; \qquad \underline{R}_{new} = \underline{S}^{-1/2}\,\underline{\tilde{R}}_{new}\,\underline{S}^{-1/2}\ ,$$

where $\underline{\tilde{T}}$ is the occupied part of $\underline{\tilde{U}}$; that is, the matrix formed from those eigenvectors of $\underline{\tilde{U}}$ corresponding to the lowest 0.5N eigenvalues (see Chapter IV).

The new Hartree-Fock matrix for the next cycle of the iterative process is set up by means of equation (X.7), with

$$\underline{R} = \underline{R}_{old} + \gamma(\underline{R}_{new} - \underline{R}_{old})\ ,$$

where $\underline{R}_{old}$ is the $\underline{R}$ matrix of the previous cycle and γ is an arbitrary coefficient ($0.0 < \gamma \leq 1.0$).

This proceduro is repeated until self-consistency is obtained; that is, $\underline{R}_{new} = \underline{R}_{old}$.

In many cases, it is advantageous to incorporate the symmetry of the nuclear configuration from the outset in order to reduce the size of the Hartree-Fock matrix*. The problem then decomposes into a number of smaller ones for which the iterative procedure is less prone to convergence difficulties. The matrices relating the relevant quantities for the self-consistent field procedure in this case are as follows:

Assuming $\underline{\chi}^{(s.o)} = \underline{\chi}^{(a.o.)} \underline{Z}$

and defining $\underline{A}^2 = (\underline{Z}^+ \underline{S} \underline{Z})$,

then

$$\underline{\chi}^{(o.s.o.)} = \underline{\chi}^{(s.o.)} \underline{A}^{-1} = \underline{\chi}^{(a.o.)} \underline{Z} \underline{A}^{-1};$$

$$\underline{h}^{(o.s.o.)} = \underline{A}^{-1} \underline{h}^{(s.o.)} \underline{A}^{-1} = \underline{A}^{-1} \underline{Z}^+ \underline{h}^{(a.o.)} \underline{Z} \underline{A}^{-1};$$

and

$$\underline{R}^{(a.o.)} = \underline{Z} \underline{A}^{-1} \underline{R}^{(o.s.o.)} \underline{A}^{-1} \underline{Z}^+$$

where (s.o.), (o.s.o.) and (a.o.) indicate ' symmetry orbital ', ' orthogonalized symmotry orbital ' and ' atomic orbital ' bases, respectively.

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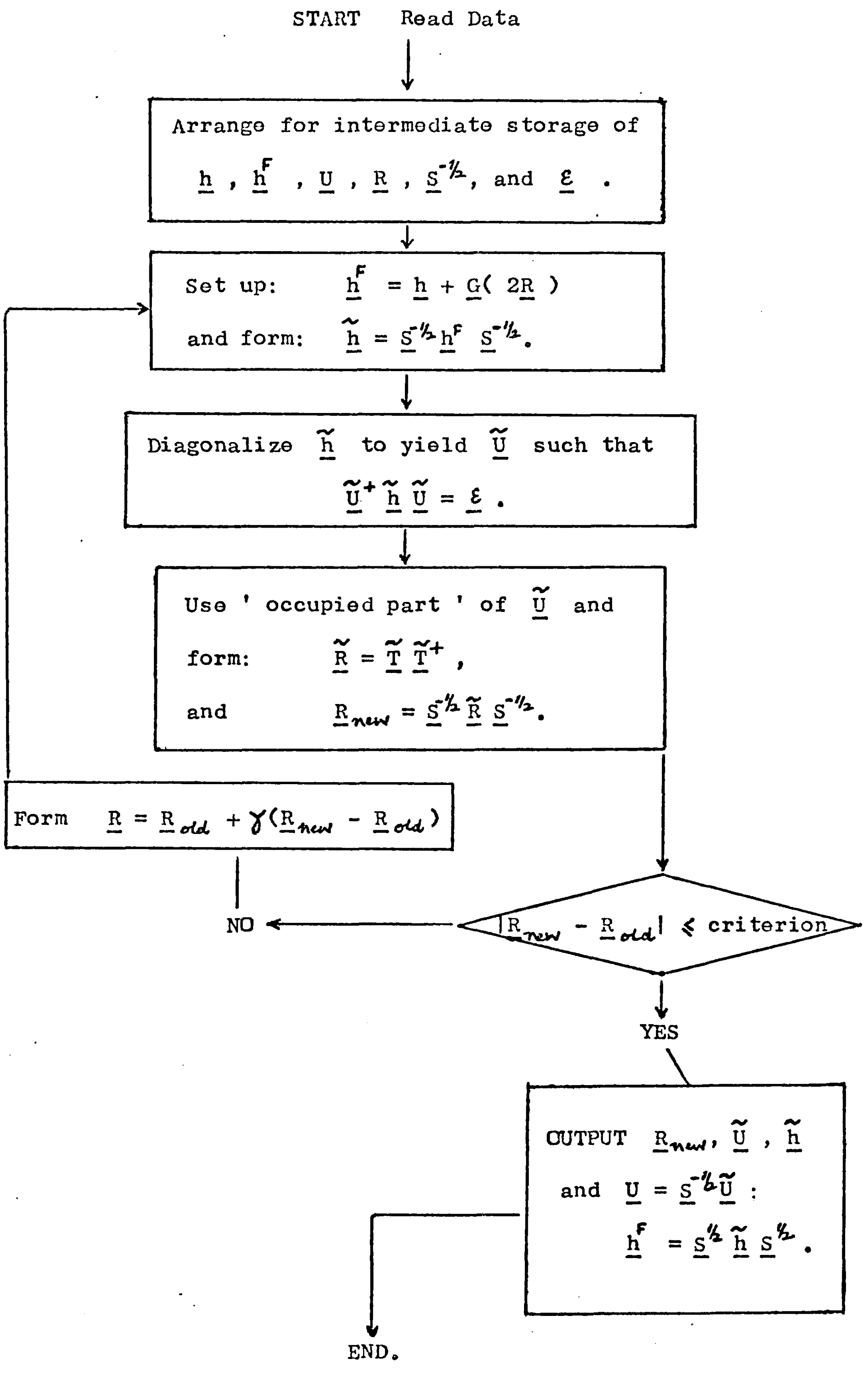
[*] This only applies to those situations for which the Hartree-Fock operator is completely symmetric with respect to all the symmetry operations of the nuclear framework.

The following is a flow-diagram describing the method used for finding the solutions of the Roothaan-Hartree-Fock equations for a closed-shell system using the procedure outlined in equations (X.4) to (X.7). The corresponding flow-diagram for the solution of equation (IV.74) follows analogously.



The input data consists of:

1.) the size of the basis set;

2.) the number of doubly-occupied molecular orbitals;

3.) $\underline{h}$ and $\underline{S}$ matrices;

4.) an initial $\underline{R}$-matrix (usually the null-matrix);

5.) the criterion;

6.) the value of γ-coefficient; and

7.) the position of the two-electron integrals on disc or tape.

A flow-diagram to compute the expression (see equation (IX.20) et. seq.):

$$\mathcal{E}_{core-core} = \sum_{\mu} \sum_{\nu(\neq\mu)} \Big(\sum_{i}^{(\mu)} \mathcal{E}_i^{\mu\nu} + 0.5\, Z_\mu Z_\nu R_{\mu\nu}^{-1} \Big),$$

where

$$\mathcal{E}_i^{\mu\nu} \approx C_i^{\mu\nu} (\alpha_i^\mu ; n_i^\mu ; \omega_i^\mu ; R_{\mu\nu})$$

$$\sum_{l,m} A_l(x) A_m(y)\, g (x_l , \eta_m , R_{\mu\nu} , \alpha_i^\mu , n_i^\mu)\, \rho_{core}^{\nu} (x_l , \eta_m)$$

$$C_i^{\mu\nu} (\alpha_i^\mu ; n_i^\mu ; \omega_i^\mu ; R_{\mu\nu}) = \frac{ (2\alpha_i^\mu)^{2n_i^\mu} (\omega_i^\mu/2) (R_{\mu\nu}/2)^{2n_i^\mu - 1} }{ (2n_i^\mu)! \;\; e^{R_{\mu\nu}\alpha_i^\mu} };$$

and $g (x_l , \eta_m , R_{\mu\nu} , \alpha_i^\mu , n_i^\mu) = (1 + \eta_m + x_l / R_{\mu\nu} \alpha_i^\mu)^{2n_i^\mu - 1} e^{-R_{\mu\nu}\alpha_i^\mu \eta_m}$

$$\rho_{core}^{\nu} (x_l , \eta_m) = - Z_\nu + \sum_{j}^{(\nu)} \omega_j^\nu \Big[1 - e^{-y} \sum_{k=0}^{2n_j^\nu - 1} (1 - k/2n_j^\nu)\, y^k / k! \Big]$$

where

$$y = \alpha_j^\nu (x_l / \alpha_i^\mu + R_{\mu\nu} (1 - \eta_m))$$

for the core-core interaction is given below. The input data consists of

1.) the coordinates of the nuclear centres;

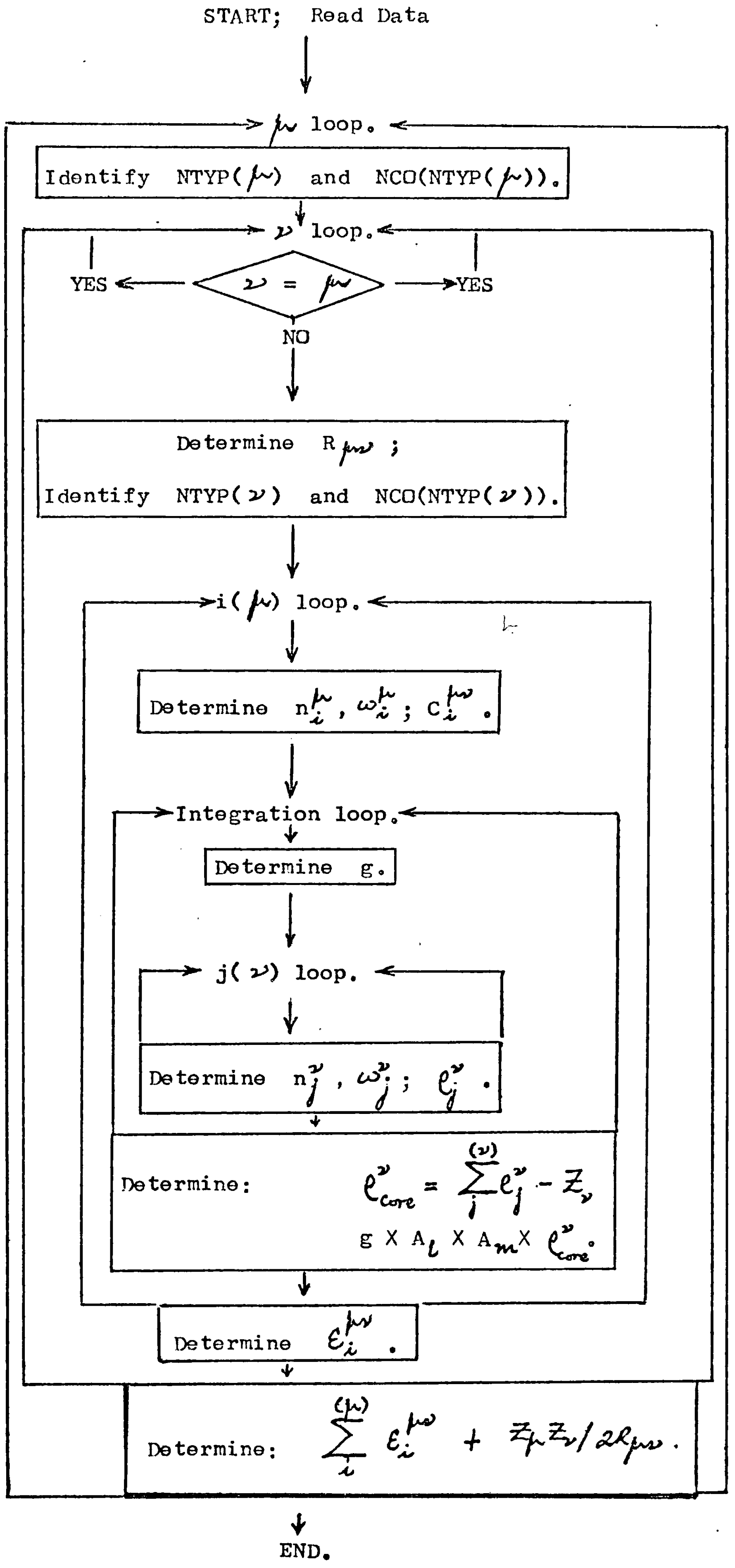
2.) the type of atom on each centre: NTYP(μ);

3.) the nuclear charge for each type of atom: Z(μ);

4.) the number of core shells for each type of atom: NCO(NTYP);

5.) the core-orbital exponents for each type of atom; and

6.) the Gauss-Legendre and Gauss-Laguerre integration points and weights.


START; Read Data
μ loop.
Identify NTYP(μ) and NCO(NTYP(μ)).
ν loop.
$\nu = \mu$
YES
YES
NO
Determine $R_{\mu\nu}$;
Identify NTYP(ν) and NCO(NTYP(ν)).
i(μ) loop.
Determine n_i^{μ}, ω_i^{μ}; $C_i^{\mu\nu}$.
Integration loop.
Determine g.
j(ν) loop.
Determine n_j^{ν}, ω_j^{ν}; ρ_j^{ν}.
Determine:
$\rho^{\nu}_{core} = \sum_j^{(\nu)} \rho_j^{\nu} - Z_\nu$
g X A_l X A_m X ρ^{ν}_{core}.
Determine $\mathcal{E}_i^{\mu\nu}$.
Determine:
$\sum_i^{(\mu)} \mathcal{E}_i^{\mu\nu} + Z_\mu Z_\nu / 2R_{\mu\nu}$.
END.

The following short algorithm is included to explain, in particular, the notation ' j(ν) loop '. This means:

```
        I = 0.5((1 + 8 X NCO(NTYP( $\nu$)))$^{1/2}$)
        DO 2    $n_j^\nu$  =  1,I
        DO 3    L  =  1,$n_j^\nu$
        $l_j^\nu$  =  L-1
        $\omega_j^\nu$ = 4 X $l_j^\nu$  + 2
        $\rho_j^\nu$  =  .....
          .
          .
          .
3           CONTINUE
2           CONTINUE
```

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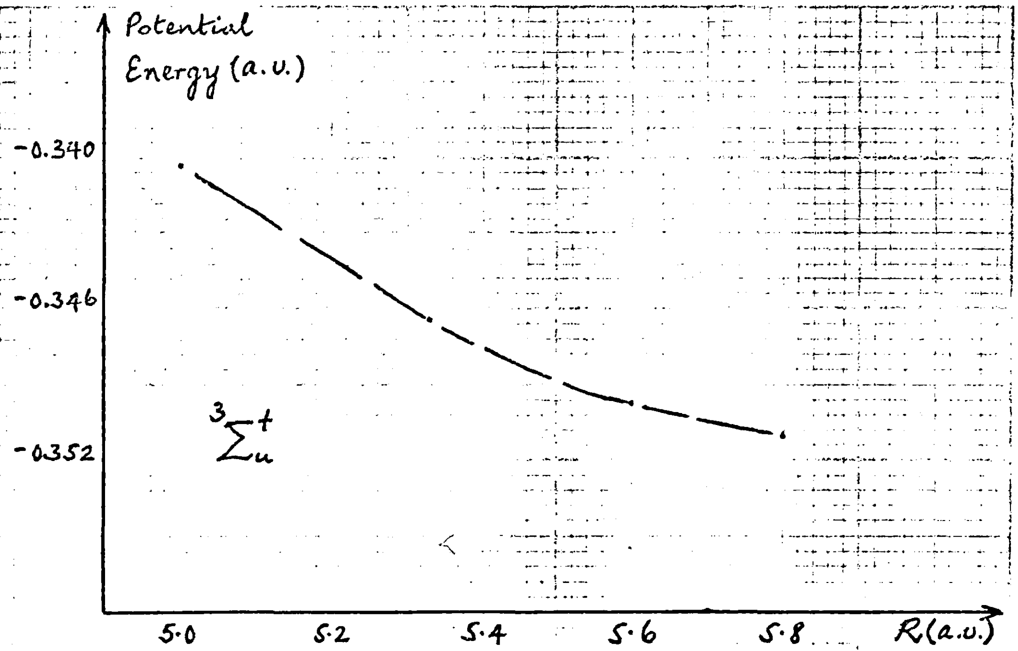
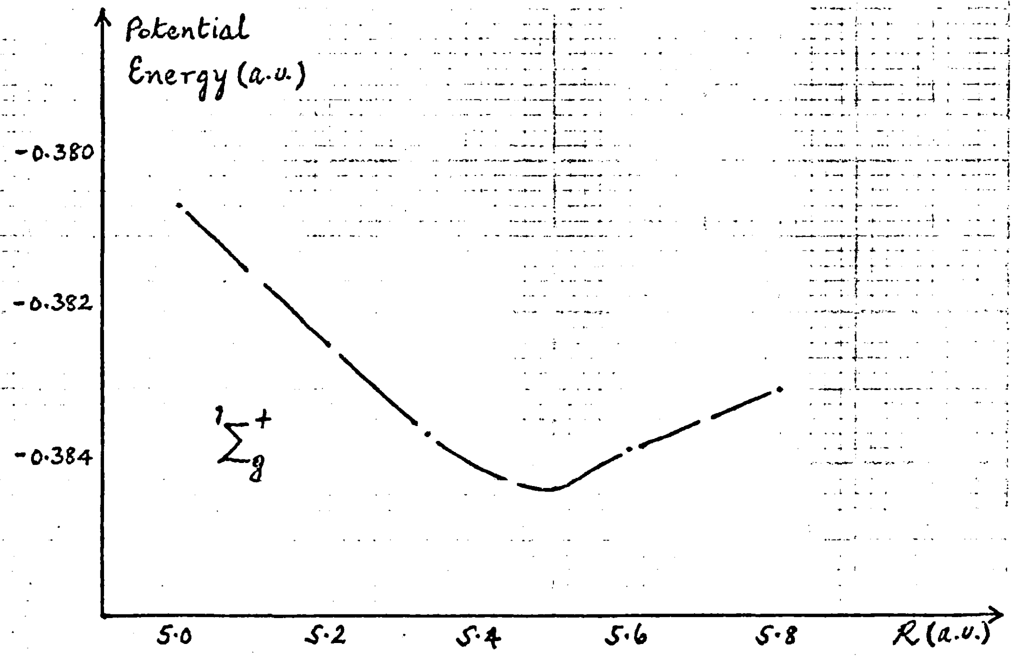
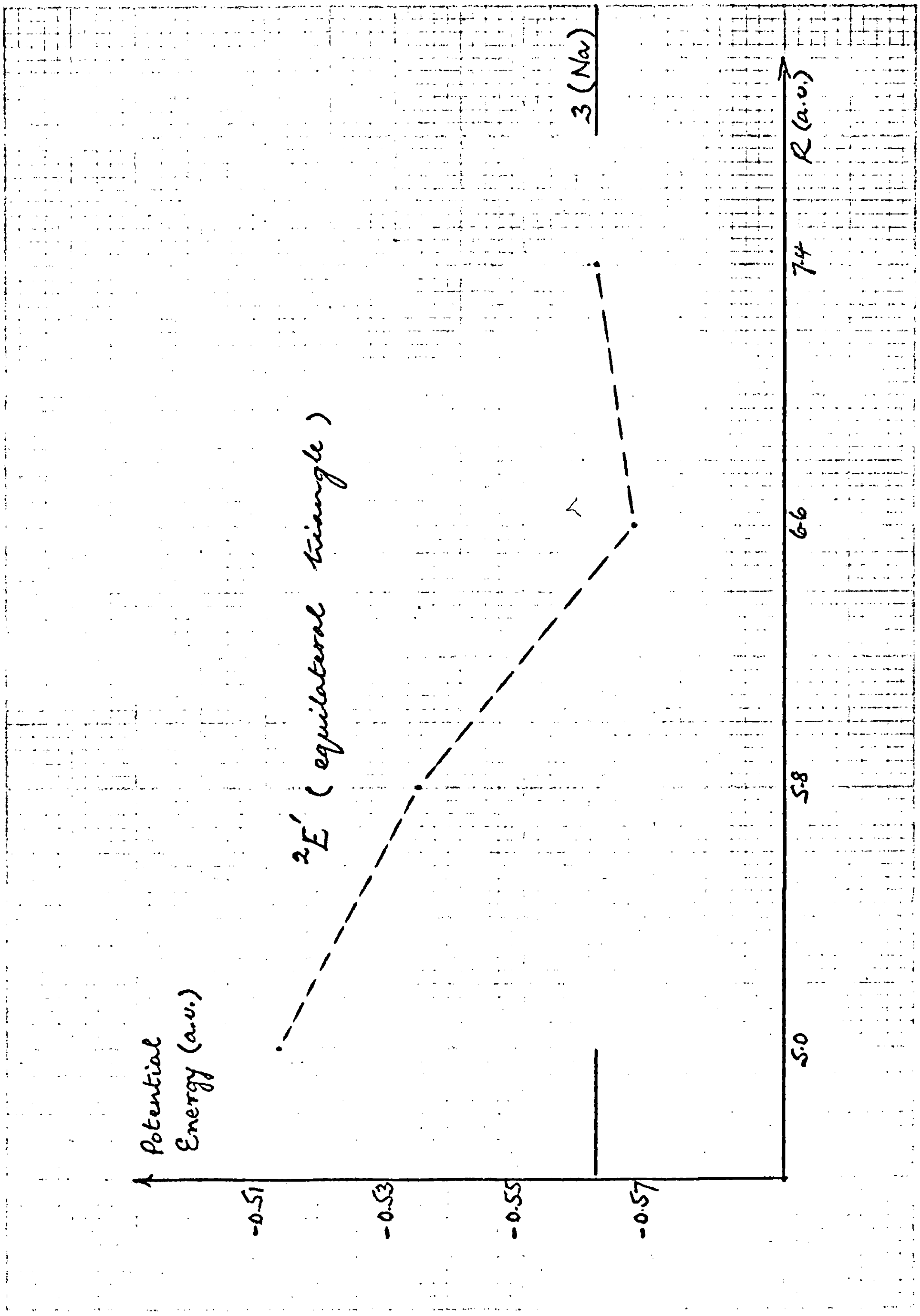


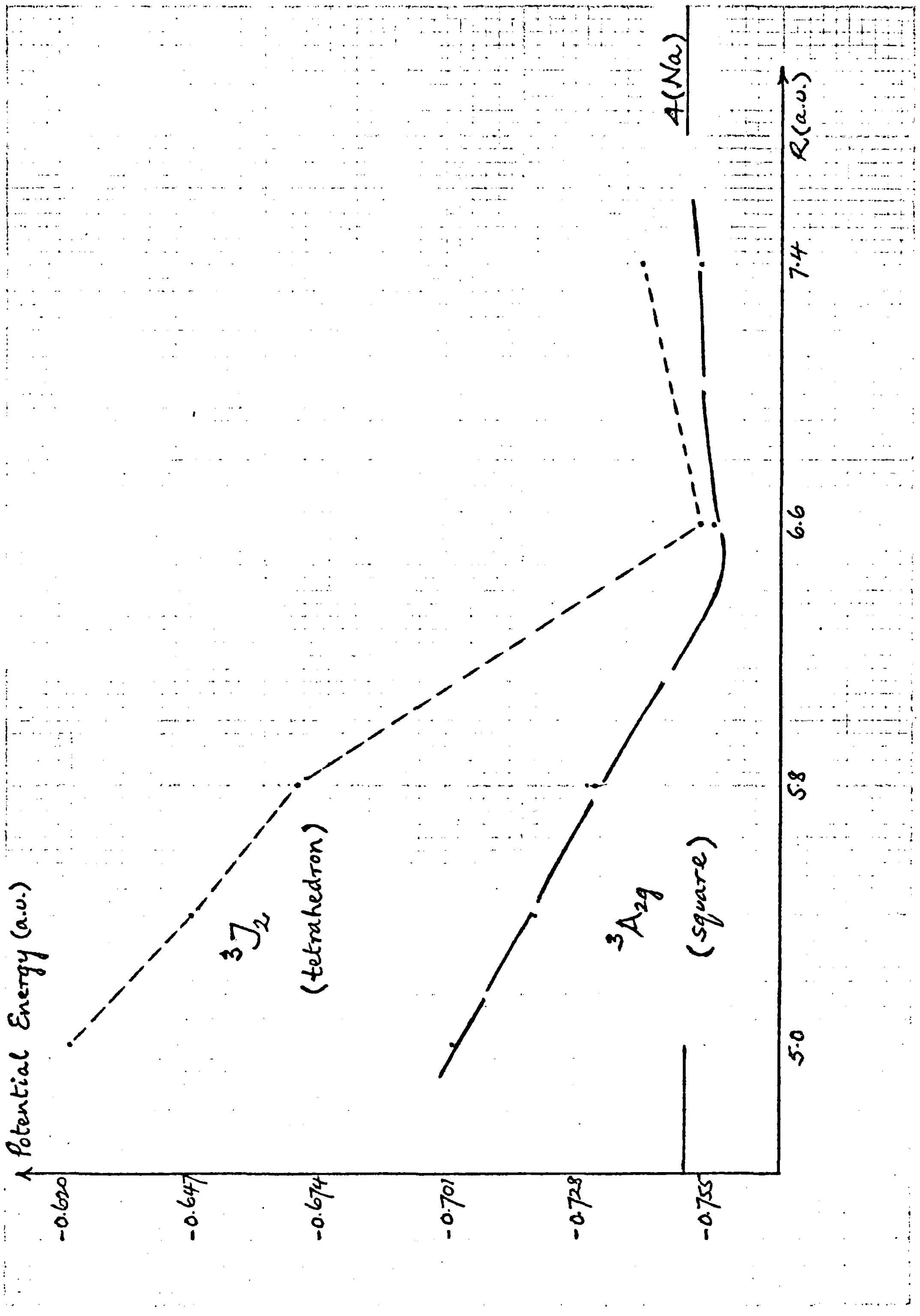


Potential Curves For Lowest States Of Dimer.

(Valence Bond Calculation.)



Potential Curve For Trimer (Valence Bond Calc.).



Potential Curves For Quadramer (V.B. Calculation)

CHAPTER XI.

CONCLUDING REMARKS.

In concluding this research project, it may be appropriate to attempt to compare some of the properties discussed earlier for small aggregates with those of the infinite solid.

As may be expected, there are striking differences in these properties. Such differences may be attributed, in large measure, to the finite sizes of the clusters. Thus, for example, it is well known that the valence charge distribution in the infinite solid is fairly uniform (see, for example, Harrison (1964)) whereas, from the discussion of Chapters VII and VIII, those for small agglomerates are expected to be much less smooth. One reason for this is that, as the system becomes larger, electrons can wander throughout a larger volume and thereby move in a lower average potential field. Simultaneously, their kinetic energies are lowered, as is implicit in the smoother spatial variations of the occupied orbitals. According to Wigner and Seitz (1955), this lowering of the kinetic energy of the valence electrons is mainly responsible for the stability of the infinite solid. It also explains the smaller value of the mean Fermi energy (Seitz (1940)) of the valence electrons in the bulk relative to the ionization potential of the free atom.

As explained earlier, the peculiar properties of an agglomerate of hydrogen atoms are believed to be due essentially to the very strong binding which results from the absence of core electrons. Also, correlation effects will tend to offset any lowering in kinetic and potential energies of the valence electrons as explained above for other monovalent systems. Under a very high pressure, a transition to a metallic form is expected; according to Mott (1949), this transition will be sharp.

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