CALCULATIONS ON THE GROUND, EXCITED AND

IONIC STATES OF SOME MOLECULES AND

MOLECULAR CRYSTALS

A Thesis submitted by

ALFRED TERRY AMOS

in partial fulfilment of the requirements
for the degree of Doctor of Philosophy in
the University of London.

Mathematics Department,
Imperial College,
ABSTRACT

In the first part the molecular orbital method is discussed and its application to π-electron systems indicated. The method is used to find self-consistent bond orders for the ground states of a number of hydrocarbons and heterocyclic molecules. The dipole moments for the heterocyclics and the C-C bond lengths for acridine are calculated and compared with experiment.

Part II develops in general terms the theory of wave functions which have the form of a single determinant, but without the restriction to doubly occupied orbitals. The unrestricted molecular orbitals and the unrestricted bond order matrices are defined and some of their properties deduced. The use of annihilators and projection operators to produce eigenfunctions of spin is investigated. The role of molecular symmetry and of a truncated set of basic functions in forcing a single determinant to be an eigenfunction of spin is discussed. The transformation properties of the unrestricted orbitals are used to define the natural spin orbitals, the natural orbitals and the corresponding orbitals and examples of these are given.

A steepest descent procedure which can be used in an iterative calculation of the unrestricted bond order
matrices for any system is devised in part III. The method is used to calculate unrestricted bond order matrices for the ions and lowest $\pi$ triplet states of naphthalene, anthracene, phenanthrene and azulene. Spin densities, charges, excitation energies and ionization potentials are found and compared with experiment.

In the final part the theory of exciton waves in molecular crystals and the dipole-dipole approximation is described. The method of long waves is applied to molecular crystals and this enables the retardation of the forces and the molecular polarizability to be included in the theory. The dispersion relation is obtained and used to study absorption and reflection in the crystals.
The author wishes to acknowledge the encouragement and interest shown by Professor G. G. Hall during the supervision of the work presented in this thesis.

He would also like to thank Dr. R. A. Buckingham for permission to use the University of London computer, the staff of the Computer Unit for running some of the programmes and Mrs. S. A. Thomas for the excellent typing of the manuscript.
CONTENTS

PART I: THE MOLECULAR ORBITAL METHOD AND ITS APPLICATION TO SINGLET GROUND STATES OF \( \pi \)-ELECTRON SYSTEMS

Chapter 1: Approximate solution of the wave equation - the molecular orbital method 8

Chapter 2: Application of molecular orbital theory to \( \pi \)-electron systems 22

Chapter 3: Ground state properties of some heterocyclics 37

PART II: THEORY OF SINGLET DETERMINANT WAVE FUNCTIONS

Chapter 4: Density Matrices 55

Chapter 5: Correlation problem and improved wave functions 70

Chapter 6: Unrestricted Hartree-Fock wave functions 78

Chapter 7: Transformation properties of the orbitals 98

PART III: ITERATIVE CALCULATION OF UNRESTRICTED BOND ORDER MATRICES - IONS AND TRIPLET STATES OF HYDROCARBONS

Chapter 8: Calculation of unrestricted bond order matrices 116

Chapter 9: Application of unrestricted method to \( \pi \)-electron systems 125

Chapter 10: Calculations on the ions and lowest \( \pi \) triplet states of some conjugated hydrocarbons 133
# PART IV: LONG WAVE THEORY OF ABSORPTION AND REFLECTION IN MOLECULAR CRYSTALS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Exciton waves and the dipole-dipole approximation</td>
<td>148</td>
</tr>
<tr>
<td>12</td>
<td>Application of the long wave method to molecular crystals</td>
<td>158</td>
</tr>
</tbody>
</table>

**APPENDIX** ................................................................. 179

**REFERENCES** ................................................................. 182
PART I

THE MOLECULAR ORBITAL METHOD AND ITS APPLICATION
TO SINGLET GROUND STATES OF \( \pi \)-ELECTRON SYSTEMS
CHAPTER I

APPROXIMATE SOLUTION OF THE WAVE EQUATION
- THE MOLECULAR ORBITAL METHOD
1.1 Introduction

The first step in any quantum mechanical theory is to solve the appropriate Schrödinger equation:

\[ H \Psi = E \Psi \]

where \( H \) is the quantum mechanical Hamiltonian obtained from the classical Hamiltonian by replacing the momentum vectors \( p_i \) with the operators \( -i\hbar \nabla_i \); \( E \) is the energy of the system and \( \Psi \) the wave function.

The Hamiltonian for a molecule will contain terms due to the nuclei and electrons in the molecule and consequently the wave function will be a function of both nuclear and electronic coordinates. Obviously to solve the Schrödinger equation accurately for any but the simplest chemical systems is prohibitively difficult and to obtain any results it is necessary to resort to approximations.

An examination of the wave equation shows that there can be two types of approximation. We can either simplify the Hamiltonian or use the variational principle to find an approximate wave function; but usually it is necessary to do both. The use of an approximate Hamiltonian implies that we make some physical assumptions which simplify the system we are considering and this simplification may apply to most chemical systems or to
just a few related systems. An example of the former is the separation of the wave function into an electronic equation and a nuclear equation and of the latter the Hückel approximation for \( \pi \)-electron systems. Only approximations of the first type will be considered in this chapter but in chapter 2 the Hückel approximation will be discussed in connection with conjugated molecules.

Even when the Hamiltonian has been simplified it is usually still very difficult to solve the wave equation exactly and it is necessary to use the variational principle to obtain reasonable wave functions and energy values. There are several ways of constructing trial wave functions which can be used with the variational principle but one of the most important is the molecular orbital method. By assuming each electron moves independently in a molecular orbital (M.O.) a trial wave function built up of one-electron terms can be constructed. In order to satisfy the Pauli principle the wave function should be in the form of a single determinant and, using the variational principle with such a wave function, the Hartree–Fock self-consistent field equations for the individual molecular orbitals can be obtained. In the final section, the self-consistent field (S.C.F.) equations will be discussed and it will be shown that
the introduction of the linear combination of atomic orbitals (L.C.A.O.) approximation allows the orbital equations to be put into a soluble form.

1.2 Approximations to the Hamiltonian

The first assumption we can make to simplify the Hamiltonian is to neglect all relativistic effects. This has the important effect that the Hamiltonian then contains no spin terms. This approximation is a very reasonable one for molecules which do not contain heavy atoms and it will certainly not affect any results for conjugated hydrocarbons and similar molecules.

Having made this approximation, the wave equation for a molecule can be written as

\[ H \Psi = \left\{ -\sum_\alpha \frac{\hbar^2}{2m_\alpha} \nabla^2_\alpha + \frac{1}{2} \sum_{\alpha \beta} \frac{Z_{\alpha} Z_{\beta} e^2}{r_{\alpha \beta}} 
- \sum_\alpha \frac{\hbar^2}{2m_\alpha} \nabla^2_\alpha - \sum_\alpha \sum_\iota \frac{Z_{\alpha} e^2}{r_{\alpha \iota}} + \frac{1}{2} \sum_{\iota j} \frac{e^2}{r_{\iota j}} \right\} \Psi = E \Psi \] (1.2.1.)

where Greek suffixes refer to the nuclei and italic to the electrons. \( m_\alpha \) is the mass of, and \( Z_\alpha e \) the charge on the nucleus \( \alpha \). \( m \) and \( e \) are the corresponding quantities for the electron.

By using atomic units (see Shull and Hall, 1959) the wave equation can be put in the simpler form:
It turns out that if we write \( \Psi = \Phi_e \Phi^*_N \)
where \( \Phi_e \) is a function of electronic coordinates only (but includes the nuclear coordinates as parameters) and \( \Phi^*_N \) of nuclear coordinates only, then the wave equation is separable into a nuclear wave equation and an electronic wave equation, the other terms vanishing if we assume the ratio of the electronic mass to the mass of the nucleus is extremely small (Born and Oppenheimer, 1927). Making this approximation, the wave equation is reduced to two equations, one involving the motion of the electrons and the other being an equation for the vibrations and rotations of the nuclei. The chemically important one is the electronic equation since this determines the structure and energy levels of the molecules. We shall, therefore, only now be concerned with solving the electronic Schrödinger equation which, using atomic units, we can write as

\[
H \Psi_e = \left\{ -\frac{1}{2} \sum_{\alpha} \nabla_{\alpha}^2 - \sum_{\alpha} \frac{Z_\alpha}{r_{\alpha e}} + \frac{1}{2} \sum_{ij} \frac{1}{r_{ij}} \right\} \Psi_e = E_e \Psi_e
\]  

(1.2.2.)
Physically this equation implies that the nuclei are fixed with their positions known and the electrons move in the field of the fixed nuclei.

1.3 The Variational Principle

Having simplified the Hamiltonian in the ways described and in any other way which may be possible for the system under consideration, it may be still difficult in practice to solve the wave equation accurately. Thus it is necessary to obtain an approximate solution to the wave equation

$$H\Psi = E\Psi$$

(1.3.1.)

where $H$ is the simplified Hamiltonian.

The variational method allows us to do this since if $\Phi$ is any trial wave function,

$$e = \frac{\int \Phi^* H \Phi \, dx}{\int \Phi^* \Phi \, dx} \geq E = \frac{\int \Psi^* H \Psi \, dx}{\int \Psi^* \Psi \, dx}$$

(1.3.2.)

The method consists of taking a trial wave function $\Phi$ containing adjustable parameters and functions and choosing these to minimise $e$. By careful choice of $\Phi$, a value of $e$ can be obtained which is very close to the true energy value $E$; and as $e \to E$, so $\Phi \to \Psi$ in the sense that the overlap integral between $\Phi$ and $\Psi$ tends to unity (Eckhart, 1930).
It should be emphasised that even though an approximate wave function \( \Phi \) may give an energy value \( \varepsilon \) which is close to the true value of \( E \), then it does not follow that the theoretical value of any other physical property derived using the function \( \Phi \) will be a good approximation to the exact value. For this reason care should be taken in choosing the form of the approximate wave function \( \Phi \) depending on which physical properties are being investigated.

The true wave function will be antisymmetrical in the electronic coordinates to satisfy the Pauli principle and it will be an eigenfunction of the spin operators \( S_z \) and \( S^2 \). Also it will belong to some irreducible representation of the symmetry group of the nuclei and will take account of the correlation between the electrons. Thus to obtain a good approximation to the true wave function the trial wave function should have as many of these properties as possible. Usually it is possible to choose a trial wave function with only some of these properties and just which of the properties it should have depends on the problem under consideration. Thus if the energy is the quantity required, in some molecules it may be thought desirable to choose a trial wave function which takes into account electron correlation
but which is not an eigenfunction of \( \sum \vec{s}^2 \); but care would be needed if such a function were used to estimate any spin properties of the molecule.

1.4 Molecular Orbitals and the S.C.F. - L.C.A.O. Approximation

The Hamiltonian for a molecule can be written in terms of one-electron operators, \( \mathcal{H}_i \) and two-electron operators, viz. \( \mathcal{H}_{ij} \). We can write with the usual notation:

\[
H = \sum_i \mathcal{H}_i + \frac{1}{2} \sum_{ij} \mathcal{H}_{ij} \quad (1.4.1)
\]

where

\[
\mathcal{H}_i = -\frac{1}{2} \nabla_i^2 - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}}
\]

and

\[
\mathcal{H}_{ij} = \frac{1}{r_{ij}}
\]

But for the inclusion of the two electron terms, it would be possible to obtain an exact solution in the form of a Hartree product:

\[
\Psi = \Psi_1(x_1) \Psi_2(x_2) \cdots \Psi_N(x_N) \quad (1.4.2)
\]

where \( \Psi_1, \ldots, \Psi_N \) are functions of the coordinates (including spin) of one electron only and are called molecular orbitals. This indicates that the Hartree
product might be used as a trial wave function, the variational method being used to obtain the orbital equations for the functions \( \{ \psi_j \} \) which would give the lowest energy. The assumption that a good trial wave function can be built up of one electron terms is the basis of the molecular orbital method.

Unfortunately the Hartree product does not have all the desirable properties of a trial wave function as described in the previous section, for it is neither antisymmetrical in the electronic coordinates nor does it take into account the correlation between the electrons. The antisymmetrical requirement can be satisfied by writing the wave function in the form of a single Slater determinant

\[
\Phi = \frac{1}{\sqrt{(N!)}} \begin{vmatrix}
\psi_1(1) & \psi_2(1) & \ldots & \psi_N(1) \\
\psi_1(N) & \psi_2(N) & \ldots & \psi_N(N)
\end{vmatrix}
\]

(1.4.3.)

Using a wave function of this kind is equivalent to replacing the two electron operator \( \hat{P}_{ij} \) by a single electron operator which appears in the equations as an "average" of the two electron terms. Physically this implies that each electron moves in the field of the
nuclei and the self consistent field (S.C.F.) formed by the "averaged" fields of the other electrons. For this reason the method is called the Hartree-Fock S.C.F. approximation.

It is easy to see that the wave function $\Psi$ is invariant with respect to any linear transformation of the $\alpha.O.'s$ among themselves and, also, the orbitals have to be linearly independent for a non-trivial solution. Hence, we can assume without loss of generality that the $\alpha.O.'s$ form an orthonormal set.

$$\int \psi_k^* \psi_l \, d\lambda = \delta_{kl} \quad (1.4.4.)$$

where the integration includes spin. With this assumption it follows that the wave function is normalised. Also, it is convenient to write each $\alpha.O.$ $\psi_{\alpha} (\lambda)$ as the product of a spacial orbital $\phi_k (\tau)$ and a spin factor which, without loss of generality, can be taken as either $\alpha$ or $\beta$.

In order to satisfy the requirement that $\Psi$ should be an eigenfunction of $\sum_{\sigma z}$ and $\sum^2$, for a singlet ground state of a $2N$ electron system the wave function has to be written as

$$\Psi = \frac{1}{(2N!)^{1/2}} \prod_e \{ \phi_1 (1) \alpha (1) \phi_2 (2) \alpha (2) \ldots \} \phi_n (N) \alpha (N) \phi_1 (N+1) \beta (N+1) \ldots \phi_n (2N) \beta (2N) \quad (1.4.5.)$$
where the spacial orbitals form an orthonormal set to satisfy (1.4.4.).

The only other form the single determinant wave function can take, if it is to be an eigenfunction of $\mathcal{H}$ has a number of doubly occupied spacial orbitals, the remainder being singly occupied by electrons with the same spin. (See section 4.4). Therefore, the most general form of a single determinant wave function, which is an eigenfunction of $\mathcal{H}$, is:

$$\Psi = \sqrt{(p+q)!} \det \left\{ \phi_{1}(1)\alpha(1) \ldots \phi_{p}(p)\alpha(p) \right\}$$

$$\phi_{1}(p+1)\beta(p+1) \ldots \phi_{q}(p+q)\beta(p+q) \right\}$$ (1.4.6.)

By applying the variational principle to this wave function, the orbital equations which the "best" h.o.'s satisfy can be derived. Lennard-Jones (1949) used the calculus of variations to show that these orbital equations are:

$$\left( \varepsilon_{n}^{\alpha} + \varepsilon_{n}^{\beta} \right) \left\{ \hbar + V \right\} \phi_{n} + \sum_{m} \left( \varepsilon_{m}^{\alpha} \varepsilon_{n}^{\alpha} \kappa_{mn}^{\alpha} + \varepsilon_{m}^{\beta} \varepsilon_{n}^{\beta} \kappa_{mn}^{\beta} \right) \phi_{m} - \sum_{m} \left( \varepsilon_{m}^{\alpha} \varepsilon_{n}^{\alpha} + \varepsilon_{m}^{\beta} \varepsilon_{n}^{\beta} \right) \left\{ \zeta_{mn} + \kappa_{mn} + J_{mn} \right\} \phi_{m} = 0$$ (1.4.7.)

where $\varepsilon_{n}^{\alpha} = 1$ or $0$ depending as $\phi_{n}$ is associated with a spin or not, and
\[ \hat{h} = -\frac{1}{2} \nabla^2 - \sum_{\lambda} \frac{\varepsilon_{\lambda}}{r_{\lambda}} \]

\[ V(x) = \sum_{\lambda} (\varepsilon_{\lambda}^s + \varepsilon_{\lambda}^p) C_{\ell\ell}(x) \]

\[ C_{\ell m n}(x_j) = \int \phi_m^*(x_j) \frac{1}{r_{ij}} \phi_n(x_j) \, dx_j \]

\[ K_{\ell mn} = \int \phi_m^* \phi_n \, dx \]

\[ J_{\ell mn} = \sum_{\lambda} (\varepsilon_{\lambda}^s + \varepsilon_{\lambda}^p) [lm|\ell n] \]

\[ K_{\ell mn} = \sum_{\lambda} \varepsilon_{\lambda} [lm|\ell n] \]

\[ \text{with} \quad [lm|n p] = \int \phi_{\ell}^*(x_i) \phi_{\ell}^*(x_j) \frac{1}{r_{ij}} \phi_n^*(x_i) \phi_p(x_j) \, dx_i \, dx_j \]

To obtain solutions of these equations is extremely difficult but in the important case of a singlet ground state (1.4.5.) with \( \rho = q \) the equations simplify considerably to give

\[ F \phi_+ = (\hat{h} + V + A) \phi_+ = E_+ \phi_+ \quad (1.4.8.) \]

where

\[ A \phi_+ = -\sum_{s} C_{\ell mn} \phi_s \]

(for full details see Roothaan, 1951)

These S.C.F. equations are more easy to solve in the atomic case because of the spherical symmetry than in the molecular case where the method of linear combination of atomic orbitals (L.C.A.O.) has to be introduced.
in order to obtain solutions. This consists of writing each L.O. as a linear combination of a basic set of \( \tilde{\omega} \) fixed functions so that

\[
\phi_s(t) = \sum_{t=1}^{M} \alpha_{st} \omega_t(t) \quad (1.4.9.)
\]

For this to be mathematically correct the set \( \{\omega_t\} \) should be complete and \( M \) should be infinite; but, by making a suitable choice of the basic set, even when \( M \) is quite small good results can be obtained. As the name of the method implies one choice of the basic orbitals is the atomic orbitals of the atoms in the molecule, but this is not essential, nor in many cases is it desirable.

Substitution in the orbital equations gives the equations which determine the coefficients, (see Hall, 1951, Roothaan, 1951)

\[
\sum_t \alpha_{st} \left\{ H_{lt} + \sum_{j=1}^{N} \sum_{k=1}^{N} a_{ij} a_{nk} \left[ 2 \langle \ell_j | t k \rangle - \langle \ell_j | k t \rangle \right] \right\} = E_s \sum_t \alpha_{st} S_{lt} \quad s = 1, \ldots, N \quad (1.4.10.)
\]

where

\[
H_{lt} = \int \omega_{t}^* \ h \ \omega_t \ dt
\]

\[
S_{lt} = \int \omega_{t}^* \ \omega_t \ dt
\]

\[
\langle \ell_j | t k \rangle = \int \omega_{t}^* (1) \omega_{j}^* (2) \frac{1}{r_{12}} \ \omega_t (1) \ \omega_k (2) \ dr_{12}
\]

These equations which are cubic in the coefficients can be solved iteratively when the integrals are known.
The integrals can be calculated numerically or, as is often the case, determined by some empirical method.

Methods of solution of these equations in the case of conjugated molecules and the use of the solutions in calculating various properties of the molecules will be considered in Chapters 2 and 3.
CHAPTER 2

APPLICATION OF MOLECULAR ORBITAL THEORY
TO π-ELECTRON SYSTEMS
2.1 Introduction

The application of molecular orbital theory to conjugated molecules and especially to conjugated hydrocarbons has been very successful mainly because only a few of the electrons are important. Most of the electrons in these molecules can be considered as moving in orbitals which are well localised around the atomic nuclei. The remainder - one per carbon atom in the case of hydrocarbons - move in orbitals which extend throughout the molecule and are antisymmetrical in the molecular plane. It turns out that most of the physical properties of the molecule are determined by this small number of mobile or $\pi$-electrons and, by considering only these electrons, the problem of finding a wave function for the molecule can be simplified considerably.

Hückel used this idea to suggest a very simple method of calculating a Hartree-product wave function for a conjugated system. In fact, by writing each M.O. as a linear combination of $2p_z$ atomic orbitals and making various assumptions about the integrals which arise, the problem can be reduced to finding the eigenvalues and eigenvectors of a certain matrix whose form depends mainly on the connectivity of the system. Because of the simplicity of the method, calculations are very easy to make and for some properties of the system good results can be obtained.
Unfortunately some of the basic assumptions of the theory are not valid and to obtain more accurate results the S.C.F. - L.C.A.O. equations of section 1.4 have to be used. The π-electron approximation allows these equations to be simplified and they can be solved iteratively by various methods. The difficulty here is the calculation of the integrals involved, but it will be shown in the final section of this chapter that, by choosing suitable basic functions, this difficulty can be overcome and good results can be obtained.

2.2 The π-electron Approximation

If we consider conjugated hydrocarbon molecules then each carbon atom has four electrons in its outer valence shell and it is bonded to three neighbouring atoms. We may, therefore, consider three of the valence electrons as moving in orbitals which overlap with orbitals from the three neighbouring atoms to give localised CC and CH bonds of σ type symmetry. The remaining electrons - one for each carbon atom - move in M.O.'s which have π-type symmetry and which may be represented as linear combinations of carbon \( \Sigma p_z \) atomic orbitals, these atomic orbitals being parallel to each other and perpendicular to the plane of the molecule.
These M.O.'s are completely delocalised, extending throughout the molecule, and have a node in the plane of the molecule. The electrons occupying these orbitals, the so-called π- or mobile electrons, can be treated separately from the σ-electrons which are localised around the atomic cores because the two types of orbitals have different symmetry in the molecular plane and so any π-σ interaction will have negligible effect on the lowest states wave functions (Moser, 1953). Also, since the electrons are delocalised and less closely bound than the σ-electrons, most of the properties of the molecule can be deduced by considering only the π-electron system. Exactly the same argument applies if a carbon atom is replaced by a hetero-atom. Thus in such a system the wave equation to be solved is:

\[ \left\{ \sum_i \frac{1}{\mu_i} + \frac{\hbar^2}{2m_e} \sum_{ij} \frac{1}{r_{ij}} \right\} \Psi = E \Psi \]  

(2.2.1.)

where the summations now refer only to π-electrons, \( E \) is the π electron energy and \( \Psi \) the π-electron wave function. The one-electron operator will now contain terms due to the nuclei and σ-electrons which are together in the inert cores.

The assumption that the π-electrons can be treated separately is essentially a method of simplifying the
Hamiltonian. Physically it implies that a conjugated molecule can be considered as consisting of \( \pi \)-electrons moving in a field due to fixed cores, these cores being built up of atomic nuclei and localised \( \sigma \)-electrons. A rigorous justification for this approximation is hard to give although attempts have been made to do so (Parr Ellison and Lykos, 1956). Perhaps its greatest justifications are the excellent results which have been obtained by using it.

2.3 Hückel Theory

Hückel (1931) used the \( \pi \)-electron approximation to give a rather naive treatment of conjugated molecules. His method is a very simple one yet it gives surprisingly accurate results for many molecular properties and, because of the ease of the calculation, it is still quite often used.

The basic assumptions made are that the \( \pi \)-electron wave function is a Hartree - product of M.O.'s and that each M.O. satisfies an eigenvalue equation

\[
H \phi_i = E_i \phi_i \tag{2.3.1.}
\]

where \( H \) is some one-electron Hamiltonian, the nature of which is not considered explicitly. The total
π-electron energy is taken to be the sum of the separate energies \( E_i \) for each M.O. included in the product. Writing each M.O. as a linear combination of \( \pi_z^2 \) atomic orbitals \( \{ \omega_j \} \), one on each core, we have, in the case of hydrocarbons,

\[
\phi_i = \sum_{j=1}^{M} a_{ij} \omega_j \tag{2.3.2.}
\]

where \( M \) is the number of carbon atoms and

\[
\sum_{j=1}^{M} a_{ij} H \omega_j = E_i \sum_{j=1}^{M} a_{ij} \omega_j \tag{2.3.3.}
\]

Multiplying by \( \omega^* \) and integrating

\[
\sum_{j=1}^{M} a_{ij} H_{kj} = E_i \sum_{j=1}^{M} a_{ij} S_{kj} \tag{2.3.4.}
\]

where

\[
H_{kj} = \int \omega_k^* H \omega_j \, dx \quad S_{kj} = \int \omega_k^* \omega_j \, dx
\]

Finally the matrix elements \( H_{kj} \) are treated as parameters, with the assumption that,

(i) \( H_{jj} = \alpha \)

(ii) \( H_{ij} = \beta \) where \( i, j \) refer to neighbouring atoms

\[ = 0 \quad \text{otherwise} \tag{2.3.5.} \]

(iii) \( S_{kj} = \delta_{kj} \)
Making use of these assumptions, the eigenvalues and eigenvectors of the matrix $H_{ij}$, whose form depends mainly on the connectivity of the molecule, will be the orbital energies and coefficients. Equations (2.3.4.) give a set of simultaneous linear equations

$$\sum_j (H_{jk} - E_i \delta_{jk}) a_{ij} = 0 \quad (2.3.6.)$$

and for consistency the determinant

$$\begin{vmatrix} H_{jk} - E_i \delta_{jk} \end{vmatrix}$$

must vanish. The roots of this determinant, which are the eigenvalues of $H_{jk}$, give the various orbital energies in terms of the parameters $\alpha$ and $\beta$, and hence the total energy will be given in terms of these. For a $2N$ electron system, there will be $2N$ eigenvectors and eigenvalues giving $2N$ H.O.'s, but, since each H.O. can be occupied by two electrons of opposite spins, only the $N$ orbitals corresponding to the $N$ lowest orbital energies are used. By taking $\alpha$ as the zero level of energy and working in units of $\beta$, it becomes clear from the eigenvector equation that the actual coefficients $\{a_{ij}\}$ are independent of the parameters $\alpha$ and $\beta$ in the case of hydrocarbons.

The extension of the theory to substituted molecules, as originally suggested by Hückel is very simple and
consists of changing the diagonal element $H_{jj}$ which refers to the hetero-atom from $\alpha$ for the carbon atom, to $\alpha + \delta.\beta$ for the substituted atom. This means that the results for hetero-atoms obtained using this method will depend on three parameters; $\alpha$ and $\beta$, as before, and the third parameter $\delta$ which represents the difference in electronegativity between the carbon atom and the substituted atom. Unfortunately the introduction of $\delta$ means that the orbital coefficients are no longer independent of the parameters, as in the hydrocarbons, but now depend on $\delta$. This makes it difficult to compare results as there is great variation in the values of $\delta$ used by various authors.

Having obtained the coefficients for the molecule under consideration it is usual to calculate the charge and bond-order matrix $P$, the elements of this being defined as:

$$P_{rs} = \sum_{\text{ALL OCCUPIED ORBITALS}} \alpha^*_{ir} \alpha_{is} \quad (2.3.7.)$$

where the sum over all occupied orbitals means that each orbital is counted twice if it is doubly occupied. The importance of this matrix lies in the fact that the diagonal elements can be identified with the charge on the atoms and the bond order $P_{rs}$ between adjacent atoms can be correlated with the bond length (see Coulson,
1939). Thus the matrix $P$ gives information about the structure of the molecule and this is especially important in the case of substituted molecules when $\pi$-electron moments and likely points of attack by charged radicals can be predicted. As well as giving information about the structure of molecules, Hückel theory can be used to calculate resonance-energies, bond-localisation-energies, atom-localisation energies and ionisation potentials. It is also possible to give predictions of the excited states of molecules by using the theory, the excitation energies being given by the differences between orbital energies. Usually these predicted values are given in terms of the parameter $\beta$ which is then chosen to give the best agreement with experiment. For details of some calculations and references see Coulson and Longuet-Higgins (1947 a, b); Coulson and Daudel (1957); Wheland (1942); Davies (1955); Wheland and Pauling (1935); Coulson (1952); Daudel, Lefebvre and Moser (1959); Streitwieser (1962).

Although many physical properties can be predicted quite well using the Hückel theory, the method has many faults and there are many discrepancies in the results. For example very different values of $\beta$ have to be taken in order that calculated values of different properties
should agree with the experimental values (compare Hückel, 1931; Lennard-Jones, 1937; Mulliken, Rieke and Brown, 1941) and also, the prediction of the excited states are often very poor (see for example, McWeeny and Peacock, 1957, p.46). In the case of substituted molecules, the value of the parameter δ as used by different authors has differed widely from 2.0 in older work to 0.40 more recently (Hameka and Liquori, 1958) and some attempts have been made to obtain better results by "sharing out" δ over a number of atoms (Heland and Pauling, 1935). Some improvement can also be obtained in the general case by including the overlap integrals \( S_{ij} \) in equations (2.3.6.) since the assumption that \( S_{ij} = \delta_{ij} \) is not correct for \( 2p_z \) atomic orbitals; but, unfortunately, this leads to theoretical difficulties in defining such quantities as charge and bond-order (McWeeny, 1951).

It has previously been shown that a wave function in the form of a Hartree-product is not a good one and this is another fault of the Hückel approximation and means that the formulae for the energy has the wrong form for some molecules. (Hall, 1952, section 4). The most serious criticism of the Hückel theory, however, is that a rigorous application of the S.C.F.-L.C.A.O. method leads to equations (1.4.10) which are
cubic in the coefficients and not linear as assumed by the Hückel theory. Hall (1952 a,b) has used equivalent molecular orbitals to reinterpret the Hückel theory in terms of the more accurate S.C.F. theory and this explains the reason for the success of the Hückel theory in some applications. But it is clear that to obtain more accurate predictions of a wide range of molecular properties the S.C.F. - L.C.A.O. equations have to be solved and this will be considered next.

2.4 Application of the S.C.F. - L.C.A.O. Method to Conjugated Systems

Defining the bond-order matrix $\mathbf{P}$ in the case of an S.C.F.-L.C.A.O. solution exactly as in the case of the Hückel theory, equation 1.4.10 can be written in the form

$$\sum_{r} a_{sr} F_{er} = \sum_{r} a_{sr} (H_{er} + G_{er}) = \sum_{r} a_{sr} \left[ H_{er} + \frac{1}{2} \sum_{jk} P_{jk} \left[ 2 (\ell_j | \tau k) - (\ell_j | k \tau) \right] \right] = E_{s} \sum_{r} a_{sr} S_{er} \quad (2.4.1)$$

and these equations can be solved iteratively by several methods once the various integrals are known. The most usual method is to assume a set of values for the coefficients, calculate the matrix $\mathbf{F}$ using these and obtain improved values by solving what is then a set of linear equations. This is repeated until consistency
is obtained. Another method suggested by Hall (1955) is based on the standard excited state; and McWeeny (1956 a, b) has put forward a steepest descents method. This latter method will be discussed in more detail in Chapter 8.

The main difficulty in solving these equations is the question of the integrals. In the simple Hückel theory there are very few parameters to be considered but in the S.C.F. - L.C.A.O. method there are a considerable number of integrals which have to be known before the calculation can proceed. Because of this the application of the method to conjugated systems has followed two paths. In the non-empirical method equations 2.4.1. have been solved using a basis of $2p_z$ atomic orbitals, one on each core, all the integrals involved being calculated numerically (see Parr, Craig and Ross, 1950). Unfortunately the results of these calculations have been very disappointing.

A much more successful method has been the semi-empirical one. Essentially this assumes that the basis of "atomic orbitals" which are used are chosen to be localised about individual atoms (or cores) so that many of the integrals vanish. The remaining integrals are then estimated using experimental data. This method
was introduced by Parser and Parr (1953) who showed that
the excited states of benzene could then be estimated
very accurately.

Assuming that localised orthonormal functions exist such that the two electron integrals have the form

\[(ab | cd) = \gamma_{ab} \delta_{ac} \delta_{bd} \quad (2.4.2.)\]

where

\[\gamma_{ab} = (ab | ab)\]

and using these functions as a basis, the equations (2.4.1.) reduce to the form:

\[\sum_{\ell}^N a_{sr} F_{\ell \ell} = E_s a_{s \ell} \quad (2.4.3.)\]

where

\[F_{rr} = H_{rr} + \sum_{s}^N P_{ss} \gamma_{rs} - \frac{1}{2} P_{ss} \gamma_{ss}\]

\[F_{rs} = H_{rs} - \frac{1}{2} P_{rs} \gamma_{rs}\]

The coefficients \([a_{sr}]\) and orbital energies \(E_s\)
are now eigenvectors and eigenvalues of the S.C.F.
Hamiltonian \(F\) which can be written in terms of the integrals \(H_{rs}\) and \(\gamma_{rs}\) and the bond order matrix \(P\).

\[\text{\textsuperscript{\textdegree}}\text{Functions of this type have been constructed by Hall (1954) and McWeeny (1955). Equation (2.4.2.) is not exactly satisfied by these functions but it is a good approximation.}\]
An examination of the integrals $\mathcal{H}_{rs}$ shows that whereas $\mathcal{H}_{rs}(r \neq s)$ will depend only on the atoms $r$ and $s$ and will be insensitive to the rest of the molecule, the reverse is true for $\mathcal{H}_{rr}$ (see McWeeny, 1955 b, pp. 78-81). This can easily be seen by writing out $\mathcal{H}_{rr}$ more fully as:

$$\mathcal{H}_{rr} = (\omega_r | -\frac{1}{2} \nabla^2 + \nu_r | \omega_r) + \sum_{s \neq r} (\omega_r | V_s | \omega_r) \quad (2.4.4.)$$

where $V_s$ represents the potential due to the core at atom $s$. Now the first term which can be written as $\epsilon_r$ depends only on atom $r$ and is insensitive to the rest of the molecule; but the second term depends very much on the extent of the molecule. McWeeny (1956 b) has suggested that a good approximation for the integral $(\omega_r | V_s | \omega_r)$ is $-Z_s \gamma_{rs}$ (c.f. Pople, 1956, who uses an inverse distance approximation). With this approximation the S.C.F. Hamiltonian has the form

$$\begin{align*}
F_{rr} &= \epsilon_r + \frac{1}{2} F_{rr} \gamma_{rr} + \sum_{s \neq r} (\rho_{ss} - Z_s) \gamma_{rs} \\
F_{rs} &= \mathcal{H}_{rs} - \frac{1}{2} \rho_{rs} \gamma_{rs} \quad (2.4.5.)
\end{align*}$$

All the parameters and integrals now depend only on the atoms or atom pairs to which they refer and are insensitive to their environment and the extent of the molecule. Therefore they can be treated as parameters, determined from experimental data and used for a wide range of molecules.
The iterative techniques used to solve these equations can easily be adapted for electronic computation and this means calculations can be made even for large conjugated molecules. Luckily many concepts carry over from the Hückel theory and, in particular, the bond-order matrix has similar properties although the relationship between the bond order and bond length is more complicated (Deas, 1955). Calculated bond lengths are usually in good agreement with experiment and the use of S.C.F. - L.C.A.O. solutions leads to much improvement in the prediction of excited states (Pariser and Parr, 1953, Pariser, 1956, McWeeny and Peacock, 1957) and ionization potentials (Pople, 1953, Hush and Pople, 1955, Hedges and Matsu, 1958). Alternant hydrocarbons have received the most attention (see, for example, Hall, 1957) and it turns out that the results are very close to those obtained using the Hückel theory. In these molecules, charges on the individual atoms (Prr) are unity and substituting \textit{this} in equation (2.3.5.) it can easily be seen that the elements of the S.C.F. Hamiltonian are close to the assumption of the Hückel theory.
CHAPTER 3

GROUND STATE PROPERTIES OF SOME HETEROCYCLICS
3.1 Introduction

In order to illustrate the S.C.F. - L.C.A.O. method, in this chapter the bond order matrices for the ground states of various hydrocarbons and heterocyclic molecules will be obtained. The method of calculation used will be the steepest descent method due to McWeeny which is discussed in some detail in chapter 8.

It has already been pointed out that the S.C.F. - L.C.A.O. method has been successfully applied to conjugated hydrocarbons and the only reason for repeating calculations on these molecules is that the results will be needed for comparison. However, there have been few calculations on heterocyclic molecules and the theory of these molecules has not yet become standardized. The prime purpose of the calculations in this chapter, therefore, is to show that the self-consistent version of molecular orbital theory can be applied to a variety of heterocyclics and will give agreement with experiment for a variety of properties. In a previous discussion of hetero-molecules the difficulty of parameter values was mentioned. The difficulty is that the nitrogen nucleus requires different parameters from the carbon nucleus and so raises the problem of the magnitude of these parameters. The fact that a wide variety of values have been used by different authors makes the situation even more difficult.
since it is impossible to compare results. In these calculations only one set of parameters, those suggested by McWeeny and Peacock (1957) will be used. This choice has been made partly because the theory used is also the same so that the results can be accumulated and partly because their criterion, namely comparison with the observed spectra of several molecules, seems more sensitive to changes in the parameters than those previously used.

3.2 Method of Calculation

The method of calculation is that described in chapter 8 with the matrices \( R \) and \( Q \) now equal. The full details of the method can be found in McWeeny's papers (1956 a, b) or they can be deduced as a special case of chapter 8. The matrix \( R \), which is exactly half the charge and bond order matrix \( R = \frac{1}{2} F \) will minimize the energy and will also be idempotent.

The iteration procedure for finding the matrix which minimises the energy can be summarised as follows:-

(i) Starting with approximate matrix \( R_0 \), the self consistent Hamiltonian (2.4.3.) \( E \) is calculated.
(ii) The matrices \( \mathbf{I} \) and \( \mathbf{J} \) are calculated and the constant \( \lambda \) determined. In this case the formulae for \( \mathbf{I} \), \( \mathbf{J} \) and \( \lambda \) are:

\[
\mathbf{I} = \mathbf{S} + \mathbf{S}^+ \quad \mathbf{J} = \mathbf{S} - \mathbf{S}^+
\]

where \( \mathbf{S} = \mathbf{F} \mathbf{R}_0 - \mathbf{R}_0 \mathbf{F} \mathbf{R}_0 \)

and

\[
\lambda = -\frac{\alpha}{2b - c}
\]

where

\[
\alpha = \text{tr} \mathbf{I} \mathbf{F} \\
\beta = \text{tr} \mathbf{I} \mathbf{J} \mathbf{F} \\
c = \sum_{\mathbf{S}^u \mathbf{V}} \mathbf{I}_{\mathbf{S}^u} \mathbf{I}_{\mathbf{U} \mathbf{V}} [\langle \mathbf{S} \mathbf{U} | \mathbf{V} \rangle - \langle \mathbf{S} \mathbf{U} | \mathbf{V} \rangle]
\]

(iii) The change \( \delta \mathbf{R}_0 \) in \( \mathbf{R}_0 \) required to minimise the energy will be given by

\[
\delta \mathbf{R}_0 = -\lambda \left( 1 + \lambda^2 \mathbf{I}^2 \right)^{-1} (\mathbf{I} + \lambda \mathbf{I} \mathbf{J})
\]

(iv) The improved matrix will be given by

\[
\mathbf{R}_0 = \mathbf{R}_0 + \delta \mathbf{R}_0
\]

but in general \( \mathbf{R}_0 \) will not be idempotent.

The final step in the process is to obtain an idempotent matrix \( \mathbf{R}_1 \) from \( \mathbf{R}_0 \) by putting

\[
\mathbf{R}_1 = \mathbf{R}_0^2 - 2 \mathbf{R}_0
\]

(v) With the new value of \( \mathbf{R}_1 \), the whole process may be repeated until consistency is obtained.
The calculation has been programmed for the University of London "Mercury" computer so that the calculation for one molecule is completed in one operation. About ten iterations were necessary for consistency to within 0.0001 for the larger molecules and took about 25 minutes. The initial matrices used in the calculation were usually based on the corresponding Hückel-type matrix for the unsubstituted hydrocarbon. For quinoline, the use of the Hückel type naphthalene values for the initial matrix did not lead to convergence but the use of the self-consistent naphthalene values with an adjustment of the charges was sufficient to give a satisfactory initial matrix.

3.3 Values of the Parameters

In section 2.3 it was shown that with suitable approximations, the self-consistent field Hamiltonian could be written in terms of the bond-order matrix \( P \) (where \( P = 2 \bar{R} \)) and various parameters, viz.

\[
F_{rr} = \bar{\omega}_r - \frac{1}{2} \gamma_{rr} + \frac{1}{2} P_{rr} \gamma_{rr} + \sum_{s \neq r} (P_{ss} - \bar{Z}_s) \gamma_{rs}
\]

\[
F_{rs} = H_{rs} - \frac{1}{2} P_{rs} \gamma_{rs}
\]

where \( \epsilon_r = \bar{\omega}_r - \frac{1}{2} \gamma_{rr} \) and \( \bar{\omega}_r \) is the energy of an electron in a localised orbital in the standard excited state.
The values of the parameters $\gamma_{rs}$ are taken from Pariser (1956) and Pariser and Parr (1953) where possible and the inverse distance approximation is used for the remaining more distant nuclei. These values were assumed to be independent of whether the nuclei were carbon or nitrogen. Some of these integrals were also satisfactory for azulene. In this molecule, however, integrals involving next-nearest neighbours were not available and had to be estimated using a rather more sophisticated approximation (Parr, 1960) than inverse distance. The values obtained were -1.222 $\beta$ in the five-membered ring; -1.105 $\beta$ in the seven-membered ring; and -1.132 $\beta$ between the two rings.

The $H_{rs}$ parameters were all taken zero except for nearest neighbours and $H_{rs}$ between a carbon and a nitrogen nucleus was taken as slightly larger than that between two carbon nuclei as recommended by Pariser and Parr.

The most important parameter is the value of $\bar{\omega}_r$, which is a measure of the electronegativity of the atom relative to that of carbon. McWeeny and Peacock (1957) have investigated different values of $\bar{\omega}_r$ and find that the agreement between the calculated and observed spectra of the heterobenzenes is best for $\bar{\omega}_r = 0.35\beta$ ($\beta = -4.79$ eV).
If the diagonal matrix element \( H_{rr} \) is expressed in the conventional Hückel form as
\[
\lambda_n = \lambda_c + \delta \beta
\]
this value of \( \delta \) corresponds approximately to
\[
\delta = 0.20
\]

This value is much lower than has been used earlier. In the first Hückel-type calculations, e.g. Wheland and Pauling (1935), and Coulon and Longuet-Higgins (1947 b), \( \delta \) has been taken as large as 2 but this is now generally considered to be too large. Orgel, Cotrell, Dick and Sutton (1951) suggest the value 1 on the ground that it leads to the correct dipole moment of pyridine. The value 0.6 has also been supported (Chalvet and Sandorfy, 1949; Lowdin, 1951; Davies, 1955) on the same basis. This criterion is not decisive, however, for it depends on the value assigned to the dipole moment of the \( \sigma \)-electrons. By estimating this contribution more accurately, Hameka and Liquori (1958) find good agreement with the dipole moments of a number of heterocyclics using \( \delta = 0.40 \). The use of the bond-order, bond-length relation to fix \( \delta \) has been proposed by Lofthus (1959) and he suggests \( \delta = 0.9 - 1.0 \). These calculations have all been of the Hückel type, though with differing conventions as to overlap integrals and so are not exactly comparable with the self-consistent ones.
3.4 **Bond Orders**

The bond orders for a variety of molecules, obtained by this calculation, are shown in Fig. 3.4. The parent hydrocarbons were also calculated and are included in Fig. 3.4 for comparison. It is clear that, while substitution does not produce large changes, its effect is more pronounced on the charges on and close to the nitrogen atoms.

As can be seen in Fig. 3.4 the atomic charges are more nearly uniform than those predicted in previous calculations. This is due in part to the smaller value of $\delta$ and in part to the self-consistent equations which penalize any large accumulation of charge. The charge on the nitrogen atoms is always about 1.10 whereas other calculations, e.g. Coulson and Longuet-Higgins (1947 b) and Hameka and Liquori (1958), give larger and more varied values. The atoms nearest to an N atom have charges of 0.96 and 0.44, the latter being assigned to the atom whose bond to the nitrogen has the larger order. The charges of the atoms in the purely carbon rings depart very little from unity and do not always have the signs of the net charge suggested by the law of alternating polarity.

Perturbation theory (Coulson and Longuet-Higgins, 1947 a; Pople, 1955; McWeeny, 1956 b) suggests that
Fig. 3.4  Calculated charges and bond orders (contd. over)

The charges are on the outside of the figures and the bond orders on the inside. The charges are the net charges i.e. \((1 - P_{rr})\) and for the alternate hydrocarbons these are zero.
Fig. 3.4 (continued, see also page 47).
Fig. 3.4  Calculated charges and bond orders (concluded).

Fig. 3.4A  Approximate charges and bond orders.
the bond orders should be little changed by substitution and this is borne out in Fig. 3.4. There are small changes, however, and these seem to follow a pattern. Of the two bonds to the nitrogen the larger bond order is reduced and the smaller increased by about 0.005. The next nearest bonds all decrease in order by amounts which vary from 0.006 to 0.002.

The reality of this pattern can be demonstrated more clearly by using the quinoline and isoquinoline results to predict the results for other molecules. This is done by superimposing the differences due to substitution of the simple molecules on to the results for the parent hydrocarbon of the larger as the position of the nitrogen dictates and if there is any overlap the results are averaged. The results obtained in this way for one molecule are shown in Fig. 3.4A. The bond orders are in very good agreement with the accurate ones given in Fig. 3.4 though the charges are not quite so accurate. This procedure is useful in improving the initial matrices required for the iteration calculation.

3.5 Dipole Moments

The contribution to the dipole moment of these molecules due to their mobile electrons is readily calculated. It must be supplemented, however, by the
dipole moment due to the $\sigma$-electrons. Hameka and Liquori (1958) have shown that the contribution is due, very largely, to the lone pairs of the nitrogen atoms. By considering approximate analytical forms for the orbitals they estimate that the lone pair dipole moment is about 1.33D greater than that of a CH bond. Such calculations are, necessarily, approximate and the results are quite sensitive to the parameters employed. For this reason it seems better to use the experimental dipole moment of one molecule to fix the $\sigma$-moment and to use this value in the remaining calculations. Pyridine has been selected since its dipole moment is most accurately known (De More et al. 1954; Jannelli and Otsini, 1956).

The dipole moments calculated in this way using the charges in Fig. 3.4 and those of McWeeny and Peacock (op. cit) are shown in table 3.5, together with the observed values and those calculated by Hameka and Liquori. The agreement with experiment is within the probable error of the experimental values. The agreement with the Hameka and Liquori calculations is also good and shows that the dipole moment is not a very sensitive criterion for $\delta$. The lone pair moment of 1.74D is not so much larger than that of Hameka and Liquori as to contradict their calculations.
<table>
<thead>
<tr>
<th></th>
<th>$\mu_\sigma$</th>
<th>$\mu_\pi$</th>
<th>$\mu_\perp$</th>
<th>$\mu$</th>
<th>$\mu_{\text{EXP}}$</th>
<th>$\mu_{\text{HL}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>1.74</td>
<td>0.41</td>
<td>(2.15)</td>
<td>2.15±0.05(a,b)</td>
<td>2.20</td>
<td></td>
</tr>
<tr>
<td>Pyrmidin</td>
<td>1.74</td>
<td>0.39</td>
<td>2.13</td>
<td>2.10±0.10(c)</td>
<td>2.19</td>
<td></td>
</tr>
<tr>
<td>Pyridazine</td>
<td>3.01</td>
<td>0.78</td>
<td>3.79</td>
<td>3.94(d)</td>
<td>3.80</td>
<td></td>
</tr>
<tr>
<td>Quinoline</td>
<td>1.74</td>
<td>0.46</td>
<td>0.05</td>
<td>2.20</td>
<td>2.16(e)</td>
<td>2.22</td>
</tr>
<tr>
<td>Isoquinoline</td>
<td>1.74</td>
<td>0.42</td>
<td>0.20</td>
<td>2.17</td>
<td>2.54(e)</td>
<td>2.38</td>
</tr>
<tr>
<td>Benzquinoline</td>
<td>1.74</td>
<td>0.49</td>
<td>0.03</td>
<td>2.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzisoquinoline</td>
<td>1.74</td>
<td>0.47</td>
<td>0.31</td>
<td>2.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acridine</td>
<td>1.74</td>
<td>0.55</td>
<td></td>
<td>2.27</td>
<td>1.95(f)</td>
<td></td>
</tr>
</tbody>
</table>

a De Mcra, Wilcox and Goldstein, 1954
b Jannelli and Otsini, 1956
c Hückel and Salinger, 1944
d Schneider, 1948
e Rau and Narayanaswamy, 1934
f Bergmann, Engel and Mayer, 1932

TABLE 3.5 Calculated and observed dipole moments (in Debyes).
3.6 Bond Lengths

The theory of the relation between bond order and bond length developed by Coulson (1939) and Deas (1955) applies only to alternant hydrocarbons. It is based on the equality, at the equilibrium internuclear distance, of the attractive force due to the mobile electrons and the repulsive force due to the compression of the \( \sigma \)-electrons. For alternant hydrocarbons there are no other forces but for other conjugated molecules there is the attractive force of electrostatic type due to the net charges on the atoms. This force is the product of the net charges and the force between the corresponding orbitals, i.e.

\[
\nabla (\chi r_s)
\]

When this force is compared with the first two, for molecules of the type considered here, it is found to be only about 1 per cent. of their magnitudes, largely because the net charges are only 0.1 at most. Thus the alternant theory applies also to bonds whose net charges are as small as this.

<table>
<thead>
<tr>
<th>( p )</th>
<th>( r )</th>
<th>( r^+_\text{exp} )</th>
<th>( r^#_{\text{exp}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.493</td>
<td>1.433</td>
<td>1.429</td>
<td>1.433</td>
</tr>
<tr>
<td>0.771</td>
<td>1.362</td>
<td>1.360</td>
<td>1.366</td>
</tr>
<tr>
<td>0.553</td>
<td>1.416</td>
<td>1.428</td>
<td>1.419</td>
</tr>
<tr>
<td>0.770</td>
<td>1.362</td>
<td>1.359</td>
<td>1.366</td>
</tr>
<tr>
<td>0.498</td>
<td>1.430</td>
<td>1.434</td>
<td>1.433</td>
</tr>
<tr>
<td>0.508</td>
<td>1.439</td>
<td>1.433</td>
<td>1.436</td>
</tr>
<tr>
<td>0.613</td>
<td>1.398</td>
<td>1.398</td>
<td>1.399</td>
</tr>
</tbody>
</table>

+ Phillips, Ahmed and Barnes, 1960

\# Phillips, 1956
Since the bond orders calculated here are the self-consistent ones and not the Coulson ones the Deas relation for bond lengths should, in principle, be revised but a graph of the experiments lengths for naphthalene and anthracene follows the Deas graph fairly closely except that the high bond orders should have slightly longer lengths. This suggests that the Deas relation should still be accurate enough.

The CC bond lengths for acridine, calculated from the Deas relation, are given in the table along with the experimental results obtained by refined calculations on the X-ray diffraction data for two different crystalline forms of acridine. The agreement with experiment is surprisingly good. This agreement also helps to confirm that δ need not be as large as 1 to give acceptable bond lengths.

3.7 Isomeric Energy Differences

In addition to the quantities already mentioned, these calculations also give the contribution of the mobile electrons to the total energy. This is not, unfortunately, a quantity susceptible of experimental measurement. One quantity which can be deduced from it and is capable of measurement is the energy difference between isomeric molecules. The values calculated are
vertical energy differences since no allowances are made for any changes in bond length between isomers. It seems likely that these changes will be small.

From these calculations, isoquinolone should be more stable than quinoline by $0.00322 \beta$ or 356 cals/mole. Similarly benzisoquinolone is more stable than benz-quinoline by 398 cals/mole and more stable than acridine by 685 cals/mole. There does not seem to be any experimental estimate to compare with these predictions.
PART II

THEORY OF SINGLE DETERMINANT WAVE FUNCTIONS
CHAPTER 4

DENSITY MATRICES
4.1 Introduction

In part II we will be mainly concerned with single determinant wave functions, but in order to discuss the properties of such wave functions most easily, it is necessary to introduce density matrices. These can be defined in terms of a quite general wave function and have a physical significance which is lacking in the wave function itself. Also, the expectation value of any symmetrical operator can be written in terms of these matrices.

The density matrices for a single determinant wave function have some very special properties and these will be discussed in detail. Especially important is the fact that all the density matrices can be written in terms of the first order matrix and, in the case of the L.C.A.O. approximation, it can be shown that the density matrices are functions of two matrices which are analogues of the charge and bond order matrix.

The most general type of single determinant wave function in which each spin orbital is written as the product of a spacial part and a spin factor $\alpha$ or $\beta$, has
the form:

$$
\psi = (N!)^{-1/2} \left\{ \phi_1(1) \alpha(1), \phi_2(2) \alpha(2), \ldots, \phi_p(p) \alpha(p),
\Theta_1(p+1) \beta(p+1), \ldots, \Theta_q(n) \beta(n) \right\}
$$

(4.1.1.)

where \( \{ \phi_i \} \) and \( \{ \Theta_i \} \) are orthonormal sets of functions and
\[ \int \phi_i(1) \Theta_i(1) d\tau \]

is not necessarily zero. Any determinantal wave function can be put in this form, and
most of the results obtained will be for this wave function. If density matrices are used to investigate its spin
properties, it turns out that it can only be an eigen-
function of \( \mathcal{S}_z \) if \( \psi_i = \Theta_i \Rightarrow \psi \), i.e. if the wave
function has the form usually assumed in the Hartree-Fock
theory (equation 1.4.6).

\*It would be conceivable to have a wave function in the
form of a Slater determinant (1.4.3) in which the spin
orbitals could not be space-spin factored but would be
in the form

$$
\psi_i(\mathbf{r}) = \psi_i^\alpha(\mathbf{r}) \alpha + \psi_i^\beta(\mathbf{r}) \beta
$$

thus having components associated with \( \alpha \)-spin and \( \beta \)-spin.
Such wave functions would not, in general, be eigen-
functions of \( \mathcal{S}_z \). However, in the special case of
\( \pi \)-electron systems with the usual Pariser and Parr
approximations, it can be easily shown that the wave
function has the form of (4.1.1.) so that the spin orbitals
do turn out to be space-spin factored. This, of course,
will only be true if the Hamiltonian is assumed to have
no spin terms.
In the final section it will be shown that projection operators can be defined which enable us to select from a general wave function another wave function with some particular property. For example, if a wave function is a mixture of spin states, then projection operators can be used to obtain a wave function which is a pure spin state. Thus projection operators can be used to obtain from the wave function (4.1.1) a wave function which is an eigenfunction of spin.

4.2 Density Matrices for a General Wave Function

Given a system of \( N \) identical antisymmetrical particles whose wave function is \( \Psi(x_1, x_2, \ldots, x_N) \) where \( x_1, x_2, \ldots, x_N \) are the coordinates (including spin) of the particles, then a set of \( N \) density matrices of various orders can be defined. If \( \rho_{++}(i', i', 1, \ldots, n) \) or \( \rho_{+}(x_1', x_2', x_3'|x_1, x_2, x_3) \) denotes the \( + \)th order density matrix, then we define

\[
\rho_{++}(i', j', \ldots, i' ||1, 2, \ldots, n) = N \int \Psi^*(t', i', \ldots, i', 1, 2, \ldots, n) \Psi^*(1, 2, \ldots, n) dx_{i'}, dx_{j'}, \ldots, dx_{n}(4.2.1)
\]

The diagonal elements of these matrices have a definite physical interpretation. \( \rho_{++}(i'|1) dx_{i'} \) for example, is \( N \) times the probability of finding a particle in the volume element \( dx_{i'} \), surrounding the point \( x_{i'} \).
when all the other particles have arbitrary positions and spins. \( \rho_2(1,2|1,2) \, d\vec{x}_1 \, d\vec{x}_2 \) is the number of pairs, times the probability of finding one particle around the point \( \vec{x}_1 \) and another around \( \vec{x}_2 \) when the remaining particles have arbitrary positions in the configuration space. Similar interpretations hold for the diagonal elements of the other matrices.

The density matrices as defined above, include the spin of the particles, but by integrating out spin, we can define spinless density matrices. Denoting the spin components by \( s \) and putting \( d\vec{X}_i = d\vec{X}_i \, d\vec{S}_i \) then the \( +1 \) order spinless density matrix is given by

\[
P_+ = \left\{ \rho_+ (1,2,3,4) \right\} \frac{d\vec{S}_1 \, d\vec{S}_2 \, d\vec{S}_3 \, d\vec{S}_4}{s_1 = s_2 = s_3 = s_4} \tag{4.2.2.}
\]

Using the antisymmetrical property of the wave function, it follows that the density matrices are antisymmetrical in each set of indices. From this we can deduce a formula for the expectation value of a physical operator which is symmetrical with respect to the particles of the system. Denoting this operator by \( Q \), we can write:

\[
Q = Q_0 + \sum_i Q_i + \frac{i}{\pi} \sum_{ij} Q_{ij} + \frac{i}{3!} \sum_{ijk} Q_{ijk} + \ldots \tag{4.2.3.}
\]

where each term is a one-, two-, or many-particle operator respectively.
Then we have, for example,

\[
\int \Psi^* \left( \frac{1}{3!} \sum_{i,j,k} \langle \hat{Q}_{ijk} \rangle \right) \Psi \, d\mathbf{x} = \frac{1}{3} N (N-1)(N-2) \int \Psi^* \Psi \, d\mathbf{x}
\]

\[= N^2 C_2 \int \left\{ \left[ \int \Psi^* \left( \sum_{i,1,\ldots,N} \langle \hat{Q}_{1N3} \Psi \rangle \right) \right]^2 \right\} \, dx_1 \, dx_2 \, dx_3 \,
\]

where \( \mathbf{x}' \) is put equal to \( \mathbf{x}_1, \mathbf{x}_2 \) to \( \mathbf{x}_2, \mathbf{x}_3' \) to \( \mathbf{x}_3 \) before integration over these variables takes place.

This can be written as

\[
\int \hat{Q}_{123} \rho_3 \left( x_1', x_2', x_3' \right) \, dx_1 \, dx_2 \, dx_3 \]

providing the convention is adopted that the operator \( \hat{Q}_{123} \) works only on the unprimed coordinates, and after this, the unprimed coordinates are put equal to the primed before the integration takes place. Extending this convention, the expectation value of \( \hat{Q} \) can be written as:

\[
\langle \hat{Q} \rangle = \hat{Q}_0 + \int \hat{Q}_1 \rho_1 \left( x_1' \right) \, dx_1 + \int \hat{Q}_{12} \rho_1 \left( x_2' \right) \, dx_2 + \int \hat{Q}_{13} \rho_1 \left( x_3' \right) \, dx_3 + \ldots
\]

In particular the expectation value of a Hamiltonian \( \mathcal{H} \), consisting of one-electron terms \( \mathcal{H}_1 \) and two electron repulsion terms, becomes

\[
\langle \mathcal{H} \rangle = \langle \hat{H}_1 \rangle + \sum_{i,j} \langle \hat{H}_{ij} \rangle = \int \mathcal{H}_1 \rho_1 \left( x_1' \right) \, dx_1 + \int \mathcal{H}_{12} \rho_1 \left( x_2' \right) \, dx_2 + \ldots
\]

If we consider the operator \( S_i^2 \), then using the formula (Dirac, 1929)
4.3 Density Matrices for a Single Determinant Wave Function

Consider a wave function \( \psi \) in the form of a single determinant built up of a set of \( N \) orthonormal orbitals \( \psi_1, \psi_2, \ldots, \psi_N \);

\[
\psi = (N!)^{-\frac{1}{2}} \text{Det} \{ \psi_1(1) \psi_2(2) \ldots \psi_N(N) \}
\]

Then from the orthonormality conditions we have,

\[
\rho_{1}(1'1) = \sum_{k}^{N} \psi_{k}^{*}(1') \psi_{k}(1) \quad \quad (4.3.1.)
\]

\[
\rho_{1}(1'2'1'2) = \frac{1}{\xi} \sum_{k}^{N} \sum_{j}^{N} \{ \psi_{k}^{*}(1) \psi_{k}(1') \psi_{j}^{*}(2) \psi_{j}(2') - \psi_{k}^{*}(1') \psi_{k}(1) \psi_{j}^{*}(2') \psi_{j}(2) \}
\]

\[
= \frac{1}{\xi} \begin{vmatrix}
\rho_{1}(1'1) & \rho_{3}(1'2) \\
\rho_{1}(2'1) & \rho_{1}(2'2)
\end{vmatrix} \quad \quad (4.3.2.)
\]
And, in general, it is easy to show by induction that
\[\rho_k (1'2'\ldots r'|i 2\ldots t) = \frac{1}{r!} \det \left\{ \rho_1 (1|1') \rho_1 (2|2') \ldots \rho_1 (+|t') \right\}\]

Then it follows from (4.2.5.) that the expectation value of the Hamiltonian \(H\) is given by:
\[\langle H \rangle = \int h_1 \rho_1 (1'|1) d\chi_1 + \frac{i}{2} \int \frac{1}{r'!} \left\{ \rho_1 (1|1) \rho_1 (2|2') - \rho_1 (1|2) \rho_1 (2|1') \right\} d\chi_1\]

and from (4.2.7.):
\[\langle S^2 \rangle = -\frac{1}{2} N (N-1) + \frac{1}{2} \int \left\{ \rho_1 (t_1 s_1 |t_2 s_2) \rho_1 (t_2 s_2 |t_1 s_1) - \rho_1 (t_2 s_2 |t_1 s_1) \rho_1 (t_1 s_1 |t_2 s_2) \right\} d\chi_1 d\chi_2\]

The wave function \(\Psi\) is invariant against unitary transformations of the spin orbitals \(\{ \psi_i \}\) and it is trivial to show that \(\rho_1 (1'|1)\) is also invariant. Hence all the density matrices are invariant and do not depend on any particular choice of \(\{ \psi_i \}\). The most convenient choice of the orbitals is to take a certain number of orbitals with \(\alpha\)-spin and a certain number with \(\beta\)-spin depending on the system. Thus denoting the spacial parts of the orbitals by \(\phi_i\) and \(\Theta_i\) the wave function can be written as
\[\Psi = (N!)^{-\frac{1}{2}} \det \left\{ \phi_1 (1) \alpha (1) , \phi_p (p) \alpha (p) , \Theta_1 (p+1) \beta (p+1) , \Theta_q (N) \beta (N) \right\}\]

(4.3.6.)
It is always possible by taking linear combinations of the \( \{ \psi_i \} \) orbitals and the \( \{ \Theta_i \} \) orbitals to make the sets \( \{ \psi_i \} \) and \( \{ \Theta_i \} \) orthonormal. The wave function and the density matrices remain invariant under these operations.

The first order density matrix now has the form:

\[
\rho_1(1'|1) = \sum_{k=1}^{p} \phi_k^*(1') \phi_k(1) + \sum_{k=1}^{q} \Theta_k^*(1') \Theta_k(1) (4.3.7)
\]

Thus the spinless density matrix \( \rho_1 \) can be put in the form:

\[
P_1(1'|1) = P_1^x + P_1^y = \sum_{k=1}^{p} \phi_k^*(1') \phi_k(1) + \sum_{k=1}^{q} \Theta_k^*(1') \Theta_k(1) (4.3.8)
\]

and it is clear that all the density matrices and consequently the expectation values of all symmetrical operators can be written in terms of \( P_1^x \) and \( P_1^y \).

In the usual L.C.A.O. approximation the spacial functions \( \phi_i \) and \( \Theta_i \) are written as linear combinations of a set of \( m \) fixed orthonormal functions \( \{ \omega_i(t) \} \).

Introducing sets of coefficients \( \{ a_{ij} \} \) and \( \{ b_{ij} \} \) we can write:

\[
\phi_i = \sum_{j=1}^{m} \omega_j a_{ji} \quad \Theta_i = \sum_{j=1}^{m} \omega_j b_{ji} \quad (4.3.9)
\]

Then,

\[
P_1^x(1'|1) = \sum_{k=1}^{p} \sum_{i,j} \phi_k^* \phi_k(1') \omega_j(1) = \sum_{i,j} R_{ij} \omega_i^*(1') \omega_j(1) (4.3.10)
\]

\[
P_1^y(1'|1) = \sum_{k=1}^{q} \sum_{i,j} \theta_k^* \theta_k(1') \omega_j(1) = \sum_{i,j} Q_{ij} \omega_i^*(1') \omega_j(1) (4.3.11)
\]
where the matrices $R$ and $Q$ are defined by

$$R_{ij} = \sum_{k=1}^{h} a^*_{jk} a_{ik}$$

$$Q_{ij} = \sum_{k=1}^{q} b^*_{jk} b_{ik}$$

(4.3.12.)

All the density matrices can be put in terms of the functions $\{\omega_i\}$ and the two matrices $R$ and $Q$; and so in this approximation $R$ and $Q$ contain all the physical information about the system. Using the orthogonality relations, it is possible to show that:

$$R^2 = R$$
$$tR = P$$

$$Q^2 = Q$$
$$tQ = Q$$

(4.3.13.)

On specialising to the ground state of an alternant hydrocarbon in the usual L.C.A.C. approximation with doubly occupied orbitals, we see that $R=Q=\frac{1}{2}P$, where $P$ is the charge and bond order matrix. Thus we may in the general case regard $R$ and $Q$ as the charge and bond order matrices for electrons with $\alpha$-spin and $\beta$-spin respectively.

4.4 Spin Properties of a Single Determinant Wave Function

*This treatment is due to Löwdin (1959, page 209).
The first order density matrix for the wave function in the form of a single determinant, with the notation adopted in the previous section, is given by:

\[
\rho_1(1\mid 2) = \rho_1^\alpha(1\mid 2) \alpha^*\beta + \rho_1^\beta(1\mid 2) \beta^*\alpha \tag{4.4.1}
\]

therefore

\[
\langle \xi^2 \rangle = -\frac{1}{4} (N-4) N + \frac{1}{4} \sum \left\{ \left[ \rho^\alpha_1(1\mid 2) \alpha^*\beta + \rho^\beta_1(1\mid 2) \beta^*\alpha \right] \beta(1) \beta(2) \right\} dx_1 dx_2 - \frac{1}{2} \sum \left\{ \left[ \rho^\alpha_1(1\mid 2) \alpha^*\beta + \rho^\beta_1(1\mid 2) \beta^*\alpha \right] \alpha(1) \beta(2) \right\} dx_1 dx_2
\]

\[
= \frac{1}{4} (p-q)^2 + \frac{1}{2} (p+q) - \frac{1}{2} \sum S_{k\ell} \tag{4.4.2}
\]

where

\[
m = \frac{1}{2} (p-q) \quad (q<p) \quad S_{k\ell} = \int \phi^*_k(1) \Theta_k(1) d^4 x_1
\]

The operator \( \xi^4 \) can be written in the form

\[
\xi^4 = \frac{1}{16} N^2(N-4)^2 - \frac{1}{4} N(N-4) \sum_{ij} \rho_{ij}^c + \frac{1}{4} \sum_{ij} \rho_{i\bar{j}} \rho_{\bar{j}i} \tag{4.4.3}
\]

and using the 4th order density matrix it can be shown that:

\[
\langle \xi^{14} \rangle = \left[ p - \frac{q}{2} \sum_{k\ell} S_{k\ell} \right] \left[ q - \frac{q}{2} \sum_{k\ell} S_{k\ell} \right] + \frac{q}{2} \sum_{k\ell} S_{k\ell} + \frac{q}{4} \sum_{k\ell} \left[ q - \sum_{k\ell} S_{k\ell} \right] \tag{4.4.4}
\]

Now consider the width \( \Delta \xi^2 \) defined by

\[
\langle \Delta \xi^2 \rangle = \langle (\xi^2 - \langle \xi^2 \rangle)^2 \rangle = \langle \xi^4 \rangle - \langle \xi^2 \rangle^2 \tag{4.4.5}
\]
This quantity vanishes if, and only if, the wave function under consideration is an eigenfunction of $S^2$. For the single determinant wave function

$$\left( \Delta S^2 \right)^2 = \left[ q - \sum_k \sum_{\ell} S_{k\ell} \right] \left[ p - \sum_k S_{k\ell}^2 \right] + 2 \sum_k \sum_{\ell} S_{k\ell}^2 - 2 \sum_{k\ell m} S_{mk} S_{m\ell} S_{n\ell} S_{nk} \quad (4.4.6.)$$

Considerations of the overlap matrix $S_{k\ell}$ lead us to the condition

$$\sum_k \sum_{\ell} S_{mk} S_{m\ell} S_{n\ell} S_{nk} \leq \sum_k \sum_{\ell} S_{k\ell}^2 \leq q \quad (4.4.7.)$$

and the equality sign only occurs when

$$\Theta_k (\mathbf{1}) = \phi_k (\mathbf{1}) \quad k = 1, 2, \ldots q$$

Hence a single determinant wave function is an eigenfunction of $S^2$ if and only if the number of doubly filled orbitals is $q$. If we use the L.C.A.O. approximation this is equivalent to the condition that

$$t^r R Q = q \quad (4.4.8.)$$

It is clear that even in the case when $\Theta_k \neq \phi_k$, the determinant is an eigenfunction of $S^2$ with eigenvalue $m = \frac{1}{2} (p - q)$ and so in the general case when

$$\langle S^2 \rangle = m(m+1) + \left[ q - \sum_k \sum_{\ell} S_{k\ell}^2 \right]$$

the determinant will be a mixture of spin states associated with quantum numbers $m, m+1, \ldots, \frac{1}{2} N$. For example,
if \( m = 1 \) then in the usual Hartree-Fock method we would have a pure triplet with \( \langle \xi^2 \rangle = 2 \) But in the case when \( \Theta_k = \phi_k \), then \( \langle \xi^2 \rangle > 2 \) and the wave function would be a mixture of spin states, i.e.

\[
\text{triplet} + \text{quintet} + \text{septet} + \ldots
\]

4.5 Projection Operators

Consider an operator \( \mathcal{T} \) which commutes with \( H \) and suppose \( \mathcal{T} \) has a finite number of eigenvalues \( \ell \) with eigenfunctions \( \psi_\ell \).

Then

\[
\mathcal{T} H = H \mathcal{T} \quad (4.5.1.)
\]

\[
\mathcal{T} \psi_\ell = \ell \psi_\ell \quad (4.5.2.)
\]

and it is clear that the operator \( (\mathcal{T} - \ell) \) acting on \( \psi_\ell \) gives the result zero. Now if an arbitrary trial function \( \psi \) can be written in the form:

\[
\psi = \sum \alpha_\ell \psi_\ell \quad (4.5.3.)
\]

then the product operator

\[
O_k = \prod \frac{\mathcal{T} - \ell}{\ell - \ell_k} \quad (4.5.4.)
\]

when applied to \( \psi \) will select the component of \( \psi \) associated with the term \( \ell = \ell_k \). Such an operator is known as a projection operator and has the following properties:

\[
O_k^2 = O_k \quad (4.5.5.)
\]
(ii) The denominator \( t_\ell - t_k \) is chosen so that the term in \( \mathcal{U} \) associated with \( \ell = k \) survives the projection unchanged.

(iii) \( O_k \) commutes with \( H \) (from 4.5.1.) and using the "turn over rule" and property (i) it follows that

\[
\int (O_k \mathcal{U})^* H (O_k \mathcal{U}) \, d\chi = \int \mathcal{U}^* O_k^+ H O_k \mathcal{U} \, d\chi
\]

\[
= \int \mathcal{U}^* H (O_k^+ O_k) \mathcal{U} \, d\chi
\]

\[
= \int \mathcal{U}^* H O_k \mathcal{U} \, d\chi
\]

If we now apply this technique to the operator \( \mathcal{J} = S^2 \) with \( \ell = \ell(\ell+1) \), the projection operator \( O_{2\lambda+1} \) for selecting a pure spin state, with quantum number \( \lambda \) and having multiplicity \( (2\lambda+1) \), from a trial wave function which is a mixture of spin states, will be given by:

\[
O_{2\lambda+1} = \prod_{k \neq \lambda} \left\{ \frac{S^2 - k(k+1)}{\lambda(\lambda+1) - k(k+1)} \right\} \quad (4.5.6.)
\]

Thus, if we consider a single determinant wave function \( \overline{\Psi} \) with \( \Theta_k = \phi_k \) so that \( \overline{\Psi} \) is a mixture of spin states, then the component of \( \overline{\Psi} \) which is associated with spin multiplicity \( (2\lambda+1) \) will be given by

\[
\overline{\Psi}_{(2\lambda+1)} = O_{2\lambda+1} \overline{\Psi} \quad (4.5.7.)
\]
and the energy will be:

\[
\langle H \rangle = \frac{\int \psi^* H O_{2n+1} \psi \, dx}{\int \psi^* O_{2n+1} \psi \, dx} \tag{4.5.8.}
\]

with similar expressions for other expectation values.

The operators $H$ and $O_{2n+1}$ can be combined together to form a new operator $Q$ which can be put in the form:

\[
Q = Q_0 + \sum_i Q_i + \sum'_j Q_{ij} + \ldots
\]

with the usual notation. Hence it follows that $\langle H \rangle$ can be expressed in terms of the density matrices associated with the function $\tilde{\psi}$.

As well as projection operators to select eigenfunctions of $S^2$, operators can be constructed to select eigenfunctions of $S_z$ and also functions adapted to the symmetry group of the nuclei for a specified irreducible representation. These projection operators are important in the study of improved wave functions since they usually simplify the problem a great deal (Löwdin, 1955, Helvin, 1956).
CHAPTER 5

CORRELATION PROBLEM AND IMPROVED WAVE FUNCTIONS
5.1 Introduction

So far we have been mainly concerned with single determinant wave functions which arise from the idea of electrons moving independently in molecular orbitals. It has been pointed out that such wave functions have many desirable properties, not least of which is the fact that they provide simple qualitative interpretations of molecules whereas such interpretations are difficult to make using more complicated, even if more accurate, wave functions. It has also been proved that for a single determinant wave function to be an eigenfunction of spin, we must have $\Theta_k = \phi_k$ i.e. doubly occupied orbitals as in the usual Hartree–Fock method. However, results from previous sections show that one way to obtain improved wave functions is to allow electrons with different spins to have different spacial orbitals and to use projection operator techniques to obtain pure eigenfunctions of spin. Thus, although the wave function in such a scheme will then be the sum of determinants, not all the simplicity of the molecular orbital idea will be lost. This method of obtaining improved wave functions will be considered in some detail in the following chapters.

That improved wave functions are needed can be seen from a consideration of the so-called correlation problem.
The presence of the two-electron repulsion terms in the Hamiltonian implies that no two electrons should come close together in space; but in the usual single determinant scheme with doubly occupied orbitals, electrons with opposite spins are forced to move in the same spacial orbitals. This means that the error in the energy due to this (the correlation error) can become quite significant and, more important, the form of the wave function can be incorrect for describing some molecular properties.

In fact a careful consideration of a single determinant wave function shows that the more accurately it represents a pure spin state, then the less accurately does it take into account the correlation between electrons with opposite spins. Thus it is clear that a single determinant wave function can never have all the desirable properties as described in section 1.3 and so to reduce the correlation error it is necessary to obtain improved wave functions. One method of doing this - the method of different orbitals for different spins - has already been mentioned. Two others, the method of configuration interaction and the use of correlated wave functions will be considered very briefly in sections 3 and 4.

5.2 **Correlation Problem**

The physical interpretation of the diagonal elements
of the second order density matrix for a molecule is as follows:

\[ p_2(1,2|1,3) d_{x_1} d_{x_2} = \text{no. of pairs} \times \text{probability of finding one electron at point } \ x_1 \ \text{and another at } x_2 \ \text{when the other electrons have arbitrary positions}. \]

The Hamiltonian for a molecule contains electron repulsion terms \[ \sum_{ij}^{'} / t_{ij} \] which represent the mutual repulsion energies between pairs of electrons. It follows that the repulsion energy becomes infinite as \[ t_{ij} \to 0 \], and this implies that electrons cannot come close together in space. Hence the probability density \[ p_2(x_1 x_2 | x_1 x_2) \] must vanish when the spacial coordinates \[ x_1 \] and \[ x_2 \] are equal; and we can say that each electron is surrounded by a Coulomb hole with respect to all the other electrons.

If we now consider the probability density \[ p_2(x_1 x_2 | x_1 x_2) \] in the case of a single determinant wave function then, when \[ x_1 = x_2 \] and \[ s_1 = s_2 \] it follows from section 4.3 that

\[ p_2(x_1 x_1 | x_1 x_1) = 0 \quad (5.2.1.) \]

and in fact this is a perfectly general result, holding for all antisymmetrical wave functions. Thus we can say each electron is surrounded by a Fermi hole with respect to all other electrons with the same spin.
However, now if we consider the case \( \mathbf{t}_1 = \mathbf{t}_1 \) but \( s_1 \neq s_2 \), then, using the notation of Chapter 4,

\[
\rho_2 \left( \mathbf{t}_1 s_1, \mathbf{t}_1 s_2 \left| \mathbf{t}_1 s_1, \mathbf{t}_1 s_2 \right. \right) \propto \sum_{i=1}^{q} \sum_{k=1}^{p} \phi_k^2(1) \Theta_k^2(1) \quad (5.2.2.)
\]

and this will certainly not be zero for all \( \mathbf{t}_1 \). Thus there is no Coulomb correlation between electrons with opposite spins for a single determinant wave function.

\[
\sum_{i=1}^{q} \sum_{k=1}^{p} \phi_k^2(1) \Theta_k^2(1) \propto \text{Prob. of finding electron with } \alpha\text{-spin at } \mathbf{t}_1 \times \text{prob. of finding electron with } \beta\text{-spin at } \mathbf{t}_1
\]

Hence it is clear that in the usual Hartree-Fock approximation when \( \phi_k \equiv \Theta_k \) these probabilities will be large and the error in the wave function and the energy due to this will be quite appreciable. Physically the error is due to forcing pairs of electrons with opposite spins into the same spatial orbital; and by relaxing the condition \( \phi_k \equiv \Theta_k \), some improvement can be obtained.

But no single determinant wave function can be an eigenfunction of spin and at the same time take into account the correlation effect. For this reason in order to get more accurate results, it is necessary to obtain improved wave functions.

Table 5.2 gives examples of the energy error - the correlation error - due to neglect of the Coulomb
correlation in the case of atoms (Fröman, 1958). It should be noticed that even though the error is usually small compared with the absolute value of the energy, since we are almost always concerned with energy differences, the error can be important. Also the neglect of correlation can produce a wave function whose form is incorrect for describing various molecular properties, for example, magnetic properties (Slater, 1951, 1953).

**Table 5.2**

<table>
<thead>
<tr>
<th>Element</th>
<th>Correlation error in e.v.</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>-1.14</td>
</tr>
<tr>
<td>H⁻</td>
<td>-1.08</td>
</tr>
<tr>
<td>Be</td>
<td>-2.37</td>
</tr>
<tr>
<td>F⁻</td>
<td>-10.69</td>
</tr>
</tbody>
</table>

5.3 **The Method of Configuration Interaction**

This method is based on the assumption that a wave function can be accurately written as a linear combination of Slater determinants. If \( \{ \psi_i(x) \} \) is a complete orthonormal set of spin orbitals and if \( \Phi_\kappa \) is a single Slater determinant built up of the N- orbitals

\[
\psi_{k_1} \psi_{k_2} \ldots \psi_{k_N}
\]

where \( \kappa \) denotes the ordered configuration defined by \( (k_1, k_2, \ldots, k_N) \) then,
assuming the series converges, the solution of the Schrödinger equation will be

$$\Psi = \sum K C_k \Phi_K$$

where the summation is over all configurations K. The coefficients $C_k$ are given by the infinite system of linear equations obtained using the variational method:

$$\sum_L (H_{KL} - E \delta_{KL}) C_L = 0 \quad \text{where} \quad H_{KL} = \int \Phi_K^* H \Phi_L dx$$

Obviously only a limited number of configurations can be considered and the difficulty in the method is to choose the basic set of orbitals so that one gets rapid convergence. Projection operators can be used to select the determinants with the correct symmetry and spin properties and this reduces the number of configurations which have to be considered.

For further details and references see the Technical Report by McWeeny (1955) and the review by Löwdin (1959).

5.4 Correlated Wave Functions

Correlated wave functions are those in which an attempt to take into account electronic correlation is made by including the interelectronic distance explicitly in the wave function. The idea is not new and in fact two of the most accurate wave functions in the whole
subject are correlated wave functions. Both the Hylleraas wave functions for the ground state of Helium (Hylleraas, 1929) and the James-Coolidge wave function for the ground state of the hydrogen molecule (James and Coolidge, 1933) are power series expansions, one of the variables being the interelectronic distance.

In applications to other two electron systems it has been found that good results can be obtained using a wave-function of the form

$$\Psi = C(t_{12}) \phi (t_1, t_2)$$

where the interelectronic distance only appears as a coordinate in the so-called correlation factor $C(t_{12})$. Even with $C(t_{12})$ taking the very simple form

$$C = 1 + \alpha t_{12}$$

some good results have been obtained and attempts have been made to extend the method to larger systems. For a review and references see Löwdin (1959).
CHAPTER 6

UNRESTRICTED HARTREE-FOCK WAVE FUNCTIONS
6.1 Introduction

The method of different orbitals for different spins can be applied to the problem of finding improved wave functions in two ways. One of these is called the unrestricted Hartree-Fock method and the other the extended Hartree-Fock method and it is the former with which we shall be concerned. The basic difference between them is that in the unrestricted form the variational principle is used with a single determinant wave function whereas in the extended form projection operators act on the single determinant to give a wave function which is an eigenfunction of spin and this wave function, which will then be the sum of determinants, is the one which is used in the variational treatment.

In the extended form of the Hartree-Fock method, therefore, the expectation value of the Hamiltonian is given by eqn. (4.5.8.).

\[
\langle H \rangle = \frac{\int \Psi^* H \Omega \Psi \, dx}{\int \Psi^* \Omega \Psi \, dx}
\]  

(6.1.1.)

where \( \Psi \) is the single determinant and \( \Omega \) the projection operator defined in eqn. (4.5.6.). Using the L.C.A.O. approximation and the results of sections 4.3 and 4.5, it follows that \( \langle H \rangle \) can be written in terms of the matrices \( R \) and \( Q \), but this expression will be very complicated. For this reason, attempts so far made to use the extended
method have been confined to cases in which the spacial orbitals are more closely defined than in the L.C.A.O. approximation. In the alternant molecular orbital method, for example, linear combinations of bonding and antibonding orbitals are taken so that only one parameter appears in the equations (Löwdin, 1954, 1955). Even with this considerable simplification, however, some excellent results have been obtained for benzene and acetylene (Itoh and Yoshizumi, 1955).

The expectation value for the Hamiltonian in the unrestricted method is given by:

\[ E = \frac{\int \Psi^* H \Psi \, dx}{\int \Psi^* \Psi \, dx} \]  

(6.1.2.)

and this too can be written in terms of \( R \) and \( Q \) although in this case the formula is quite simple. By using the variational method, the equations which the coefficients of the "best" \( \text{M.O.}'s \) satisfy can be derived and the matrices \( R \) and \( Q \) which give the minimum value of \( E \) can be obtained by a steepest descents method. Unfortunately it turns out that for a singlet ground state one solution of these equations is \( R = Q \) which implies that the best possible single determinant singlet ground state wave function is one with doubly occupied orbitals, exactly as is usually assumed. But for doublet and triplet states, for example, the best \( \text{M.O.}'s \) will be
those in which there are different orbitals for electrons with different spins.

For these states, the single determinant wave function will, unfortunately, be a mixture of spin states but it will take into account electron correlation and it is likely to give better energy values than the usual Hartree-Fock wave functions (c.f. Pratt, 1956). Projection operators can be used to make the wave function an eigenfunction of spin and, although this will hardly give the best wave function possible since the variational method will have been used before instead of after the projection, it will certainly lead to some improvement. In the final section, therefore, various formulae will be obtained, in the case when this is done with the assumption that the projection operator

\[ O_{\alpha \lambda 1} = \prod_{k \neq \lambda} \left( \frac{S^2 - k(k+1)}{\lambda(\lambda+1) - k(k+1)} \right) \]  

(6.1.3.)

which is needed to make the wave function represent a pure spin state can be approximated by the annihilator

\[ A_{\alpha \lambda 1} = \frac{\lambda^2 - (m+1)(m+2)}{m(m+1) - (m+1)(m+2)} \]  

(6.1.4.)

If we require a pure triplet, for example, this is equivalent to assuming that the single determinant wave
function is a mixture of triplet and quintet states when in fact it is a mixture of triplet, quintet, septet, etc. In other words we assume that the contributions in the single determinant from the septet state and the states of higher multiplicity are negligible.

6.2 The Equations for the Molecular Orbital Coefficients

Consider a system of N electrons and suppose the wave function \( \Psi \) for the system can be written in terms of \( N \) H.O.'s \( \psi_1, \psi_2, \ldots, \psi_N \) where the \( \{\psi_i\} \) include spin and are orthogonal

\[
\Psi = \left( N! \right)^{-\frac{1}{2}} \text{Det} \left\{ \psi_1(1) \psi_2(2) \ldots \psi_N(N) \right\} \quad (6.2.1.)
\]

The total Hamiltonian \( H \) can be written as (see 1.4.1)

\[
H = \sum_i \mathcal{H}_i + \frac{i}{2} \sum_{ij} \mathcal{H}_{ij}
\]

and the total energy is given by

\[
E = \int \overline{\Psi} H \Psi \, dx = \sum_i \mathcal{H}_{ii} + \frac{i}{2} \sum_{ij} \left[ \mathcal{H}_{ij} \right] - \left[ \mathcal{H}_{ji} \right] \quad (6.2.3.)
\]

where

\[
\mathcal{H}_{ii} = \int \psi_i^*(1) \mathcal{H}_i \psi_i(1) \, dx_1
\]

\[
\left[ i,j \mid k,l \right] = \int \psi_i^*(1) \psi_j^*(2) \frac{1}{h} \psi_k(1) \psi_l(2) \, dx_1 \, dx_2
\]

If we assume that there are \( p \) orbitals associated with \( \alpha \)-spin and \( q \) with \( \beta \)-spin, then the energy simplifies
to:
\[
E = \sum_{i}^p \varepsilon_i \phi_i + \sum_{j}^q \varepsilon_j \phi_j + \frac{1}{2} \sum_{ij}^p \{ [\phi_i|\phi_j] - [\phi_j|\phi_i] \} + \frac{1}{2} \sum_{ij}^q \{ [\phi_i|\phi_j] - [\phi_j|\phi_i] \} + \sum_{\alpha}^p \sum_{j}^q \{ [\phi_i|\phi_j] - [\phi_j|\phi_i] \}
\]
(6.2.4.)

where \( \sum_{\alpha} \) is the sum over orbitals with \( \alpha \)-spin only.

Now as in the usual L.C.A.O. method we can write the spacial parts of the orbitals as a linear combination of \( M \) basic orbitals which we will assume form an orthonormal set. We can write
\[
\Psi_i(1) = \sum_{s=1}^M a_{si} \omega_s(1) \alpha(1) = \phi_i(1) \alpha(1)
\]
(6.2.5.)
and
\[
\Psi_j(1) = \sum_{s=1}^M b_{sj} \omega_s(1) \beta(1) = \phi_j(1) \beta(1)
\]
where we assume \( \Psi_i \) is associated with \( \alpha \)-spin and \( \Psi_j \) with \( \beta \)-spin (c.f. equation 4.3.6.).

Then substituting in (6.2.4.)
\[
E = \sum_{i}^p \sum_{s=1}^M a_{si} \phi_i \phi_{ts} + \sum_{j}^q \sum_{s=1}^M b_{sj} \phi_j \phi_{ts} + \sum_{i}^p \sum_{j}^q a_{si} b_{sj} \phi_i \phi_{ts} + \frac{1}{2} \sum_{i}^p \sum_{j}^q \{ \alpha_i | \alpha_j \} \phi_i \phi_j \phi_{tv} \phi_{su}
\]
(6.2.6.)
with the notation of (1.4.10.).

The energy formula (6.2.3.) was derived using the assumption that the M.O.'s are orthonormal. The orthogonality between an orbital associated with \( \alpha \)-spin

...
and one with \( \beta \)-spin arises solely because of the orthogonality of the spin parts. For M.O.'s with the same spin the spacial parts must be orthonormal and the conditions for this are:

\[
\sum_{s=1}^{M} a_{s\iota}^{*} a_{s\jota} = \delta_{\iota\jota} \tag{6.2.7.}
\]

and

\[
\sum_{s=1}^{M} b_{s\iota}^{*} b_{s\jota} = \delta_{\iota\jota}.
\]

Using the variational principle, the "best" M.O.'s are those which minimise the energy expression (6.2.6.) subject to the condition (6.2.7.). Introducing Lagrangean multipliers \( \lambda_{\iota\jota} \) and \( \mu_{\iota\jota} \), it follows that the equations, which the coefficients of the best M.O.'s must satisfy, are given by minimising

\[
E - 2 \sum_{\iota,\jota}^{M} \lambda_{\iota\jota} a_{s\iota}^{*} a_{s\jota} - 2 \sum_{\iota,\jota}^{M} \mu_{\iota\jota} b_{s\iota}^{*} b_{s\jota} \tag{6.2.8.}
\]

Differentiating this quantity with respect to \( a_{s\iota} \) and putting the result equal to zero, we have:

\[
\sum_{t=1}^{M} \left\{ \sum_{j}^{P} \sum_{k}^{M} a_{s\iota}^{*} (tu|sv) - (tu|sv) a_{s\jota} - \sum_{j}^{M} b_{s\iota}^{*} (tu|sv) b_{s\jota} \right\} \lambda_{t\jota} = \tag{6.2.9.}
\]

And similarly after differentiating with respect to \( b_{s\iota} \).

It is easily seen that the equations must be invariant to mixing amongst orbitals with the same spin and since the matrix \( \lambda \) refers to \( \alpha \)-spin only, we can
apply a unitary transformation to the set of orbitals
with $\alpha$-spin, and to the matrix $\hat{A}$ so that $\hat{A}$ is diagonalised. Similarly for the set of equations involving $\mu$. Hence, introducing the matrices $R$ and $Q$ equation (6.2.9.) becomes

$$\sum_{t=1}^{M} \left\{ H_{t} + \sum_{uv} R_{vu} \left[ (t|u|sv) - (t|v|su) \right] + \sum_{uv} Q_{vu} (t|v|su) \right\} a_{si} = \lambda_{i} a_{ui} \quad (6.2.10)$$

$$\sum_{t=1}^{M} \left\{ H_{t} + \sum_{uv} Q_{vu} \left[ (t|u|sv) - (t|v|su) \right] + \sum_{uv} R_{vu} (t|v|su) \right\} b_{si} = \mu_{i} b_{ui}$$

The orbitals which satisfy these equations, i.e. the orbitals for which equations (6.2.9.) reduce to eigenvalue form, are known as the unrestricted molecular orbitals. With the obvious notation the unrestricted molecular orbitals for $\alpha$-spin and for $\beta$-spin will be the eigenvectors of the matrices $F^\alpha = (H + G^\alpha)$ and $F^\beta = (H + G^\beta)$, respectively.

Koopman's theorem (1933) that the molecular orbitals are the orbitals best suited to describing ionization applies equally well to the unrestricted molecular orbitals and gives them their physical significance. On ionization an electron is to be regarded as removed from one of the unrestricted molecular orbitals and the ionization potential is $-\lambda_{i}$ if its spin is $\alpha$ and $-\mu_{i}$ for $\beta$-spin.
For each orbital the coefficients can be put in the form of a column vector \( a_i \) or \( b_i \) and the vectors can be collected into two matrices \( \mathbf{A} \), size \( M \times \mathbf{P} \), and \( \mathbf{B} \) size \( M \times \mathbf{Q} \), the former referring to \( \alpha \)-spin and the latter to \( \beta \)-spin.

It follows that
\[
\mathbf{R} = \mathbf{A} \mathbf{A}^\dagger \quad \mathbf{Q} = \mathbf{B} \mathbf{B}^\dagger
\]  
(6.2.11.)

and from the orthogonality relations
\[
\mathbf{A}^\dagger \mathbf{A} = 1 \quad \mathbf{B}^\dagger \mathbf{B} = 1
\]  
(6.2.12.)

Combined together these give
\[
\mathbf{R}^2 = \mathbf{R} \quad \mathbf{Q}^2 = \mathbf{Q}
\]  
(6.2.13.)

i.e. \( \mathbf{R} \) and \( \mathbf{Q} \) are idempotent matrices.

Also from (6.2.11.) and (6.2.12.)
\[
\text{Trace} \mathbf{R} = \mathbf{P} \quad \text{Trace} \mathbf{Q} = \mathbf{Q}
\]  
(6.2.14.)

The energy can be expressed, using the matrices \( \mathbf{R} \) and \( \mathbf{Q} \), as
\[
\mathbf{E} = \sum_{st} (\mathbf{R}_{ts} + \mathbf{Q}_{ts}) \mathbf{H}_{st} + \frac{1}{2} \sum_{stuv} [\mathbf{R}_{us} \mathbf{R}_{vt} + \mathbf{Q}_{us} \mathbf{Q}_{vt} - (\mathbf{H}_{st} \mathbf{H}_{uv})] + \sum_{stuv} \mathbf{R}_{us} \mathbf{R}_{vt} (\mathbf{H}_{st} \mathbf{H}_{uv})
\]
i.e.
\[
\mathbf{E} = \text{tr} (\mathbf{R} \mathbf{H}) + \mathbf{tr} (\mathbf{Q} \mathbf{H}) + \frac{1}{2} \text{tr} (\mathbf{R} \mathbf{G}^x) + \frac{1}{2} \text{tr} (\mathbf{Q} \mathbf{G}^y)
\]  
(6.2.15.)

From this bond order matrices can be found directly by minimizing \( \mathbf{E} \) subject to conditions (6.2.13.) and (6.2.14.).
6.3 **Symmetry**

The symmetry of a molecule has various consequences for its orbitals. The electron density will be taken to have the full symmetry of the group, and, since the spin functions are eigenfunctions of the spin-free Hamiltonian, the density associated with \( \alpha \)-spin alone, \( P^\alpha_1(1|1) \) and with \( \beta \)-spin alone, \( P^\beta_1(1|1) \) (see section 4.3) must also be fully symmetrical. This makes the operators on the left-hand sides of equations (6.2.10.) fully symmetrical. Thus the unrestricted molecular orbitals are determined by eigenvalue equations with symmetrical operators and so must be symmetry orbitals transforming according to the various irreducible representations of the group.

It follows from group theory that, if \( P^\alpha_1 \) and \( P^\beta_1 \) are to be fully symmetrical, the orbitals with \( \alpha \)-spin and those with \( \beta \)-spin must each span an integral number of representations completely. If the representations are not completely spanned there will be spatial degeneracy among the wave functions and the Jahn-Teller theorem will imply the instability of the nuclear configuration.

Just as the single determinant used in this theory need not be an eigenfunction of \( \mathcal{S}^z \) so the theory can be extended to include determinants which do not, by themselves, satisfy the symmetry requirements. One
such determinant gives an electron density which does not have the full symmetry of the molecular group though it may of a subgroup. The unrestricted molecular orbitals are symmetry orbitals, then, but only of this subgroup. The full wave function is a linear combination of several determinants (see Nesbet, 1961).

6.4 Molecular Ground States

Almost all molecules have an even number of electrons which are coupled together to give a fully symmetric singlet wave function for the ground state. This singlet character forces the number of \( \alpha \) orbitals to equal the number of \( \beta \) orbitals so that

\[
\rho = \varphi
\]  

(6.4.1.)

Under these conditions the solution of equations (6.2.5.) and (6.2.10.) has

\[
\Theta_\uparrow \equiv \Phi_\uparrow
\]  

(6.4.2.)

unless, as for some excited states, the \( \Theta_\uparrow \) span irreducible representations not all identical with those of the \( \Phi_\uparrow \). Thus the more general form of the wave function leads to the same result as if the orbitals had been originally assumed to be doubly occupied.
On the other hand, molecules, ions or radicals, which have an odd number of electrons, will have \( p \neq q \) and the orbitals, in general, will be different. Furthermore, the first excited state of most molecules is the lowest triplet state and the \( S_z = 1 \) component of this has \( p = q + 2 \) so that the degeneracy is again prevented.

These results explain why a number of general theorems which are valid for molecular ground states in the Hartree-Fock theory are valid for ions, radicals, etc., only in the unrestricted molecular orbital theory. These theorems include Koopman's theorem already mentioned, Brillouin's theorem (Nesbet, 1961) and the stability theorem (Hall, 1961).

6.5 *Refinements of Single Determinant Wave Functions*

As we have seen in chapter 4, the single determinant wave function of the unrestricted molecular orbital method is not, in general, an eigenfunction of \( S_z^2 \). The mean value of \( S_z^2 \) is given by

\[
\langle S_z^2 \rangle = \frac{1}{4} (p-q)^2 + \frac{1}{2} (p+q) - L \tag{6.5.1}
\]

where

\[
L = \text{tr} \ R Q = \sum_{rs} R_{rs} Q_{sr} \tag{6.5.2}
\]

may be interpreted as the number of doubly occupied orbitals. The wave function is a mixture of components of various
multiplicities but the values of \((\mathbf{p} - q)\) puts a lower limit to the spin quantum number so that
\[
\frac{1}{2} (p + q) > \mathcal{S}' > \mathcal{S}'_z = \frac{1}{2} (p - q) \quad (6.5.3.)
\]

To remove these unwanted components and improve the wave function the use of a projection operator has been suggested by Löwdin (1955). From chapter 4 we know that
\[
A_{2n+1} = \mathcal{S}^2 - n(n+1) \quad (6.5.4.)
\]
acting on a mixture of components will annihilate the component of multiplicity \((2n+1)\). This can be repeated for all the unwanted components and, since these components have higher energies, their removal will improve the energy as well as the spin properties. On the other hand, the high multiplicities have energies so high that they can contribute little to the wave function. The annihilation of the lower multiplicities is therefore the more important.

The projection operator \(O_{2n+1}\) which selects out the spin eigenfunction of multiplicity \(2n+1\) is a product of these annihilators, namely,
\[
O_{2n+1} = \prod_{m>2} A_{2m+1} \quad (6.5.5.)
\]
while the energy of the spin eigenfunction projected from the single determinant \(\Psi\) is
\[
\langle H \rangle = \mathcal{W} = \frac{\int \Psi^* H O_{2n+1} \Psi \, dx}{\int \Psi^* O_{2n+1} \Psi \, dx} \quad (6.5.6.)
\]
The operators $O_{2n+1}$ and $H O_{2n+1}$ are, therefore, of the many electron type and their integrals involve high-order density matrices. For the single determinant these can all be expressed in terms of $R$ and $Q$ so that $R$ and $Q$ remain fundamental quantities in the more general theory although they no longer have the same connexion with the first order density matrix. The order of density matrix required in the energy formula depends on the number of annihilators used in $O_{2n+1}$ and this in turn depends on the number of electrons in the molecule and its symmetry. If $k$ is the number of annihilators used the highest order required will be $2k+2$. Nevertheless, the complicated form of $O_{2n+1}$ makes it difficult to evaluate (6.5.6.) and so find the best possible $R$ and $Q$ by minimization.

**TABLE 6.5 CLASSIFICATION OF REFINEMENTS OF MOLECULAR ORBITAL THEORY**

<table>
<thead>
<tr>
<th>method</th>
<th>wave functions used to find</th>
<th>$\mathbf{E, Q}$</th>
<th>$\mathbf{W}$</th>
<th>eigen-function of $\mathbf{G^2}$</th>
<th>energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.o.</td>
<td></td>
<td>det</td>
<td>det</td>
<td>yes</td>
<td>$W_1$</td>
</tr>
<tr>
<td>unrestricted m.o.</td>
<td></td>
<td>det</td>
<td>det</td>
<td>no</td>
<td>$W_2 &lt; W_1$</td>
</tr>
<tr>
<td>unrestricted m.o. with $A_{2n+3}$</td>
<td></td>
<td>det</td>
<td>$A_{2n+3}$ det</td>
<td>no</td>
<td>$W_2 &lt; W_2$</td>
</tr>
<tr>
<td>unrestricted m.o. with $O_{2n+1}$</td>
<td></td>
<td>det</td>
<td>$O_{2n+1}$ det</td>
<td>yes</td>
<td>$W_4 &lt; W_3$</td>
</tr>
<tr>
<td>extended m.o. with $A_{2n+3}$</td>
<td>$A_{2n+3}$ det</td>
<td>$A_{2n+1}$ det</td>
<td>no</td>
<td></td>
<td>$W_5 &lt; W_3$</td>
</tr>
<tr>
<td>extended m.o. with $O_{2n+1}$</td>
<td>$O_{2n+1}$ det</td>
<td>$O_{2n+1}$ det</td>
<td>yes</td>
<td></td>
<td>$W_6 &lt; W_5$</td>
</tr>
</tbody>
</table>
There are two possible ways of applying these refinements to obtain better energies. In the first, which is less accurate but easier, the $\mathbf{R}$ and $\mathbf{Q}$ of the unrestricted molecular orbital method are kept fixed but the wave function and the energy are improved by using $A_{2n+3}$ or $O_{2n+1}$. Because of the results in section 6.4 this method is not generally useful for molecular ground states. In the second method the energy is corrected using $A_{2n+3}$ or $O_{2n+1}$ before the best $\mathbf{R}$ and $\mathbf{Q}$ are found by minimization. This may be called the extended molecular orbital method. These various possibilities are shown in table 6.5. Examples of the unrestricted methods will be given in section 6.6.

The Hylleraas-Eckart wave functions and the alternant molecular orbitals (Löwdin, 1955) are examples of extended molecular orbitals with $O_{2n+1}$.

6.6 Wave Functions with a Single Annihilator

A determinantal wave function whose major component has a spin quantum number $A$ can be refined by using $A_{2n+3}$ to annihilate the next component. Higher components, with spin $n+2$, etc., are often negligible because of their much higher energy. When this is so, $A_{2n+3}$ can be treated as idempotent and the energy is then

$$W = \int \Psi^* H \left[ g^2 - (n+1)(n+2) \right] \Psi \, dx \sqrt{\int \Psi^* \left[ g^2 - (n+1)(n+2) \right] \Psi \, dx} \quad (6.6.1)$$
and will involve density matrices of up to the fourth order. In terms of $\mathbf{R}$ and $\mathbf{Q}$ its value is

$$W = W_0 - \frac{1}{2\chi} \left[ 2 \text{tr} (\mathbf{R} \mathbf{Q} \mathbf{R} + \mathbf{Q} \mathbf{R} \mathbf{Q} - 2 \mathbf{R} \mathbf{Q}) \right] +$$

$$+ \sum_{stuv} \left\{ [\mathbf{R} \mathbf{Q} \mathbf{R} - \mathbf{Q} \mathbf{R} \mathbf{Q}]_{st} [\mathbf{R} + \mathbf{Q}]_{uv} \right\} (tv|us) - \sum_{stuv} \left\{ [\mathbf{R} \mathbf{Q} \mathbf{R}]_{st} R_{uv} \right\}$$

$$+ [\mathbf{Q} \mathbf{R} \mathbf{Q}]_{st} Q_{uv} + [\mathbf{Q} \mathbf{Q}]_{st} [\mathbf{R} + \mathbf{Q}]_{uv} (tv|su)$$

(6.6.2.)

where $W_0$ is the energy for a single determinant and

$$\chi = (\lambda + 1)(\lambda + 2) - \frac{1}{4} (p - q)^2 - \frac{1}{2} (p + q) + L$$

The mean value of $\mathbf{F}^2$ now improves to

$$\langle \mathbf{F}^2 \rangle = \frac{1}{2} (p - q)^2 + \frac{1}{2} (p + q) - L - \frac{1}{2} \chi \left( (p - L)(p + L) + 2L - 2U \right)$$

and the first-order density matrix is

$$\chi_{(1|2)} = \sum_{rs} J_{rs} \omega_s^x (1) \omega_t (2) \gamma (1) \alpha (2) + \sum_{rs} K_{rs} \omega_s^x (1) \omega_t (2) \beta (4) \beta (5)$$

where

$$J = \mathbf{R} - \left( \mathbf{R} \mathbf{Q} \mathbf{R} - \frac{1}{2} \mathbf{R} \mathbf{Q} - \frac{1}{2} \mathbf{Q} \mathbf{R} \right) / \chi$$

$$K = \mathbf{Q} - \left( \mathbf{Q} \mathbf{R} \mathbf{Q} - \frac{1}{2} \mathbf{Q} \mathbf{R} - \frac{1}{2} \mathbf{R} \mathbf{Q} \right) / \chi$$

The energy cannot be expressed in terms of $\mathbf{J}$ and $\mathbf{K}$ alone but their introduction enables it to be put into the simpler form

$$W = \text{tr} (\mathbf{J} + \mathbf{K}) + \frac{1}{2} \text{tr} \mathbf{J}^2 + \frac{1}{2} \text{tr} \mathbf{K}^2 - C$$

where

$$C = -\frac{1}{2\chi} \sum_{stuv} \left\{ [\mathbf{R} (\mathbf{R} - \mathbf{Q})]_{st} [\mathbf{R} (\mathbf{Q})]_{uv} (tv|us) \right\}$$
The final correction term $C$ is generally small.

The single determinant wave function $\Psi$ is a mixture of pure spin states and can be written as

$$\Psi = c_0 \Psi_{2\alpha+1} + c_1 \Psi_{2\alpha+3} + c_2 \Psi_{2\alpha+5} + \ldots \quad (6.6.3.)$$

where $c_0 = \frac{1}{2} (p - q)$ and $\Psi_{2\alpha+1}$ is a spin eigenstate with eigenvalue $\lambda(\alpha + 1)$. Thus, for example, if $p - q = 2$, the main contribution to $\Psi$ will be from the triplet $\Psi_3$ but mixed in with this will be a quintet $\Psi_5$, a septet $\Psi_7$, and so on.

We anticipate the results of part III to give a few examples. For those considered here, components higher than $\Psi_{2\alpha+5}$ cannot occur and $c_0^2$, $c_1^2$, and $c_2^2$ can be calculated from $\langle S^2 \rangle$ and $\langle S^4 \rangle$. The results are shown in table 6.6 and illustrate the rapid decrease in the coefficients. Table 6.6A shows the effect on the energy $W$ and on $\langle S^2 \rangle$ of one annihilator $A_{2\alpha+3}$ and of $O_{2\alpha+1}$. The energies given are relative to the energies of the localized orbitals and are multiples of $\beta(= -4.79 \text{ eV})$. The use of $A_{2\alpha+3}$ is seen to produce appreciable improvements in both $W$ and $\langle S^2 \rangle$ but the remaining annihilators in $O_{2\alpha+1}$ have little effect on $W$ despite the improvement in $\langle S^2 \rangle$. Further examples are given in chapter 10.
### TABLE 6.6

**RELATIVE WEIGHTS OF HIGHER SPIN STATES IN SINGLE DETERMINANT WAVE FUNCTIONS.**

<table>
<thead>
<tr>
<th>Molecular State</th>
<th>$s$</th>
<th>$C_0^2$</th>
<th>$C_1^2$</th>
<th>$C_2^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allyl radical</td>
<td>$\frac{1}{2}$</td>
<td>0.9628</td>
<td>0.0372</td>
<td>0</td>
</tr>
<tr>
<td>Butadiene lowest triplet</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pyridine lowest $\pi$ triplet</td>
<td>1</td>
<td>0.9568</td>
<td>0.0427</td>
<td>0.0005</td>
</tr>
<tr>
<td>Pyrazine lowest $\pi$ triplet</td>
<td>1</td>
<td>0.9556</td>
<td>0.0439</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

### TABLE 6.6A

**ENERGIES AND $\langle S^2 \rangle$ FOR UNRESTRICTED M.O. WAVE FUNCTIONS**

<table>
<thead>
<tr>
<th>Molecular State</th>
<th>$\langle S^2 \rangle$</th>
<th>$\langle S^2 \rangle$</th>
<th>$\langle S^2 \rangle$</th>
<th>$\langle S^2 \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allyl radical</td>
<td>8.58</td>
<td>0.8612</td>
<td>8.61</td>
<td>0.75</td>
</tr>
<tr>
<td>Butadiene lowest triplet</td>
<td>13.83</td>
<td>2</td>
<td>unchanged</td>
<td>unchanged</td>
</tr>
<tr>
<td>Pyridine lowest $\pi$ triplet</td>
<td>35.58</td>
<td>2.1708</td>
<td>35.62</td>
<td>2.0022</td>
</tr>
<tr>
<td>Pyrazine lowest $\pi$ triplet</td>
<td>35.97</td>
<td>2.1755</td>
<td>36.02</td>
<td>2.0026</td>
</tr>
</tbody>
</table>

6.7 **Forced Eigenfunctions**

Although these more general determinantal wave functions are not generally eigenfunctions of $\langle S^2 \rangle$ there are several ways in which they can be forced to be. These derive from the fact that the orbitals are expressed as linear combinations of a limited number of basis functions. The symmetry of the molecule also introduces considerable restrictions.
The simplest example of a forced eigenfunction occurs when the unrestricted molecular orbitals are uniquely determined by symmetry alone. In this event the $\Theta_\uparrow$ are either identical with some of the $\Phi_\uparrow$ or are spatially orthogonal to them. Thus the orbitals are either doubly occupied or singly occupied. If the singly occupied orbitals all have the same spin the single determinant is an eigenfunction of spin. This type of forcing occurs frequently among the states of benzene although for some excited states the spatial symmetry requires wave functions with several determinants so that the argument is made more complicated.

Forcing can still occur, however, when the molecular orbitals are not fully determined by symmetry. If there are sufficient molecular orbitals of one spin and one irreducible representation to span completely the space of all functions of that symmetry then, in particular, the molecular orbitals of the opposite spin and the same symmetry can be expressed in terms of them. Thus, although the unrestricted molecular orbitals themselves may be different, it is possible to transform them into orbitals some doubly occupied and some singly occupied. If all the molecular orbitals satisfy this condition or are uniquely determined by symmetry the determinant will be forced to be an eigenfunction of $\mathbf{S}^2$. 
The lowest triplet state of butadiene, for example, has two electrons of \( \alpha \) spin in two symmetrical orbitals and one in an antisymmetrical orbital. The single \( \beta \) electron is in a symmetrical orbital but since the \( \alpha \) orbitals span the two-dimensional space of symmetrical orbitals they can be transformed to give a doubly occupied and a singly occupied symmetrical orbital and, consequently, the determinant is an eigenfunction of \( S_z^2 \) (see tables in the previous section).

Even when the symmetry and the truncation are not sufficient to force the determinant to be an eigenfunction they may restrict it considerably. Thus, instead of being resolvable into a mixture of components with a wide range of multiplicities, the determinant may be restricted to a few components of the lower multiplicities. A few annihilators will then suffice to produce a spin eigenfunction.
CHAPTER 7

TRANSFORMATION PROPERTIES OF THE ORBITALS
7.1 Introduction

Because the unrestricted wave function is in the form of a single determinant, the wave function is invariant with respect to transformations of the orbitals among themselves. In particular if the $\alpha$-spin orbitals are transformed among themselves and the $\beta$-spin orbitals among themselves with unitary transformations

$$\chi_{\alpha} = \sum_{s} \phi_{s} U_{\alpha}$$

$$\eta_{\beta} = \sum_{s} \Theta_{s} V_{\beta}$$

(7.1.1.)

then $\Psi$ is unaltered. These degrees of freedom for the orbitals were used in the previous chapter to bring the orbital equations (6.2.9.) to eigenvalue form (6.2.10.) and so define the unrestricted molecular orbitals. However, these are not the only interesting type of orbital. The natural spin orbitals, which diagonalize the first order density matrix, and the natural orbitals, which enable the spinless first order density matrix to be diagonal are also of importance.

Most quantities associated with the wave function are also invariant with respect to (7.1.1.). For example, if a projection operator is used to improve the wave function, then $\hat{O} \Psi$ will be unchanged although the individual determinants in the sum $\hat{O} \Psi$ will change. We already have from section 4.3 that the first order
density matrix is invariant and so are the components \( p_1^\alpha \) and \( p_1^\beta \) of the spinless density matrix, i.e.

\[
p_1^\alpha (1|2) = \sum_{\nu} \phi_{1}^\nu (1) \phi_{1}^\nu (2) = \sum_{\nu} \chi_{s}^\nu (1) \chi_{s}^\nu (2)
\]

\[
p_1^\beta (1|2) = \sum_{\nu} \Theta_{1}^\nu (1) \Theta_{1}^\nu (2) = \sum_{\nu} \eta_{s}^\nu (1) \eta_{s}^\nu (2)
\]

(7.1.2.)

From this it is clear that the bond order matrices \( \mathbf{R} \) and \( \mathbf{Q} \) must be invariant. This can also be seen from the definitions of \( \mathbf{R} \) and \( \mathbf{Q} \) in terms of the matrices \( \mathbf{A} \) and \( \mathbf{B} \) (6.2.11.). The transformations (7.1.1.) turn \( \mathbf{A} \) into \( \mathbf{A} \mathbf{U} \) and \( \mathbf{B} \) into \( \mathbf{B} \mathbf{V} \) but \( \mathbf{R} \) and \( \mathbf{Q} \) remain unchanged since \( \mathbf{U} \) and \( \mathbf{V} \) are unitary. On the other hand, a transformation of the \( \omega_{1} \) to new orthonormal functions \( \mathbf{U} \) with

\[
\sum_{\xi} \omega_{\xi}^\ast T_{1} = \mathbf{U}
\]

(7.1.3.)

turns \( \mathbf{A} \) into \( \mathbf{T} \mathbf{A} \) and \( \mathbf{B} \) into \( \mathbf{T} \mathbf{B} \) while \( \mathbf{R} \) becomes \( \mathbf{T} \mathbf{R} \mathbf{T}^\dagger \) and \( \mathbf{Q} \) becomes \( \mathbf{T} \mathbf{Q} \mathbf{T}^\dagger \).

We shall use some of these transformation properties to discuss the natural orbitals and to introduce a new type of orbital - the corresponding orbital. These are the orbitals for which the overlap matrix between the \( \alpha \)-spin orbitals and the \( \beta \)-spin orbitals has diagonal form. The corresponding orbitals are, therefore, the unrestricted orbitals most reminiscent of doubly occupied orbitals. The idea of corresponding orbitals will also
be applied to open shell orbitals and alternant molecular orbitals. In section 7.4 the transformation properties of unrestricted orbitals will be illustrated using the results of a calculation on the naphthalene positive ion.

7.2 Natural Orbitals

For the wave function \( \Psi \) the first-order density matrix is

\[
\rho_d(1|2) = \sum_r \phi_r^*(1) \phi_r^*(2) \phi_r(1) \phi_r(2) + \sum_s \theta_s^*(1) \theta_s^*(2) \theta_s(1) \theta_s(2) \quad (7.2.1)
\]

This is already in diagonal form and, since the spin orbitals are orthonormal, they are natural spin orbitals. The natural spin orbitals are not unique, however, since the unitary transformations (7.1.1.) leave the form of (7.2.1.) invariant.

From (4.3.8.) the spinless density matrix is

\[
\rho_s(1|2) = \sum_r \phi_r^*(1) \phi_r(2) + \sum_s \theta_s^*(1) \theta_s(2) \quad (7.2.2)
\]

and would be in diagonal form except that the \( \phi_r \) and \( \theta_r \) are not spatially orthogonal. The unitary transformations (7.1.1.) also leave the form of (7.2.2.) invariant and can be used to define orbitals that are more nearly orthogonal. When \( \underline{U} \) and \( \underline{V} \) are determined as in the appendix then the new orbitals have the property that their spatial overlap integral
\[
T_{rs} = \int \chi^*_r \eta_s \, dx
\]  
(7.2.3.)

is diagonal
\[
T_{rs} = T_r \delta_{rs}
\]  
(7.2.4.)

These orbitals will be called corresponding orbitals because of this property. The existence of such orbitals has been suggested, without proof, by Löwdin (1958, private communication). In terms of the basic functions \( \omega_r \) the corresponding orbitals \( \chi_r \) and \( \eta_r \) are readily shown to be the eigenvectors of the matrices \( R Q R \) and \( Q R Q \), respectively. The non-zero eigenvalues of these matrices are equal and give the values of \( T_r \).

In terms of these corresponding orbitals the reduced density matrix is
\[
P_{\perp}(1|2) = \sum_r \chi^*_r(1) \chi_r(2) + \sum_s \eta^*_s(1) \eta_s(2)
\]  
(7.2.5.)

where the \( \chi_r \) are spatially orthogonal to each other and to the \( \eta_s \) except when \( r = s \). If these functions are replaced by the orthonormal combinations
\[
\lambda_r = (\chi_r + \eta_r)(2 + 2T_r)^{-1/2}
\]  
(7.2.6.)

\[
\mu_r = (\chi_r - \eta_r)(2 - 2T_r)^{-1/2}
\]  
(7.2.7.)

then all the functions are orthonormal and (7.2.5.) becomes
\[
P_{\perp}(1|2) = \sum_r \lambda^*_r(1) \lambda_r(2) + \sum_s \mu^*_s(1) \mu_s(2)
\]  
(7.2.8.)

\[
+ \sum_{t=r+1}^p \chi^*_t(1) \chi_t(2)
\]
These functions \( \lambda_r, \mu_s, \gamma_L \) are therefore the natural orbitals. The corresponding orbitals are thus the natural spin orbitals which are most easily related to the natural orbitals and their overlap integrals determine the occupation numbers of the natural orbitals.

The reduced density matrix can be written directly in terms of the \( \mathcal{W}_F \) as

\[
P_{\perp}(1|2) = \sum_{rs} \omega_r(2) \left( R_{rs} + Q_{rs} \right) \omega_s^*(1) \quad (7.2.9)
\]

Since both \( R \) and \( Q \) are symmetrical this quadratic form can be diagonalized by a unitary change of variables and the new orbitals will be the natural orbitals. To relate this definition to the previous one, the partitioned matrix \( C \), of order \( M \times N \), is considered

\[
C = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \quad (7.2.10)
\]

From equations (6.2.11.) and (6.2.12.) it follows that

\[
CC^+ = R + Q \quad (7.2.11)
\]

and from the appendix this has the same non-zero eigenvalues as \( C^+C \). Now \( C^+C \) has the partitioned form

\[
C^+C = \begin{pmatrix} I_p & 0 \\ 0 & S^+ \end{pmatrix} \begin{pmatrix} I_q & 0 \\ 0 & S \end{pmatrix} \quad (7.2.12)
\]

where \( I_p \) is the unit matrix of order \( p \), and the unitary matrices \( U \) and \( V \) enable it to be brought to the form

\[
\begin{pmatrix} U^+ & 0 \\ 0 & V^+ \end{pmatrix} \begin{pmatrix} I_p & S^+ \mid I_q \\ \end{pmatrix} \begin{pmatrix} U & 0 \\ 0 & V \end{pmatrix} = \begin{pmatrix} I & I \\ I^+ & I \end{pmatrix} \quad (7.2.13)
\]
There are, then, \(2q\) eigenvalues of the form
\[1 \pm \frac{1}{r}\] (7.2.14.)
and \((p-q)\) eigenvalues are unity exactly as in (7.2.8.)

7.3 Corresponding Orbitals

In the previous section corresponding orbitals were introduced mainly as an aid in obtaining the natural orbitals but they are interesting in their own right. Because the overlap matrix between the \(\alpha\)-spin and \(\beta\)-spin corresponding orbitals is diagonal the corresponding orbitals will be the unrestricted orbitals most closely related to the doubly occupied orbitals of the ordinary Hartree–Fock method. Perhaps because of their name, the unrestricted molecular orbitals have generally been regarded as analogous to the doubly occupied molecular orbitals but since the unrestricted molecular orbitals and are not in general corresponding orbitals this will not be so.

It has been shown in section 6.3 that the unrestricted molecular orbitals for a molecule will be symmetry orbitals transforming according to the various irreducible representations of the symmetry group of the molecule. This has several consequences for the overlap matrix since the overlap between orbitals of different symmetry will be zero. This can make it considerably easier to
find the corresponding orbitals from the molecular orbitals. More important, however, it implies that the unrestricted corresponding orbitals will also be symmetry orbitals.

To indicate another reason why corresponding orbitals are important in the unrestricted method it should be pointed out that it is only by obtaining the corresponding orbitals that we can be sure that we are using different orbitals for electrons with different spins. If the unrestricted molecular orbitals for the lowest \( \pi \) triplet state of butadiene are obtained, the one \( \beta \)-spin orbital will be different from each of the three \( \alpha \)-spin orbitals. However, when the \( \alpha \)-spin molecular orbitals are transformed into corresponding orbitals, one of them becomes identical with the \( \beta \)-spin orbital (c.f. section 6.7). In other cases it may turn out that some of the corresponding orbitals are doubly occupied while the remaining ones are not. This is very useful to know when the projection operator is to be used to improve energy values or other expectation values since many of the determinants in the sum \( \sum \psi \psi \) will vanish if there are any doubly occupied orbitals. The presence of doubly occupied orbitals will also reduce the number of spin eigenstates which make up the wave function \( \psi \) so that the number of annihilators used in \( \Theta \) will be reduced with a consequent simplification.
7.4 **Unrestricted orbitals for the Naphthalene Positive Ion**

Using the methods described in part III it is possible to find the unrestricted bond order matrices for the naphthalene positive ion. Because of the transformations (7.1.1.) the bond orders do not determine the orbitals uniquely but, having obtained $\mathbf{R}$ and $\mathbf{Q}$, by calculating $\mathbf{H}$, $\mathbf{C}^\alpha$ and $\mathbf{C}^\beta$ from (6.2.11.) and solving the eigenvector equations it is possible to obtain the unrestricted molecular orbitals. This has been done and the results are given in table 7.4.

It is evident from an inspection of table 7.4 that the orbitals for $\alpha$-spin electrons and for $\beta$-spin electrons are indeed different. This can be made even clearer if the overlap matrix $\mathbf{S}$ is calculated.

$$
\mathbf{S} = \begin{pmatrix}
0.99460 & 0 & 0 & -0.06616 \\
0 & 0.98888 & 0 & 0 \\
0 & 0 & 0.98890 & 0 \\
0.06850 & 0 & 0 & 0.99729 \\
0 & 0 & 0 & 0
\end{pmatrix}
$$

where

$$
S_{rs} = \int \phi^*_r \ \Theta_s \ d\chi
$$

Since $\mathbf{S}$ does not have diagonal form not all the unrestricted molecular orbitals will be corresponding orbitals. However, because of the symmetry of the orbitals there are a large number of zero elements and
## Table 7.4 Unrestricted molecular orbitals

<table>
<thead>
<tr>
<th>i</th>
<th>$\phi_i$</th>
<th>$\Theta_i$</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a_{1i}$</td>
<td>$a_{2i}$</td>
<td>$a_{3i}$</td>
</tr>
<tr>
<td>1</td>
<td>0.3155</td>
<td>0.2232</td>
<td>0.4487</td>
</tr>
<tr>
<td>2</td>
<td>-0.2904</td>
<td>-0.4070</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.4087</td>
<td>0.1735</td>
<td>0.3253</td>
</tr>
<tr>
<td>4</td>
<td>-0.0227</td>
<td>-0.3976</td>
<td>0.4275</td>
</tr>
<tr>
<td>5</td>
<td>0.4398</td>
<td>0.2378</td>
<td>0</td>
</tr>
</tbody>
</table>

The orbitals $\phi_i$ for $\alpha$-spin and $\Theta_i$ for $\beta$-spin are given as linear combinations of functions $\{\omega_r\}$ centred on the carbon atoms, viz.:

$$\phi_i = \sum_r a_{1i} \omega_r$$
$$\Theta_i = \sum_r b_{1i} \omega_r$$

The numbering system for the carbon atoms is the usual one (see fig.10.3) and only coefficients corresponding to atoms 1,2,9 are given, the remainder being obtained from these using the symmetry of the orbitals.
in fact the orbitals numbered 2, 3 and 5 will be corresponding orbitals. In general none of the molecular orbitals will be corresponding orbitals.

Using the method given in the appendix all the corresponding orbitals have been calculated and are given in table 7.4A. The most striking feature of this table is the fact that the orbitals $\kappa_1$ and $\eta_1$ are identical so that one of the corresponding orbitals is doubly occupied. This fact was in no way apparent from the molecular orbitals and this indicates how useful it is to calculate the corresponding orbitals. Because one orbital is doubly occupied there will be one less possible eigenstate included in the wave function. Consequently the projection operator $\hat{U}$ will be the product of four annihilators instead of five. The overlap matrix for the corresponding orbitals will have the diagonal form:

$$T = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 0.98888 & 0 & 0 \\
0 & 0 & 0.98890 & 0 \\
0 & 0 & 0 & 0.99643 \\
0 & 0 & 0 & 0
\end{bmatrix}$$

From the corresponding orbitals it would be possible to calculate the natural orbitals using equations
Table 7.4A  Corresponding Orbitals

<table>
<thead>
<tr>
<th>i</th>
<th>$\chi_i$</th>
<th>$\eta_i$</th>
<th>$\bar{\eta}_i$</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha_{1i}$</td>
<td>$\alpha_{2i}$</td>
<td>$\alpha_{4i}$</td>
<td>$b_{1i}$</td>
</tr>
<tr>
<td>1</td>
<td>0.0788</td>
<td>-0.3061</td>
<td>0.5479</td>
<td>0.0788</td>
</tr>
<tr>
<td>2</td>
<td>-0.2904</td>
<td>-0.4070</td>
<td>0</td>
<td>-0.2266</td>
</tr>
<tr>
<td>3</td>
<td>0.4087</td>
<td>0.1735</td>
<td>0.3253</td>
<td>0.3796</td>
</tr>
<tr>
<td>4</td>
<td>0.3065</td>
<td>0.3383</td>
<td>0.2896</td>
<td>0.2725</td>
</tr>
<tr>
<td>5</td>
<td>0.4398</td>
<td>0.2378</td>
<td>0</td>
<td>---</td>
</tr>
</tbody>
</table>
(7.2.6 and 7). However, because the coefficients of the $\alpha$-spin orbitals and $\beta$-spin orbitals are fairly close together and because the $T_i$ are close to unity, it is impossible to find the orbitals $\mu_i$ without the loss of all significant figures. It is possible to calculate the occupation numbers of the natural orbitals and these will be: 2, 1.9888, 1.98890, 1.99643, 1, 0.00357, 0.01110, 0.01112, zero. With the usual interpretation of the occupation numbers this implies that one natural orbital is doubly occupied, three contain almost two electrons, one contains one electron, three contain hardly any electrons and the remaining orbital is unoccupied.

7.5 **Open Shell Orbitals**

It is interesting to consider the transformation properties of the orbitals in open shell wave function. In the theory of these wave functions they are usually taken to have the form (1.4.6.) and the only transformations considered are those of the doubly occupied orbitals among themselves and the singly occupied orbitals among themselves so that the doubly occupied nature of the wave function is retained. However, it is quite legitimate to use the transformations (7.1.1.) so that the $\alpha$-spin orbitals become different from the $\beta$-spin orbitals, giving a wave function superficially similar to that
of the unrestricted method. Such transformations might be used to obtain \(\alpha\)-spin orbitals localised on some atoms with the \(\beta\)-spin orbitals localised on the remainder as in the scheme suggested by Hirst, Hopton and Linnett (1962).

If the wave function (1.4.6.) is taken then the overlap matrix between \(\alpha\)-spin and \(\beta\)-spin open shell orbitals will have diagonal form with all diagonal elements unity so that these will be corresponding orbitals. Moreover, any unitary transformations of the doubly occupied orbitals among themselves and the singly occupied orbitals among themselves will leave the overlap matrix unchanged and so the corresponding orbitals of the open shell wave function will not be unique.

When the transformations (7.1.1.) are taken, however, the overlap matrix will be changed and the new orbitals will not be corresponding orbitals. Therefore, given any open shell wave function in the form (4.3.6.) it is possible to put it into the usual form (1.4.6.) by finding the corresponding orbitals. Since the corresponding orbitals must be doubly occupied, this imposes a condition on \(R\) and \(Q\) for the open shell scheme. From section 7.2 it follows that \(RQR\) and \(Q\bar{R}Q\) each have \(q\) eigenvalues of unity and the same eigenvectors (the \(q\)-fold degeneracy shows again that the corresponding
orbitals are not unique with respect to unitary transformations). The necessary and sufficient condition for this is that \( RQ = Q \). Therefore in the open shell method \( RQ = Q \) which is the condition obtained from the wave function (1.4.6.) by McLeod (1957).

7.6 **Alternant Molecular Orbitals**

The definition given for corresponding orbitals applies equally well in the extended method. However, the extended corresponding orbitals will not be natural spin orbitals nor will they have a close connection with the natural orbitals as was found with the unrestricted corresponding orbitals. Even so it might still be useful to find the extended orbitals so as to compare with the orbitals in the unrestricted method and also to simplify calculations if any of the orbitals are doubly occupied. Use might also be made of the concept of corresponding orbitals in the analysis needed to minimise (6.1.1.).

So far the only attempts to find extended orbitals have used the Alternant Molecular Orbital method (Löwdin 1954, Paunoz 1962). This method assumes that for states of an alternant hydrocarbon the extended orbitals have the form

\[
\Theta_i = \cos \alpha \Omega_i + \sin \alpha \Omega_i'
\]

\[
\Phi_i = \cos \alpha \Omega_i - \sin \alpha \Omega_i'
\]
where $\alpha$ is a parameter and $\Omega_-$ and $\Omega_-'$ are the bonding and anti-bonding orbitals for the ground state of the molecule. The value of $\alpha$ is found by minimizing the energy (6.1.1.), and the resulting orbitals are called alternant molecular orbitals. As a refinement to the method a set of parameters $\{\alpha_i\}$ can be used instead of just one.

If the overlap matrix between $\alpha$-spin and $\beta$-spin alternant M.O.'s defined in section 7.4 is obtained, then it can be seen that it already has diagonal form with $T_i = \omega \cdot 2\alpha_i$ if one parameter is used, and $T_i = \omega \cdot 2\alpha_i$ if there is a set of parameters. Thus the alternant M.O.'s are already corresponding orbitals.

However, if the "odd" and "even" atoms in the alternant, considered separately, do not have the symmetry of the whole molecule, then the alternant M.O.'s will not be symmetry orbitals of the molecule and so will be completely different from the unrestricted corresponding orbitals for the same molecule. In such a case it is very important to use the fully projected wave function with the alternant M.O.'s to calculate all the required expectation values otherwise the symmetry will not be correct. For example, if the alternant M.O.'s for the naphthalene positive ion were found, then it would be necessary to use the fully projected wave function when
finding spin densities to ensure that atoms in similar positions had the same spin densities.

On the other hand, if the sets of "odd" and of "even" atoms have the same symmetry as the complete molecule, as is found in many odd alternants, then the alternant M.O.'s will be symmetry orbitals and can be compared with unrestricted corresponding orbitals. Because the alternant M.O.'s have the correct symmetry, the full projection need not be used to obtain other expectation values but approximations can be made. It would, for example, be possible to use only one annihilator in the projection operator (see table 6.5) and simplifications can also be made in calculating spin densities as was found by Lefebvre, Dearman and McConnell (1960) who ignored terms in tan²α and higher order terms when finding spin densities in hydrocarbon radicals. Since the alternant M.O.'s and the unrestricted corresponding orbitals have the same symmetries it would even be possible to use the alternant M.O.'s as approximate unrestricted orbitals, the value of α being obtained by minimising (6.1.2.).
PART III

ITERATIVE CALCULATION OF UNRESTRICTED BOND ORDER
MATRICES - IONS AND TRIPLET STATES OF
HYDROCARBONS
CHAPTER 8

CALCULATION OF UNRESTRICTED BOND ORDER MATRICES
8.1 **Introduction**

The unrestricted Hartree-Fock method has recently received considerable attention in the literature and in part II the theory of the method has been developed in some detail. So far, however, the discussions of the method have been qualitative and there have been few calculations. To improve on this unsatisfactory state of affairs, in this and the following two chapters a method of calculation will be devised and applied to calculating some properties of the ions and triplet states of π-electron systems.

In this particular chapter we describe a method of calculating the unrestricted bond order matrices for any system and not only π-electron systems. The method is essentially an extension of McWeeny's steepest descents iteration procedure for calculating the charge and bond order matrix for a singlet ground state. In fact the McWeeny method can be deduced as a special case of the one devised here and most of the comments which apply to his method also apply to this one. In particular, second order terms are taken into account giving better convergence than first order iteration procedures such as the Roothaan method.
8.2 Calculation of the Bond Order Matrices

In any actual calculation using the unrestricted method, one procedure is to apply the Roothaan technique to the eigenvalue equations (6.2.10.) so as to obtain the unrestricted molecular orbitals (Pople and Nesbet, 1954; Roothaan, 1951). Once these have been found the bond order matrices $\mathbf{R}$ and $\mathbf{Q}$ and any other required quantities can be calculated. However, since the first-order density matrix and consequently the density matrices of all other orders can be written in terms of $\mathbf{R}$ and $\mathbf{Q}$ only, it follows that the bond order matrices are fundamental quantities in the theory and there is no real need to calculate the orbitals at all.

Therefore a second method of calculation is to find directly matrices $\mathbf{R}$ and $\mathbf{Q}$ which minimize $E$. Providing they also satisfy the conditions (6.2.13 and 14) they will be the bond order matrices. A similar situation in ordinary Hartree-Fock theory led McWeeny (1956 a, b) to develop a steepest descent method of solution which it is possible to adapt to the present requirements. This gives an iteration procedure for calculating $\mathbf{R}$ and $\mathbf{Q}$ which takes into account second-order terms.

This can be seen by considering variations $\delta \mathbf{R}$ and $\delta \mathbf{Q}$ in $\mathbf{R}$ and $\mathbf{Q}$ with resulting changes $\delta \mathbf{C}^\alpha$ in $\mathbf{C}^\alpha$ and
If the net result is a change $\delta E$ then from equation (6.2.15.),

$$
\delta E = \text{tr}(\delta R \cdot H) + \text{tr}(\delta Q \cdot H) + \frac{1}{2} \text{tr}(\delta R \cdot G^\alpha) + \frac{1}{2} \text{tr}(\delta Q \cdot G^\beta) - \text{tr}(\delta R \cdot C^\alpha) - \text{tr}(\delta Q \cdot C^\beta)
$$

(8.2.1)

Because of the symmetry of the integrals in $C^\alpha$ and $C^\beta$ it is clear that:

$$
\text{tr}(\delta R \cdot C^\alpha) + \text{tr}(\delta Q \cdot C^\beta) = \text{tr}(\delta R \cdot G^\alpha) + \text{tr}(\delta Q \cdot G^\beta)
$$

(8.2.2)

and therefore

$$
\delta E = \text{tr}(\delta R \cdot F^\alpha) + \text{tr}(\delta Q \cdot F^\beta) + \frac{1}{2} \text{tr}(\delta R \cdot G^\alpha) + \frac{1}{2} \text{tr}(\delta Q \cdot G^\beta)
$$

(8.2.3)

This implies that to first order the variation in $E$ is equivalent to two separate independent variations in

$$
\epsilon_1 = \text{tr}(R \cdot F^\alpha)
$$

(8.2.4)

and

$$
\epsilon_2 = \text{tr}(Q \cdot F^\beta)
$$

(8.2.5)

where $F^\alpha$ and $F^\beta$ are to be regarded as fixed matrices. Thus the method analogous to Roothaan's is correct to first order, the dependence of $F^\alpha$ and $F^\beta$ on $R$ and $Q$ and of $R$ and $Q$ on each other appearing only as second-order terms. Expressing this in terms of the method of steepest descents, equation (8.2.1.) implies that for a
direct descent of the $E$ surface the initial direction and rate of descent for $R$ is exactly the same as for the descent of the $E_1$ surface, and for $Q$ exactly the same as for the descent of the $E_2$ surface. The only difference is in the curvatures of the descents which differ due to the second order terms. However, these second-order terms are not trivial but have important effects on the rate of convergence of any iteration process and neglect of them can even lead to divergence (see McWeeny, op.cit.).

McWeeny has used steepest descent methods to show that if $R$ and $Q$ are matrices which approximately minimize $E_1$ and $E_2$ respectively, then improvements $\delta R$ in $R$ and $\delta Q$ in $Q$ are given by

$$
\delta R = \left[ \sum_{m=1}^{\infty} (-1)^m \lambda^m (I^2)^{m-1} \right] I - \left[ \sum_{m=0}^{\infty} (-1)^m \lambda^m (I^2)^m \right] I
$$

and

$$
\delta Q = \left[ \sum_{m=1}^{\infty} (-1)^m \mu^m (K^2)^{m-1} \right] K - \left[ \sum_{m=0}^{\infty} (-1)^m \mu^m (K^2)^m \right] K
$$

where

$$
I = s + s^+ \quad J = s - s^+
$$

$$
K = t + t^+ \quad L = t - t^+
$$

$$
\delta = F^{\alpha} R - R F^{\alpha} R
$$

$$
\ell = F^{\beta} Q - Q F^{\beta} Q
$$
and $\lambda$ and $\mu$ are parameters which represent the curvatures of the descents of the $\xi_1$ and $\xi_2$ surfaces respectively and which satisfy

$$\frac{\partial}{\partial \lambda} (\delta \xi_1) = 0 ; \frac{\partial}{\partial \mu} (\delta \xi_2) = 0 \quad (8.2.7.)$$

The same formulae can be used for the minimization of $E$ since for the descent of the $E$ surface, $R$ and $Q$ have the same directions and rates of descent as for descents of the $\xi_1$ and $\xi_2$ surfaces. However, the curvatures are not the same and $\lambda$ and $\mu$ must now be chosen so that

$$\frac{\partial}{\partial \lambda} (\delta E) = 0 \quad \frac{\partial}{\partial \mu} (\delta E) = 0 \quad (8.2.8.)$$

and in this way second-order terms are taken into account.

It can hardly be emphasized too much that equation (8.2.8.) allows for the changes in $\zeta_\alpha$ and $\zeta_\beta$ due to the small changes $\delta R$ and $\delta Q$ in $R$ and $Q$, whereas to obtain equation (8.2.7.) $\zeta_\alpha$ and $\zeta_\beta$ are taken as constant.

To obtain values for $\lambda$ and $\mu$, equations (8.2.6.) are substituted in (8.2.3.) and if cubic and higher powers of $\lambda$ and $\mu$ are neglected this gives

$$\delta E = -\lambda^2 br \left( I^a I^d F^d \right) - \lambda br \left( I F^d \right) - \mu^2 tr \left( k L E^d \right) - \mu tr \left( k E^d \right) + \frac{1}{2} \sum_{stuv} \left\{ \lambda^2 I_{st} I_{uv} + \mu^2 k_{st} k_{uv} \right\} (su|tv) - (sv|uv) \right\} + \lambda \mu \sum_{stuv} I_{st} k_{uv} (su|tv) = -\lambda^2 a - \lambda b - \mu^2 \alpha' \mu b + \frac{1}{2} \lambda c + \frac{1}{2} \mu c + \lambda \mu d \quad (8.2.9.)$$
with the obvious notation.

The conditions (8.2.8.) give

\[
\left\{ \begin{array}{l}
d^{2} - (2a' - c)(2a' - c') \lambda = (2a - c) b + b'd \\
d^{2} - (2a' - c')(2a - c) \mu = (2a' - c') b' + b'd
\end{array} \right. \tag{8.2.10.}
\]

8.3 The Iteration Procedure

The iteration procedure to calculate the bond order matrices by the method just described starts with approximate matrices \( R \) and \( Q \) and then iterates using (8.2.6.) until there is consistency. However, even though \( R \) and \( Q \) may minimize \( E \), they will not be the correct bond order matrices unless the conditions (6.2.13 and 14) are also satisfied. Thus it is most important that the original approximate matrices should satisfy these conditions and after each iteration the new matrices should also be made to satisfy them. The idempotency condition arises also in McWeeny's original treatment and the difficulty can be solved here in the same way. In practice, the other condition does not prove very troublesome and can be satisfied by making minor alterations to the diagonal elements of the matrices after each iteration.

The complete iteration procedure can now be summarized as follows:
(i) Starting with approximate 'guessed' matrices \( R(0) \) and \( Q(0) \) the matrices \( F^{\alpha}(0) \) and \( F^{\beta}(0) \) are calculated.

(ii) The matrices \( I, J, K, L \), are found and the constants \( \lambda \) and \( \mu \) determined from (8.2.6.) and (8.2.10.).

(iii) The improvement \( \delta R(0) \) in \( R(0) \) and \( \delta Q(0) \) in \( Q(0) \) will be given by

\[
\delta R(0) = -\lambda (1 + \lambda I J) (I + \lambda I J)
\]

\[
\delta Q(0) = -\mu (1 + \mu K L) (K + \mu K L)
\]

which are equivalent to (8.2.6.).

(iv) The improved bond order matrices will be

\( \sigma(0) = R(0) + \delta R(0) \quad \rho(0) = Q(0) + \delta Q(0) \)

but in general \( \sigma(0) \) and \( \rho(0) \) will not be idempotent nor will their traces be correct. Idempotent matrices will be given by

\[
\sigma(1) = \left[ \sigma(0) \right]^2 \left[ 3 - 2 \sigma(0) \right]
\]

\[
\rho(1) = \left[ \rho(0) \right]^2 \left[ 3 - 2 \rho(0) \right]
\]

(see LcWeney, 1956a).

The final step is to obtain matrices \( R(1) \) and \( Q(1) \) whose traces are correct by writing

\[
R(1) = \sigma(1) + a \frac{1}{M} \quad Q(1) = \rho(1) + b \frac{1}{M}
\]

where \( a \) and \( b \) are the usually very small quantities

\[
a = \left[ \rho - \text{tr}\sigma(1) \right] / M \quad b = \left[ q - \text{tr}\rho(1) \right] / M
\]
(v) With these new values of $\mathbf{R}$ and $\mathbf{Q}$ the whole process is repeated until consistency is obtained.

Ideally (iv) should be repeated several times in each iteration until (6.2.13 and 14) are exactly satisfied but, in practice, it seems that to use it just once is sufficient.

The special case of a singlet ground state can readily be deduced from this by putting $\mathbf{R} = \mathbf{Q} = \frac{1}{2} \mathbf{P}$ where $\mathbf{P}$ is Coulson's charge and bond order matrix. The iteration procedure will then be the same as that of McWeeny as used in chapter 3 of this thesis.
CHAPTER 9

APPLICATION OF UNRESTRICTED METHOD

TO $\pi$-ELECTRON SYSTEMS
9.1 **Introduction**

The preceding results in chapter 8 are perfectly general and apply to any system, but since our main purpose is to discuss conjugated hydrocarbon molecules it is appropriate at this point to consider the simplifications which can be made for $\pi$ electron systems.

The obvious one is that only $\pi$ electrons need be considered so that $N$ is the number of $\pi$ electrons and $\mathbf{H}$ represents the field due to the atom cores. If the usual Pariser and Parr approximations are used together with the simplifications of Pople and Brickstock and McWeeny (see section 2.4), then $\mathbf{F}^\alpha$ and $\mathbf{F}^\beta$ have the much simpler form.

\[
\mathbf{F}^\alpha_{rs} = \beta_{rs} - \delta_{rs} \sum_t \chi_{rt} + \delta_{rs} \sum_t (R_{tt} + Q_{tt}) \gamma_{rt} - R_{rs} \gamma_{rs} \tag{9.1.1.}
\]

\[
\mathbf{F}^\beta_{rs} = \beta_{rs} - \delta_{rs} \sum_t \chi_{rt} + \delta_{rs} \sum_t (R_{tt} + Q_{tt}) \gamma_{rt} - Q_{rs} \gamma_{rs}
\]

The use of these approximations implies that the functions $\omega_r$ are chosen to be localized around the atom cores so that $(\mathbf{R} + \mathbf{Q})_{rr}$ will represent the total $\pi$ electron charge and $(\mathbf{R} - \mathbf{Q})_{rr}$ the spin density at the atom core $r$. If the annihilator is used to improve the wave function then the predicted values for the charge and spin densities will change to $(\mathbf{F}^\alpha + \mathbf{F}^\beta)$ and $(\mathbf{F}^\alpha - \mathbf{F}^\beta)_{rr}$.

With $\mathbf{F}^\alpha$ and $\mathbf{F}^\beta$ in the form (9.1.1.) it is possible to obtain some interesting results especially for
alternant hydrocarbons. In some states of these molecules there is a pairing between occupied and unoccupied orbitals which gives rise to uniform charge distribution on the atoms of these molecules and this is discussed in the next section. Also in this chapter the idea of ambiguity in the bond orders due to the cubic nature of the eigenvalue equations is extended to the unrestricted method and the possibility of obtaining approximate bond order matrices using perturbation theory is considered.

9.2 'Pairing of Orbitals' in Alternants

It is well known that Hückel theory and self-consistent theory predict that there will be unit \( \pi \)-electron charge on each atom core for many states of alternant molecules. The underlying reason for this is that the atoms in each molecule can be divided into two sets which means that for every orbital \( \{ a_{is} \} \) there is also a 'paired orbital' \( \{ \pm a_{is} \} \), the plus sign being used for atoms in one set and the minus sign for atoms in the other.

Pople and Brickstock (1954) have shown that similar results apply to unrestricted calculations of doublet ground states of odd alternants but the same is also true for many other states as a simple extension of their proof shows. Using their methods, it is clear that if
the matrices $F^\alpha$ and $F^\beta$ satisfy the relations

\[ F_{rs}^\alpha = -F_{rs}^\beta, \quad r, s \text{ in the same set}, \tag{9.2.1.} \]
\[ F_{rs}^\alpha = F_{rs}^\beta, \quad r, s \text{ in different sets}, \]

then there will be a pairing between the occupied $\alpha$-spin orbitals and the unoccupied $\beta$-spin orbitals and vice versa. This imposes on $R$ and $Q$ the conditions:

\[ R_{rs} + Q_{rs} = \delta_{rs}, \quad r, s \text{ in the same set} \tag{9.2.2.} \]
\[ R_{rs} = Q_{rs}, \quad r, s \text{ in different sets}, \]

and so for states in which (9.2.1.) is satisfied the unrestricted method predicts uniform atomic charges.

To decide for which states of an alternant (9.2.1.) holds, the eigenvalue equations (6.2.10.) together with the simplification (9.1.1.) should be examined. These show that if $R$ and $Q$ are being calculated by an iteration process and at any stage (9.2.1.) and (9.2.2.) are satisfied, then any first-order correction will not change this. Since the second-order terms of equation (8.2.3.) are based on first-order ones, it follows that the conditions will remain satisfied throughout the iteration. It is always possible to begin an iteration using matrices based on the appropriate Hückel or self-consistent ones and so, assuming convergence, if the
self-consistent method gives results which satisfy (9.2.1.) and (9.2.2.) for any state, then so will the unrestricted method. This means in particular that the lowest triplet states of even alternants will have unit π-electron charge on each atom and will therefore be non-polar.

There is also a 'pairing of orbitals' theorem associated with the positive and negative ions of alternants. McLachlan (1960) has pointed out that there are pairings between the occupied α-spin orbitals of the positive ion and the unoccupied β-spin orbitals of the negative ion and so on. Therefore the spin densities of the positive and negative ions are the same and the charges differ only in sign.

9.3 Ambiguity in the Unrestricted Bond Orders

Hall (1960) has pointed out that there is an ambiguity in the determination of self-consistent bond orders due to the fact that the same equations can often be obtained for the bond orders of several different states. A similar situation is found in the unrestricted method and can be illustrated by a calculation of the ground state of allyl. If the orbitals are chosen to have the form:

\[
\begin{align*}
\psi_1 &= (2 + k^2)^{-\frac{1}{2}} \omega_1 + k(2 + k^2)^{\frac{1}{2}} \omega_2 + (2 + k^2)^{-\frac{1}{2}} \omega_3 \\
\psi_2 &= 2^{-\frac{1}{2}} \omega_1 - 2^{-\frac{1}{2}} \omega_3 \\
\phi_1 &= (2 + l^2)^{-\frac{1}{2}} \omega_1 + l(2 + l^2)^{\frac{1}{2}} \omega_2 + (2 + l^2)^{-\frac{1}{2}} \omega_3
\end{align*}
\]

(9.3.1.)
then from (8.2.1.) it follows that $KL = 2$. The equation determining $L$ will be

$$L^4 + 2L^3(\gamma - \gamma_{12}) + 2L(2\gamma_{12} - \gamma_{13} - \gamma_1) - 4 = 0 \quad (9.3.2.)$$

where all the $\beta_{rs}$ integrals are taken to be zero except that $\beta_{12} = \beta_{23} = 0.5$ (in units of $\beta = 4.79$ eV). The quartic equation for $L$ has two real roots and taking the reduced values of the Pariser and Parr integrals, the real roots will be

$$L = +2 \quad \text{or} \quad -1.21$$

which give

$$K = +1 \quad \text{or} \quad -1.65 \quad (9.3.3.)$$

The positive values correspond to the ground state but the negative values satisfy the same equations. Thus there still remains ambiguity even though the form of the orbitals was specified very closely by (9.3.1.).

Denoting the orbitals in order of their energies as 1, 2, 3 for $\alpha$-spin and 1', 2', 3' for $\beta$-spin, the ground state will be $[12, 1']$ and the bond orders which satisfy the same equations as those of the ground state correspond to $[23, 2']$. If this treatment had begun with the general equations while still retaining (9.2.2.) there would be further ambiguity due to the state $[13, 2']$. In a perfectly general treatment there would also be solutions associated with states such as $[12, 2']$ for which there is no pairing of orbitals.
9.4 Perturbation Calculation of \( \mathbf{R} \) and \( \mathbf{Q} \)

It would be very desirable to have a method for calculating approximate unrestricted bond order matrices and at first sight the perturbation theory of Coulson and Longuett-Higgins (1947) seems an obvious way to do this. In the ions and triplet states of alternant hydrocarbons, for example, the unrestricted H.O.'s might be expected to be close to the self consistent ones. If this were so the \( \mathbf{R} \) and \( \mathbf{Q} \) of the unrestricted method could be calculated from the self consistent H.O.'s with the exchange terms in \( \mathbf{\zeta}^\alpha \) and \( \mathbf{\zeta}^\beta \) treated as perturbations.

Mclachlan (1960) has used such a method to calculate spin densities in the ions of alternant hydrocarbons. Applying his method to a negative ion, the major contribution to the spin density is due to the lowest antibonding self-consistent H.O. but there will be a correction to this due to the difference in exchange terms in \( \mathbf{\zeta}^\alpha \) and \( \mathbf{\zeta}^\beta \) and this can be found using perturbation theory. Unfortunately, if Hückel polarizabilities are used, perturbation theory has to be applied several times since any changes in \( \mathbf{R} \) and \( \mathbf{Q} \) cause further changes in \( \mathbf{\zeta}^\alpha \) and \( \mathbf{\zeta}^\beta \) and these can be significant. This is not because they are very large but because they alter the relative magnitude of the perturbation at different atoms and their effect is accumulative.
For the negative ion of naphthalene, perturbation theory has to be applied at least six times before $R$ and $Q$ and $\mathcal{E}^\alpha$ and $\mathcal{E}^\beta$ are reasonably consistent and therefore McLachlan's calculations in which perturbation theory is used once only, while qualitatively correct, are not very accurate quantitatively. The situation may be improved by using self-consistent polarizabilities (they are usually very different from Hückel ones) but these are not readily available. With Hückel polarizabilities, the calculations are really too tedious even though the final results are in fair agreement with the correct ones reported in the following chapter.
CHAPTER 10

CALCULATIONS OF THE IONS AND LOWEST $\pi$-TRIPLET STATES OF SOME CONJUGATED HYDROCARBONS
10.1 Introduction

In this chapter the iteration procedure described in chapter 8 is used to obtain unrestricted bond order matrices for the ions and lowest $\pi$ triplet states of a number of conjugated hydrocarbons. From these spin densities and net charges on each carbon atom in these molecules together with triplet excitation energies and ionization potentials can be found. By comparing the theoretical values of these properties with the few available experimental values it is possible to discuss how successful the unrestricted method is.

10.2 Parameters and Calculations

The iteration procedure of section 8.3 was used to obtain the unrestricted bond order matrices for the ions and triplet states of naphthalene, anthracene, phenenthrene and azulene. The whole calculation was programmed for the University of London 'Mercury' Computer and the approximations of section 9.1 were assumed to be correct, the values of the parameters used being those given in section 3.3.

To begin the iterations, the initial matrices were based on the appropriate Hückel orbitals and to give accuracy to three decimal places took about 10 iterations and 30 min machine time for naphthalene and azulene and
correspondingly longer for the larger molecules. The machine time used was about twice as much as for a corresponding ground state calculation as might be expected. The results of the calculations of the bond order matrices given in the following section are correct to three decimals for the ten membered rings but for the 14 membered rings, to conserve machine time, the iterations were stopped sooner, so there may be slight error in the third decimal place. This does not affect any other quantity since \( \langle S^2 \rangle \), \( \langle S^4 \rangle \) and energy values were given accurately to several decimals after a very few iterations.

Without doubt the amount of time used in these calculations could be reduced. For example, in the triplet states of the alternants, equation (9.2.2.) shows that only one of the matrices \( R \) and \( Q \) is independent so that the iterations could proceed with one bond order matrix only, reducing the calculation time by about a half. Also the symmetrical properties of the matrices could be used to halve the number of matrix elements involved with a corresponding decrease in computing time. A further improvement would be to choose better initial matrices since those based on the Hückel orbitals do not turn out to be very good approximations.

Several checks and trial runs were made to test both the programme and method of calculation. In one of
these the bond order matrices for the allyl radical were calculated and compared with the results of section 9.3. As a more complete check the bond order matrices of the naphthalene ion were computed to about four-figure accuracy and then used to form $F^\alpha$ and $F^\beta$. The eigenvectors of these matrices were then found and the appropriate number recomposed to form $R$ and $Q$. The agreement between the initial and final bond order matrices was nowhere worse than 0.00005 (see also section 7.4).

10.3 **Charges and Spin Densities**

The spin densities and net charges at the carbon atoms for the positive ions of naphthalene, anthracene and phenanthrene and for the positive and negative ions of azulene are given in the following tables. From section 9.2 it follows that the spin densities in the negative ions of the alternants will be the same as in the positive ions while the charges change only in sign. Azulene, however, is not an alternant and, as can be seen from results, its positive and negative ions are completely different. Two sets of spin densities are given for each molecule. Those before annihilation (B.A.) are associated with the wave function $\Psi^+$ while those after a single annihilation (A.S.A.) are associated with $(6.1.4.)$ and are given by $(\mathbf{S} - \mathbf{K})_{rr}$. 
Corresponding to these two sets of spin densities are two sets of charges but it is found that annihilation changes the charges hardly at all and so only the charges before annihilation are given.

The hydrogen hyperfine splittings at different ring positions in the naphthalene and anthracene ions have recently been measured by Carrington (1959). These are proportional to the spin density on the nearest carbon atom (McConnell and Chesnut, 1958) and using the constant of proportionality suggested by work on the benzene negative ion (Weissman, Tuttle and De Boer, 1957; McConnell and Dearman, 1958) experimental values for the spin densities can be found. If these are compared with the theoretical values it will be seen that the qualitative agreement is good and the quantitative agreement less so. The main error occurs at position 2 in both molecules where the theoretical spin densities are much too low. It is interesting to note that in these two molecules the use of the annihilator improves the agreement with experiment.

Figure 10.3 Numbering system for the molecules.
Naphthalene positive ion

<table>
<thead>
<tr>
<th>Atom</th>
<th>1</th>
<th>2</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin density B.A.</td>
<td>0.269</td>
<td>0.021</td>
<td>-0.081</td>
</tr>
<tr>
<td>Spin density A.S.A.</td>
<td>0.243</td>
<td>0.032</td>
<td>-0.055</td>
</tr>
<tr>
<td>Spin density Exp†</td>
<td>0.218</td>
<td>0.081</td>
<td>-0.098</td>
</tr>
<tr>
<td>Net charge</td>
<td>+0.179</td>
<td>+0.101</td>
<td>-0.061</td>
</tr>
</tbody>
</table>

Anthracene positive ion

<table>
<thead>
<tr>
<th>Atom</th>
<th>1</th>
<th>2</th>
<th>9</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin density B.A.</td>
<td>0.143</td>
<td>0.010</td>
<td>0.328</td>
<td>-0.067</td>
</tr>
<tr>
<td>Spin density A.S.A.</td>
<td>0.126</td>
<td>0.018</td>
<td>0.298</td>
<td>-0.043</td>
</tr>
<tr>
<td>Spin density Exp†</td>
<td>0.122</td>
<td>0.070</td>
<td>0.247</td>
<td>-0.065</td>
</tr>
<tr>
<td>Net charge</td>
<td>0.089</td>
<td>0.090</td>
<td>0.206</td>
<td>-0.031</td>
</tr>
</tbody>
</table>

Phenanthrene positive ion

<table>
<thead>
<tr>
<th>Atom</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin density B.A.</td>
<td>0.229</td>
<td>-0.118</td>
<td>0.178</td>
<td>-0.014</td>
<td>0.216</td>
<td>-0.039</td>
<td>0.047</td>
</tr>
<tr>
<td>Spin density A.S.A.</td>
<td>0.190</td>
<td>-0.079</td>
<td>0.147</td>
<td>0.005</td>
<td>0.209</td>
<td>-0.014</td>
<td>0.042</td>
</tr>
<tr>
<td>Net charge</td>
<td>0.111</td>
<td>0.038</td>
<td>0.134</td>
<td>0.058</td>
<td>0.176</td>
<td>-0.023</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Azulene positive ion

<table>
<thead>
<tr>
<th>Atom</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin density B.A.</td>
<td>0.432</td>
<td>-0.195</td>
<td>-0.068</td>
<td>0.185</td>
<td>-0.111</td>
<td>0.104</td>
</tr>
<tr>
<td>Spin density A.S.A.</td>
<td>0.398</td>
<td>-0.133</td>
<td>-0.042</td>
<td>0.149</td>
<td>-0.075</td>
<td>0.099</td>
</tr>
<tr>
<td>Net charges</td>
<td>0.126</td>
<td>0.017</td>
<td>0.150</td>
<td>0.113</td>
<td>0.137</td>
<td>0.032</td>
</tr>
</tbody>
</table>

†Experimental results from Carrington et al. (1959).
Azulene negative ion

<table>
<thead>
<tr>
<th>Atom</th>
<th>Spin density B.A.</th>
<th>Spin density A.S.A.</th>
<th>Net charges</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.015</td>
<td>0.103</td>
<td>-0.229</td>
</tr>
<tr>
<td></td>
<td>0.012</td>
<td>0.088</td>
<td>-0.154</td>
</tr>
<tr>
<td></td>
<td>-0.165</td>
<td>-0.157</td>
<td>-0.065</td>
</tr>
<tr>
<td></td>
<td>0.351</td>
<td>0.306</td>
<td>-0.027</td>
</tr>
<tr>
<td></td>
<td>0.457</td>
<td>0.416</td>
<td>-0.139</td>
</tr>
<tr>
<td></td>
<td>0.083</td>
<td>0.084</td>
<td>-0.095</td>
</tr>
</tbody>
</table>

If the charges are considered, the theory predicts negative charges on all the carbon atoms in the azulene negative ion and positive charges in the positive ion. On the other hand, for the positive ions of the alternants the results rather surprisingly show negative charges at some positions. Nevertheless the general effect is for each atom to have positive charge as might be expected.

Results have also been obtained for the lowest $\pi$ triplet states of the same molecules. The net charge on each carbon atom in the alternants is zero, as in the ground state, but the non-alternant azulene molecule has different charges in its ground and lowest triplet states. Spin densities both before and after a single annihilation are given but again it is found that annihilation does not change the charges.

Naphthalene triplet

<table>
<thead>
<tr>
<th>Atom</th>
<th>1</th>
<th>2</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin density B.A.</td>
<td>0.488</td>
<td>0.098</td>
<td>-0.174</td>
</tr>
<tr>
<td>Spin density</td>
<td>0.470</td>
<td>0.096</td>
<td>-0.132</td>
</tr>
</tbody>
</table>
Anthracene triplet

<table>
<thead>
<tr>
<th>Atom</th>
<th>1</th>
<th>2</th>
<th>9</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin density B.A.</td>
<td>0.184</td>
<td>0.060</td>
<td>0.658</td>
<td>-0.074</td>
</tr>
<tr>
<td>Spin density A.S.A.</td>
<td>0.170</td>
<td>0.057</td>
<td>0.648</td>
<td>-0.049</td>
</tr>
</tbody>
</table>

Phenanthrene triplet

<table>
<thead>
<tr>
<th>Atom</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin density B.A.</td>
<td>0.350</td>
<td>-0.194</td>
<td>0.292</td>
<td>-0.098</td>
<td>0.644</td>
<td>-0.178</td>
<td>0.184</td>
</tr>
<tr>
<td>Spin density A.S.A.</td>
<td>0.314</td>
<td>-0.147</td>
<td>0.254</td>
<td>-0.070</td>
<td>0.623</td>
<td>-0.133</td>
<td>0.159</td>
</tr>
</tbody>
</table>

Azulene triplet

<table>
<thead>
<tr>
<th>Atom</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin density B.A.</td>
<td>0.478</td>
<td>-0.136</td>
<td>0.355</td>
<td>-0.111</td>
<td>0.432</td>
<td>0.131</td>
</tr>
<tr>
<td>Spin density A.S.A.</td>
<td>0.457</td>
<td>-0.096</td>
<td>0.331</td>
<td>-0.076</td>
<td>0.407</td>
<td>0.133</td>
</tr>
<tr>
<td>Net charge</td>
<td>0.100</td>
<td>-0.132</td>
<td>-0.063</td>
<td>0.101</td>
<td>-0.100</td>
<td>-0.021</td>
</tr>
<tr>
<td>Ground state charges</td>
<td>-0.112</td>
<td>0.010</td>
<td>0.130</td>
<td>-0.044</td>
<td>0.084</td>
<td>-0.021</td>
</tr>
</tbody>
</table>

These results may be compared with recent open-shell calculations by Hoyland and Goodman (1962). The spin densities given by the two calculations are different, of course, since the open-shell method cannot give rise to negative spin densities. In this sense, therefore, the unrestricted method is the better one. The net charges predicted by the two methods are in very good agreement, the open-shell calculations also giving zero net charge on each carbon atom in the triplet state and negative charge at the γ position in the positive ions of naphthalene and anthracene.
10.4 Spin Properties.

If the unrestricted wave function is written formally as in equation (6.6.3.) then by using the normalizing condition and the expectation values of $\bar{S}^2$ and $\bar{S}^4$, upper bounds on the values $C_1, C_2, \ldots$ can be obtained which in turn give a lower bound to $C_0$. In practice, for $C_0, C_1$ and $C_2$ these bounds will be almost exactly the actual values of the coefficients but the upper bounds to the remaining coefficients will not be so good. The estimated values of $C_0^2, C_1^2, C_2^2$ for the various unrestricted wave functions are given in table 10.4 (c.f. table 6.6). The best estimate for $C_3^2$ which can be obtained from $\langle \bar{S}^2 \rangle$ and $\langle \bar{S}^4 \rangle$ is about a half of the value given for $C_2^2$ with correspondingly smaller values for the remaining coefficients. However, these are likely to overestimate the weights of the higher spin states.

<table>
<thead>
<tr>
<th>Molecular state</th>
<th>$C_0^2$</th>
<th>$C_1^2$</th>
<th>$C_2^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allyl radical</td>
<td>0.9628</td>
<td>0.0372</td>
<td>0</td>
</tr>
<tr>
<td>Naphthalene positive ion</td>
<td>0.9828</td>
<td>0.0170</td>
<td>0.0001</td>
</tr>
<tr>
<td>Anthracene positive ion</td>
<td>0.9792</td>
<td>0.0207</td>
<td>0.0001</td>
</tr>
<tr>
<td>Phenanthrene positive ion</td>
<td>0.9723</td>
<td>0.0273</td>
<td>0.0002</td>
</tr>
<tr>
<td>Azulene positive ion</td>
<td>0.9716</td>
<td>0.0280</td>
<td>0.0002</td>
</tr>
<tr>
<td>Azulene negative ion</td>
<td>0.9551</td>
<td>0.0441</td>
<td>0.0004</td>
</tr>
<tr>
<td>Naphthalene lowest $\pi$ triplet</td>
<td>0.9805</td>
<td>0.0193</td>
<td>0.0001</td>
</tr>
<tr>
<td>Anthracene lowest $\pi$ triplet</td>
<td>0.9866</td>
<td>0.0132</td>
<td>0.0001</td>
</tr>
<tr>
<td>Phenanthrene lowest $\pi$ triplet</td>
<td>0.9469</td>
<td>0.0509</td>
<td>0.0011</td>
</tr>
<tr>
<td>Azulene lowest $\pi$ triplet</td>
<td>0.9791</td>
<td>0.0207</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

Table 10.4 Relative weights of spin states in single determinant wave functions.
From table 10.4 it can be seen that only $c_2^2$ and $c_4^2$ are large and $c_2^2$ is very small in comparison. Therefore except possibly for the lowest triplet state of phenanthrene the assumptions involved in equation (6.6.1.) are satisfied for all the wave functions considered in this paper.

Table 10.4A shows the expectation values of $\langle S^2 \rangle$ corresponding to the wave function $\psi$ and to the wave function after the annihilation of the spin state $\psi_{2\alpha+3}$. The annihilation considerably improves the value of $\langle S^2 \rangle$ but it cannot reduce it completely to the correct value since $\psi_{2\alpha+5}$, $\psi_{2\alpha+7}$, etc. will still be present in the wave function (c.f. table 6.6A).

<table>
<thead>
<tr>
<th>Molecular state</th>
<th>$S$</th>
<th>$\langle S^2 \rangle$ for $\psi$</th>
<th>$\langle S^2 \rangle$ for $\psi_{2\alpha+3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allyl radical</td>
<td>3</td>
<td>0.8612</td>
<td>0.75</td>
</tr>
<tr>
<td>Naphthalene positive ion</td>
<td>2</td>
<td>0.8011</td>
<td>0.7523</td>
</tr>
<tr>
<td>Anthracene positive ion</td>
<td>2</td>
<td>0.8160</td>
<td>0.7548</td>
</tr>
<tr>
<td>Phenanthrene positive ion</td>
<td>2</td>
<td>0.8320</td>
<td>0.7550</td>
</tr>
<tr>
<td>Azulene positive ion</td>
<td>2</td>
<td>0.8340</td>
<td>0.7547</td>
</tr>
<tr>
<td>Azulene negative ion</td>
<td>2</td>
<td>0.8822</td>
<td>0.7596</td>
</tr>
<tr>
<td>Naphthalene lowest $\pi$ triplet</td>
<td>1</td>
<td>2.0770</td>
<td>2.0027</td>
</tr>
<tr>
<td>Anthracene lowest $\pi$ triplet</td>
<td>1</td>
<td>2.0530</td>
<td>2.0025</td>
</tr>
<tr>
<td>Phenanthrene lowest $\pi$ triplet</td>
<td>1</td>
<td>2.2038</td>
<td>2.0295</td>
</tr>
<tr>
<td>Azulene lowest $\pi$ triplet</td>
<td>1</td>
<td>2.0828</td>
<td>2.0029</td>
</tr>
</tbody>
</table>

Table 10.4A $\langle S^2 \rangle$ before and after a single annihilation.

10.5 Energies.

When the bond order matrices are known the total
energy can be calculated from equation (6.2.15.). If the ground-state energies are also known (see chapter 3), then triplet excitation energies and ionization potentials can be found. It is also interesting to use equation (6.6.2.) to find the energy after a single annihilation and this will lead to different values for the excitation energies and ionization potentials.

The triplet excitation energies both before and after a single annihilation are shown in table 10.5 together with experimental values. The agreement with experiment is not particularly good but this is only to be expected when small differences between large quantities are being calculated. The results are in any case not noticeably worse than those of other calculations (Pariser, 1956 a, b; Hall, 1952) even though some of these were able to use adjustable parameters to improve agreement with experiment.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Excitation energies (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B.A.</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>2.50</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1.44</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>2.41</td>
</tr>
<tr>
<td>Azulene</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Table 10.5      Triplet excitation energies.

*Experimental results taken from McClure (1949).
The ionization potentials cannot be obtained as directly as the excitation energies since the total energies for the ions and for the ground states are calculated using different zero energy levels. To allow for this $\beta_{rr}$ should be added to the difference between the total energies in the ground state and in the ion. Although it would be possible to calculate $\beta_{rr}$ it seems better to find it empirically. It has therefore been chosen to give the best agreement between the calculated ionization potentials of naphthalene, anthracene and phenanthrene and the recent experimental values obtained by Wacks and Dibeler (1959). In this way there will be two possible values of $\beta_{rr}$ depending on whether energies before or after a single annihilation are used; the difference between them will of course represent the averaged lowering of the total energy of the ions obtained by using the annihilator. In table 10.5A the calculated and experimental ionization potentials are given. The agreement between them is good and is improved when energies after a single annihilation are used.

The value obtained for $\beta_{rr}$ using energies before annihilation was 4.132 eV and using energies after a single annihilation, 4.242 eV.
Table 10.5A  
Ionization potentials.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ionization Potentials (eV)</th>
<th>B.A.</th>
<th>A.S.A.</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allyl</td>
<td></td>
<td>8.51₉</td>
<td>8.72₃</td>
<td>9.05[ᵇ]</td>
</tr>
<tr>
<td>Naphthalene</td>
<td></td>
<td>8.2₉₀</td>
<td>8.2₂₈</td>
<td>8.2₆[a]</td>
</tr>
<tr>
<td>Anthracene</td>
<td></td>
<td>7.₄₇₄</td>
<td>7.₅₄₇</td>
<td>7.₅₅[a]</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td></td>
<td>8.₀₇₅</td>
<td>8.₀₆₄</td>
<td>8.₀₃[a]</td>
</tr>
<tr>
<td>Azulene</td>
<td></td>
<td>7.₂₃₂</td>
<td>7.₂₇₉</td>
<td>-</td>
</tr>
</tbody>
</table>


10.6 Conclusion

It is difficult to draw any general conclusions from the results presented in this chapter since there are few experimental values available for comparison. It does seem clear, however, that the unrestricted Hartree-Fock method can give good qualitative agreement with experiment for various properties. In this, the unrestricted wave function is an improvement on other single determinant wave functions since it can give lower energy values and predicts negative spin densities at some atoms.

The quantitative agreement with experiment is quite good for most properties but the obvious exception is in the calculation of spin densities, some of which are predicted to be far too small. On reflection this is not very surprising for the unrestricted wave function.
is not an eigenfunction of spin and so it might be expected that spin properties would be predicted rather poorly. The fact that the use of a single annihilator improves the spin densities tends to confirm this view. Presumably if the bond order matrices were obtained by minimizing (6.6.2.) instead of (6.2.15.), i.e. if extended bond order matrices with $A_{2n+3}$ were found, then the calculated spin densities would be much better.

There is, however, another possibility and this is that the values of the Pariser and Parr integrals used are not the most satisfactory for unrestricted calculations. That the values of the spin densities obtained depend very much on the integrals can be seen from the allyl calculation in section 9.3. The empirical values of the integrals were originally obtained by a comparison between experimental excitation energies of benzene and theoretical excitation energies calculated with configuration interaction. Since configuration interaction wave functions and unrestricted wave functions differ from the accurate wave functions in completely different ways it would be more suitable to use different values of the integrals for the two methods.
PART IV

LONG WAVE THEORY OF ABSORPTION AND

REFLECTION IN MOLECULAR CRYSTALS
CHAPTER 11

EXCITON WAVES AND THE DIPOLE–DIPOLE APPROXIMATION
11.1 Introduction

The first three parts of this thesis have dealt with ground and excited states of free molecules. In this and the following chapter which make up part IV we shall study the properties of molecular crystals and, in particular, the theory of their excited states.

Molecular crystals include most organic molecules in crystal form and they differ from other types of crystal in that the molecules in the crystal are held together by weak forces so that, as a first approximation, the electronic states of each molecule can be considered as unchanged by the crystal field. In this approximation when the crystal is excited then the excitation is localised on one molecule. When the intermolecular forces are considered, however, their effect is to allow this excitation to move from one molecule to another throughout the crystal. We can, therefore, speak of a wave of excitation moving through the crystal.

A considerable part of the theory of molecular crystals has to do with the evaluation of the energies associated with their optically excited states so that the theoretical values may be compared with those observed in the crystal spectra. The change from the free molecule values depends on the interactions between the molecules in the crystal and to determine this involves
the calculation of long range dipole-dipole interactions. In sections 2, 3 and 4 a brief account of the theory will be given together with its extension to the case of two molecules per unit cell, while section 5 will consist of a short review of the applications of the theory.

11.2 Exciton Waves

The simplest model of a molecular crystal is the oriented gas. If the molecules in the crystal are taken to be orientated but non-interacting, then the wave function for the ground state of the crystal will be the product of the wave functions of the individual molecules:

$$\Psi^g = \prod_{s} \psi^g_s$$  (11.2.1.)

and, similarly, the crystal excited state corresponding to the \( p \) th excited state of the free molecule, with the excitation localised on the \( s \) th molecule in the crystal, will be,

$$\Psi^p_s = \psi^p_s \prod_{s \neq r} \psi^g_s$$  (11.2.2.)

where \( \psi^g_s \) and \( \psi^p_s \) are the free molecule wave functions for the ground state and \( p \) th excited state of the \( s \) th molecule and the product is taken over all the \( N \) molecules in the crystal. Evidently (11.2.2.) is \( N \)-fold degenerate corresponding to the \( N \) possible values of \( r \).
However, in real crystals, there will be interactions between the molecules and this will split the degeneracy. The correct wave functions will be found by taking linear combinations of the wave functions (11.2.2.) and the coefficients will be the eigenvectors of the crystal Hamiltonian. Since the crystal Hamiltonian will have the full symmetry of the crystal lattice, the correct wave functions can be shown to be, (c.f. Frenkel, 1931, 1936; Peierls, 1932; Seitz, 1940; Winston, 1951)

\[ \phi^p (\mathbf{k}) = \frac{1}{\mathcal{N}} \sum_{\mathbf{r}} \alpha_{\mathbf{k}} \phi(\mathbf{k}, \mathbf{r}) \hat{\mathbf{r}}^p \]  

(11.2.3.)

where \( \mathbf{k} \) is a vector in the reciprocal lattice and \( \mathbf{r} \) is the position of the \( \mathbf{r} \)th molecule in the crystal lattice. There are \( \mathcal{N} \) wave functions of the type (11.2.3.) corresponding to the \( \mathcal{N} \) values of \( \mathbf{k} \) in the first Brillouin zone but since \( \mathcal{N} \) is large \( \mathbf{k} \) can be taken as effectively continuous.

Physically (11.2.3.) implies that the excitation is no longer confined to one molecule but, on the contrary, moves from one molecule to another so that there are waves of excitation (exciton waves) set up in the crystal. Each exciton wave can be identified by its wave vector \( \mathbf{k} \) and the energy associated with it will be a function of \( \mathbf{k} \), say \( W(\mathbf{k}) \). By allowing \( \mathbf{k} \) to take all its possible values we can see that to each molecular
excited level there will correspond a band \( W(k) \) in the crystal.

The optically observed transitions will occur between the ground state and the exciton state whose wave vector \( \mathbf{k} \) satisfies the relation

\[
\mathbf{k} + \mathbf{q} = \mathbf{0}
\]

where \( \mathbf{q} \) is the wave vector of the exciting light wave (see Hochstrasser, 1961). Usually this relation is simplified to \( \mathbf{k} = \mathbf{0} \) since \( \mathbf{q} \) is small. The problem of understanding the spectrum of a molecular crystal, in the context of the simple theory just developed, therefore, consists of calculating the values of \( W(0) \) for the various excited states.

11.3 The Energy Levels

Ignoring the effect of vibration-electronic interaction and also the interaction between different molecular electronic states, the energy corresponding to the wave function (11.2.3.) can be written as:

\[
W(k) = W + \sum_{s \neq r} H_{rs} \exp \left[ \mathbf{k} \cdot (s - r) \right]
\]

where the energy is measured relative to the ground state, \( W \) is the molecular excitation energy and \( H \) is that part of the crystal Hamiltonian which involves the intermolecular interactions. The matrix elements \( H_{rs} \) are
given by:

\[ H_{rs} = \int \bar{\Psi}_r^* H \bar{\Psi}_s \, dt \]  \hspace{1cm} (11.3.2.)

More complete formulae including the explicit form for \( H \) can be found elsewhere (Craig and Hobbins, 1955; Fox and Schnepp, 1955; Hall, 1958). Here we need only note that, for the crystals of interest to us, the value of the matrix elements \( H_{rs} \) can be estimated by expanding the potentials in inverse powers of the intermolecular distance. The first and most important term will be (see Perrin, 1936, Carlson and Rushbrooke, 1950):

\[ H_{rs} = -\frac{1}{R^3} \left\{ p_x(r)p_x(s) + p_y(r)p_y(s) - 2p_z(r)p_z(s) \right\} + O\left(\frac{1}{R^4}\right) \]  \hspace{1cm} (11.3.3.)

where \( R = |r - s| \); \( p(t) \) and \( p(s) \) are the transition moments of the two molecules \( r \) and \( s \); and \( x, y, z \) are orthogonal axes with \( z \) lying along the line joining \( r \) and \( s \). Thus once the magnitude and direction of the transition dipole in the free molecule is known, then from knowledge of the crystal structure all the terms in (11.3.3.) are known.

It is important to note that \( H_{rs} \) is exactly the same as the potential energy of two electrostatic dipoles \( p(t) \) and \( p(s) \) so that the evaluation of the sum in (11.3.1.) is equivalent to finding the sum of dipole-dipole interactions. Similar summations arise in other crystal problems and in particular in the theory of ionic
crystals. In the following chapter some of the techniques used in the study of ionic crystals will be applied to molecular crystals.

11.4 Molecular Crystals with Two Molecules per Unit Cell

To obtain the results of the previous sections we have tacitly assumed that the crystals had only one molecule per unit cell. However, many of the most interesting molecular crystals, anthracene and naphthalene, for example, have two molecules per unit cell and the theory has to be modified to take account of this. The full details are given by Davydov (1948), Craig and Hobbins (1955), Winston (1951) and McClure (1959) and the last two named also deal with crystals with more than two molecules per unit cell. Here we briefly sketch the theory.

Associated with each site (a and b) in the unit cell there will be one-site excitons, viz.

\[ \phi_a^p = \frac{1}{\sqrt{N}} \sum \psi(x) \text{e}^{i\mathbf{k} \cdot \mathbf{r}_a} \Phi_r^p \]

\[ \phi_b^p = \frac{1}{\sqrt{N}} \sum \psi(x) \text{e}^{i\mathbf{k} \cdot \mathbf{r}_b} \Phi_r^p \quad (11.4.1.) \]

where the summation is over all unit cells but in \( \phi_a^p \) the excitation is only allowed to be on molecules at the site a and in \( \phi_b^p \) only on those at site b. The vectors \( \Phi_r^p \) now refer to the unit cells, the suffices a and b
being used to distinguish the different site positions.

The crystal wave functions can be obtained by taking the correct combinations of the one-site excitons and these will be given by the eigenvectors of the \(2\times2\) matrix formed from the matrix elements of the crystal Hamiltonian with respect to the one-site excitons. In the case when \(k_z = 0\) the combinations will be

\[
\phi^+ = \frac{1}{\sqrt{2}} (\phi^p_a + \phi^p_b) \\
\phi^- = \frac{1}{\sqrt{2}} (\phi^p_a - \phi^p_b)
\]

(11.4.2.)

We shall take these as correct throughout even when \(k\) is not zero although strictly speaking this will only be so if the crystal has a symmetry plane and \(k\) lies in this plane (c.f. Fox and Yatsiv, 1957).

The wave functions (11.4.2.) show that each free molecule excited state will give rise to two distinct bands in the crystal. Therefore to each free molecule transition there will be two allowed crystal transitions with different energies (and also different polarizations) given by:

\[
W^\pm(k) = W + I^\pm J
\]

(11.4.3.)

where

\[
I = \sum_s' H_{ra} s_a e^{i \mathbf{k} \cdot (s_a - r_a)} \\
J = \sum_s H_{ra} s_b e^{i \mathbf{k} \cdot (s_b - r_a)}
\]
The formula (11.3.3.) still holds so that $I$ represents the dipole-dipole sum over translationally equivalent molecules while $J$ is taken over translationally inequivalent molecules. The quantities normally calculated are the splitting $S$ (called the Davydov or factor group splitting) of the two levels and the net shift $D$ from the free molecule value. These are given by:

$$D = I, \quad S = 2J$$

11.5 Applications of the Theory

The theory of the previous sections has been applied to a few molecules and an excellent review of the results has been given by McClure (1959). Almost all calculations have been made with $k = 0$ and the summations have usually included only those molecules in a sphere of finite radius ($\sim 20\AA$) but good convergence is said to be found (Craig and Hobbins, 1955). Attempts have also been made to use the Ewald method of evaluating dipole-dipole sums (Craig and Walsh, 1956, 1958).

Before making the calculations the magnitude and direction of the appropriate free molecule transitions have had to be known. The magnitude of the transition moments have invariably been obtained from the spectrum of the free molecule but usually their directions are
not so easy to find. In some cases the fact that the Davydov splitting and the shift term depend on the direction of the transition dipole can be used to find this direction if it is not already known. For example the strong transition in anthracene at 2,500Å is split by 16,000 cm\(^{-1}\) in the crystal. This can only be explained if the transition in the free molecule is polarized in the long-axis direction.

For strong transitions the agreement between the calculations and the experimental results has been quite satisfactory but in the case of weak transitions in the free molecule the theory so far described is not accurate enough. This is because in the crystal there is coupling with any neighbouring stronger transitions and this can have an important effect. Also the theory had had to be extended to include vibrational-electronic states and the polarization of transitions in crystals. Further details and references are given in the review by McClure.
CHAPTER 12

APPLICATIONS OF THE LONG WAVE METHOD TO
MOLECULAR CRYSTALS
12.1 Introduction

Since the problem of calculating energy levels in molecular crystals can be reduced to the summation of dipole-dipole interactions, it becomes analogous to other problems in crystal theory. In particular the equations are very similar to those which arise in the calculation of the energy of vibration of an ionic crystal and this, too, involves the treatment of long range forces.

An elegant theory of vibrations in ionic crystals has been developed by Born and Huang (1954) using the method of long waves. The application of the theory to molecular crystals has been made by Hall (1962) who has studied the coupling between electromagnetic and exciton waves in the crystals.

The method of long waves enables the magnitude and direction of \( k \) to be included in the equations and then, by introducing the electric and magnetic fields, the retardation of the interaction potentials can be treated. Since \( k \) and \( \omega \) are included throughout a dispersion relation between the frequency and the dielectric constant can be obtained and this can be used to consider absorption and reflection.

Our purpose in the next chapter will be to extend Hall's treatment to include crystals with two molecules
per unit cell and to use the dispersion relation to consider what modifications have to be made to the simple Davydov treatment in the light of the more accurate long wave theory. Calculations will be made on the strong transitions of naphthalene and anthracene to illustrate these changes.

12.2 Replacement of the Dipole-Dipole Interactions by an Effective Field

In section 11.3 it was emphasised that the matrix element \( H_{rs} \) was in the form of an interaction energy between the transition dipoles \( \mathbf{p}(\uparrow) \) and \( \mathbf{p}(s) \). The electric field at \( \mathbf{r} \) due to a dipole \( \mathbf{p}(s) \) at \( s \), is

\[
E(s) = -R^3 \mathbf{p}(s) + 3 R^{-5} \left[ \mathbf{p}(s) \cdot \mathbf{R} \right] \mathbf{R}
\]

(12.2.1.)

and Hall (1962) has pointed out that because of this \((11.3.3.)\) becomes

\[
H_{rs} = -\mathbf{p}(\uparrow) \cdot E(s)
\]

(12.2.2.)

So that in the case of one molecule per unit cell the energy formula \((11.3.1.)\) can be written as

\[
W(k) = W - \mathbf{p}(\uparrow) \cdot E_{\text{eff}}(\uparrow)
\]

(12.2.3.)

where \( E_{\text{eff}}(\mathbf{r}) \) is the field which acts on the molecule at \( \mathbf{r} \) due to all the other dipoles suitably modulated. We have, therefore,
The extension of Hall's treatment to crystals with two molecules per unit cell is almost immediate. Corresponding to (11.4.3.) we have

\[ W^\pm (k) = W - F(t_0) \cdot E_{eff} (t_0) \] (12.2.5.)

so that the same formula can be used for both \( W^+ \) and \( W^- \) but \( E_{eff} \) will have different meanings in the two cases. For \( W^+ \), \( E_{eff} \) will be the field at \( t_0 \) due to the suitably modulated dipoles \( F(s_a) \exp ik \cdot R \) at the \( a \) sites in all the other unit cells except the one considered \( (r) \) and also due to the dipoles \( F(s_b) \exp ik \cdot R \) at the \( b \) sites in all the unit cells including \( r \). The effective field in the formula for \( W^- \) will have a similar definition but the dipoles at the \( b \) sites in all the unit cells will change direction and become 

\[ -F(s_b) \exp ik \cdot R. \] 

The equation (12.2.5.) is, of course, independent of \( t_0 \) and, therefore, we choose \( t_0 \) to be the origin of the coordinates and equal to zero. This has the effect of removing the term \( \exp ik \cdot t_0 \) which would otherwise modulate all the quantities in the equations. The problem is now to find the effective
field at a site position $a$ due to all other transition dipoles, the energy being given by

$$\mathcal{W}^{\pm}(k) = \mathcal{W} - \mathbf{p}_{a} \cdot \mathbf{E}^{\pm} \quad (12.2.6.)$$

12.3 **Evaluation of the Effective Field**

There are several conceivable ways of evaluating the effective field. One would be to calculate it by direct summation of the contributions from individual molecules but this leads to theoretical difficulties concerning convergence. Another way would be to use the Ewald method.

If we were concerned with an isotropic medium or crystals with tetrahedral symmetries there would be no problem since the Lorentz-Lorenz formula gives:

$$E_{\text{eff}} = E + \frac{4}{3} \pi P \quad (12.3.1.)$$

where $E$ is the electric field in the medium and $P$ the polarization. The long wave theory of crystals for which (12.3.1.) is satisfied has been developed by Hall (1958).

For crystals with more complicated symmetries such as most molecular crystals have, (12.3.1.) is not at all correct and a more complicated relation must be used.
A similar situation arises in the theory of ionic crystals (Born and Huang, 1954) and in the theory of ferroelectrics (Jaynes, 1953). Using the Ewald method we can write for the x-component of the effective field at the molecule in the a site position \( a^\alpha \),

\[
E_x + \sum_\mathbf{b} \sum_\mathbf{y} Q_{\alpha y} (\kappa; \alpha, \mathbf{b})(\mathbf{p}_\mathbf{b})_\mathbf{y} \quad (12.3.2.)
\]

where the sum \( \sum_\mathbf{b} \) is taken over all possible sites in the unit cell. The components of the tensor \( Q \) can be evaluated for a given crystal and a given value of \( \kappa \) and formulae for this have been obtained by Born and Huang (op.cit. page 254).

The point of writing \( E_x \) in the form (12.3.2.) is that the first term \( E_x \) is a non-analytic function of \( \kappa \) as \( \kappa \to 0 \) and in fact depends on the direction of \( \kappa \). On the other hand the second term is a regular function of \( \kappa \) at the origin and for long waves (\( \kappa \) small) can be taken as constant and equal to the value when \( \kappa = 0 \). This relation for \( E_x \) is, however, difficult to work with and so in order to treat retardation of forces we use a simpler relation.

If we divide the crystal into two parts by a sphere around the point \( \frac{1}{a} \) and treat the region outside the sphere as an infinite dielectric while summing the
contributions from the dipoles inside the sphere individually, the effective field will be

\[ E_{\text{eff}} = E + \mathcal{I} + \frac{4}{3} \pi \mathcal{P} \]  

(12.3.3.)

where \( \mathcal{I} \) is the field due to the dipoles inside the sphere (c.f. Hall, 1962). Evidently the radius of the sphere should be taken large enough for \( \mathcal{I} \) to converge. However, we do not wish it to be so large that the retardation over the sphere will become important and it should be small enough for \( \mathbf{k} \) to be effectively constant throughout the sphere for the limit of long waves. Luckily if the radius is taken to be about 10 - 20 Å all our requirements will be satisfied (see, for example, Craig and Walsh, 1958; Anex and Simpson, 1960). Moreover \( \mathcal{I} \) will be a regular function of \( \mathbf{k} \) as \( k \to 0 \) and, therefore, in the limit of long waves we can take it as constant and equal to \( \mathcal{I} (k = 0) \). In the remaining terms in (12.3.3.), however, we cannot do this because they will depend on the direction of \( \mathbf{k} \) as \( k \to 0 \).

In effect by using (12.3.3.) we assume that the effects of the anisotropy of the crystal can be included in \( \mathcal{I} \) and that the remainder of the crystal acts as a homogeneous dielectric. This cannot be completely correct, of course, but the adoption of such a model
enables the retardation of the potentials to be allowed for by using electric and magnetic fields. Firstly, however, we develop an electrostatic theory using (12.3.3).

12.4 Electrostatic Solutions

In order to proceed we now need the equations relating the macroscopic quantities $E$ and $P$ and also an explicit formula for $P$. The macroscopic polarizability for the crystal will depend on the transition moments (dipoles) which give rise to it and there will be a second term due to all the other virtual transitions of the molecules. Therefore, we have

$$\mathbf{P} = \frac{1}{V} (\mathbf{P}_a \pm \mathbf{P}_b) + \alpha \mathbf{E} \mathbf{u}_f$$

(12.4.1.)

and using (12.3.3.) this becomes

$$\mathbf{P} \left(1 - \frac{4}{3} \pi \alpha \right) = \left\{ \frac{1}{V} (\mathbf{P}_a \pm \mathbf{P}_b) + \alpha \mathbf{I} \right\} + \alpha \mathbf{E}$$

(12.4.2.)

where $V$ is the volume and $\alpha$ is the polarizability per unit volume of the unit cell. Since organic molecules have anisotropic polarizabilities $\alpha$ should strictly be a tensor but, for convenience, we assume that it is scalar.

If we now exclude the time dependence of the fields the electrostatic equations relating $E$ and $P$ reduce
to:

$$E = - \frac{4\pi}{k^2} (P \cdot k) k$$

(Born and Huang, 1954, page 248).

Even without writing the equation (12.2.6.) explicitly in terms of $E$ and $k$ we can see that it will be non-analytic for $k = 0$. The energy will depend on the direction of $k$ for the limit of long waves and it is, therefore, inadmissible to discuss the case of $k \to 0$ without specifying the directions involved.

From (12.4.3.) it is clear that $E$ must be parallel to $k$ and thus the solutions given by (12.4.3.), (12.4.2.) and (12.2.6.) correspond to longitudinal waves. There is another possibility, namely that $E$ vanishes. As we shall see later this corresponds to a transverse wave in the electromagnetic theory.

Assuming that $I$ is parallel to $p_a \pm p_b$, the vanishing of $E$ occurs when $k$ is perpendicular to $p_a \pm p_b$ and the energy associated with this is

$$W^\pm (k) = W - p_a \cdot I - \frac{4\pi}{3} \left\{ \frac{1}{(p_a \pm p_b) + \alpha \cdot p_a \cdot I} \right\} \left\{ -\frac{4\pi \alpha}{3} \right\}^{-1}$$

$$= W_c^\pm - \overline{W}^\pm \left\{ -\frac{4\pi \alpha}{3} \right\}^{-1}$$

(12.4.4.)

where $W_c^\pm = W - p_a \cdot I$, which we notice is exactly the value of $W^\pm (k)$ which would be obtained by summing the dipole-dipole interactions over a finite sphere,
If we now consider the longitudinal wave with \( k \) parallel to \( \Phi_a \pm \Phi_b \) then its energy will be

\[
W_c^\pm(k) = W_c^\pm + 2 \bar{W}^\pm \left[ 1 + \frac{2}{3} \pi \alpha \right]^{-1} \quad (12.4.5)
\]

12.5 **Electromagnetic Solutions**

Because the electrostatic solutions do not admit the possibility of transverse waves, they are not very useful when the optical properties of crystals are being considered. To improve on this the time dependence of the fields and the wave function has to be taken into account. This allows the retardation of the fields to be included in the theory through the introduction of a magnetic field \( \mathbf{H} \) whereas the electrostatic theory treats all the fields as instantaneous.

The time dependent wave function is written as

\[
\Phi^\pm = \sum \alpha_r e^{-i\omega t} \left[ \psi_{r_a} \pm \psi_{r_b} \right] 
\quad (12.5.1)
\]

where the \( \alpha_r \) are functions of position and \( \omega \) is the frequency of the excitation waves. The time dependent Schrödinger equation with (12.5.1.) gives the formula for the \( \alpha_r \) as

\[
\hbar \omega \alpha_r = W a_r - \Phi_a \cdot E_{\text{eff}}
\]

and if the \( \alpha_r \) are treated as a continuous function
of position this becomes

$$k \omega a = W a - \mathbf{P}_a \cdot \mathbf{E}_{stat}$$  \hspace{1cm} (12.5.2.)

The formula for the polarization will also change to

$$\mathbf{P} = \frac{\alpha}{V} \left( \mathbf{P}_a \pm \mathbf{P}_b \right) + \alpha \mathbf{E}_{stat}$$  \hspace{1cm} (12.5.3.)

It is important to realize that $\mathbf{E}_{stat}$ is now the effective field due to the modulated dipoles $\mathbf{P}_a$, so that it is a function of the amplitude of the excitation. In particular $\mathbf{I}$ will also be a function of $a$. However, for long waves $a$ will be effectively constant throughout the sphere which defines $\mathbf{I}$ so that we have

$$\mathbf{E}_{stat} = \mathbf{E} + \alpha \mathbf{I} + \frac{4 \pi}{3} \mathbf{P}$$  \hspace{1cm} (12.5.4.)

where $\mathbf{I}$ is now the field due to the dipoles $\mathbf{P}_a$, $\mathbf{P}_b$ in the sphere and is independent of $a$. Combining (12.5.2.), (12.5.3.) and (12.5.4.) gives

$$(k \omega - W_c) a = - \mathbf{P}_a \cdot \left( \mathbf{E} + \frac{4 \pi}{3} \mathbf{P} \right)$$  \hspace{1cm} (12.5.5.)

$$\mathbf{P} = \alpha \left\{ \frac{1}{V} \left( \mathbf{P}_a \pm \mathbf{P}_b \right) + \alpha \mathbf{I} \right\} + \alpha \left( \mathbf{E} + \frac{4 \pi}{3} \mathbf{P} \right)$$  \hspace{1cm} (12.5.6.)

For a plane wave the Maxwell equations give the relations between $\mathbf{H}$, $\mathbf{E}$ and $\mathbf{P}$ as

$$\frac{\omega}{c} \mathbf{H} = \mathbf{k} \times \mathbf{E}$$

$$\mathbf{k} \times \mathbf{H} = - \frac{\omega}{c} \left( \mathbf{E} + 4 \pi \mathbf{P} \right)$$
from which \( H \) can be eliminated to give

\[
k^2 \mathbf{E} - (\mathbf{k} \cdot \mathbf{E}) \mathbf{k} = \frac{\omega^2}{c^2} \left( \mathbf{E} + 4\pi \mathbf{P} \right)
\]  

(12.5.7.)

It is immediately obvious that one solution of the electromagnetic equations will have \( a = 0 \) and \( \mathbf{k} \) lying in the plane of \( \mathbf{P}_a \) and \( \mathbf{P}_b \) with \( \mathbf{E} \) perpendicular to this plane. This corresponds to a pure electromagnetic wave refracted through the crystal and the dispersion relation in this case will be

\[
\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi \alpha
\]

(12.5.8.)

where \( n = c k / \omega \). Born and Huang have pointed out that the other transverse solutions of the electromagnetic equations arise because of the interaction of the pure electromagnetic wave (12.5.8.) and the electrostatic solution corresponding to \( \mathbf{E} = 0 \). These will be the waves which are important in optical phenomena.

Eliminating \( \mathbf{P} \) and \( a \) from (12.5.5.), (12.5.6.) and (12.5.7.) gives the relation

\[
\left\{ c^2 k^2 \left( 1 - \frac{4}{3} \pi \alpha \right) - \omega^2 \left( 1 + \frac{8}{3} \pi \alpha \right) \right\} \mathbf{E} - c^2 \left( 1 - \frac{4}{3} \pi \alpha \right) (\mathbf{k} \cdot \mathbf{E}) \mathbf{k}
\]

(12.5.9.)

\[
= \frac{4\pi}{3(k_\omega - W_c)} \left\{ c^2 (\mathbf{P}_a \cdot \mathbf{k})(\mathbf{k} \cdot \mathbf{E}) - (2\omega + c^2 k^2)(\mathbf{P}_a \cdot \mathbf{E}) \right\} \left\{ \frac{1}{15} \left( \mathbf{P}_a + \mathbf{P}_b \right) + \alpha \mathbf{I} \right\}
\]

which can be written as three linear homogeneous equations in the components of \( \mathbf{E} \). For consistency the determinant of the coefficients must vanish and this gives
rise to the dispersion relation. However, two special solutions can be isolated immediately.

The first of these has \( \mathbf{K} \) and \( E \) all parallel. For this (12.5.9.) reduces to

\[
\tan \omega = W_c + 2 \bar{\Omega} (1 + \frac{4\pi}{3} \omega^2)^{-1} \tag{12.5.10.}
\]

and also the magnetic field \( \mathbf{H} \) vanishes. This, then, corresponds to a longitudinal wave of excitation exactly as in the electrostatic case.

The second solution represents a transverse wave with \( E \) parallel to \( \mathbf{F}_a \) and perpendicular to \( \mathbf{F}_b \). Hence from (12.5.9.)

\[
\tan \omega = W_c + \bar{\Omega} \left( 2 + \frac{2k^2}{\omega^2} \right) \left\{ (1 + \frac{4\pi}{3} \omega) - \frac{c^2k^2}{\omega^2} (1 + \frac{4\pi}{3} \omega) \right\}^{-1} \tag{12.5.11.}
\]

This wave represents the coupling between (12.4.4.) and (12.5.8.) and this is shown clearly in Fig. 12.5 on page 171. To understand the spectral properties of this solution we now consider the dispersion relation.

12.6 The Dispersion Relation

In terms of the refractive index (12.5.11.) becomes

\[
\frac{n^2 - 1}{n^2 + 1} = \frac{4\pi}{3} \frac{\bar{\Omega}}{\omega_c - \omega} + \frac{\bar{\Omega}}{\omega_c - \tan \omega} \tag{12.6.1.}
\]

\[
= \frac{4\pi}{3} \frac{\bar{\Omega}}{\omega_c - \omega} + \frac{\bar{\Omega}}{\omega_c - \omega}
\]
Fig. 12.5  Coupling between the electromagnetic wave and the exciton wave.

--- electrostatic solutions
--- electromagnetic solutions

a  Electrostatic solution with $E = 0$
b  Longitudinal wave
c  Electromagnetic wave
dd' Transverse wave which arises from the coupling between a and c at the point P.
and the equation can be used for crystals with one molecule or with two molecules per unit cell. For crystals with two molecules per unit cell there will be two equations (12.6.1.) corresponding to each free molecule transition given by the different values of $\bar{\omega}$ and $\omega_c$ i.e. $\bar{\omega}^+$ and $\omega_c^+$ and then $\bar{\omega}^-$ and $\omega_c^-$. 

Equation (12.6.1.) shows that $n^2$ will be negative in the region $\omega_L < \omega < \omega_H$ where

$$\omega_H = \omega_c + 2\bar{\omega} \left(1 + \frac{8}{3}\pi\alpha\right)^{-1}$$

$$\omega_L = \omega_c - \bar{\omega} \left(1 - \frac{4}{3}\pi\alpha\right)^{-1}$$  (12.6.2.)

and so $\omega_H$, $\omega_L$ represent the high and low frequency limits of metallic reflection. With $\alpha = 0$ these are exactly the same results as obtained by Anex and Simpson (1960) who treated retardation by using the Hertz vector.

The same authors have used the dispersion relation:

$$\frac{n^2 - 1}{n^2 + 2} = \zeta + \frac{\omega_p^2/3}{\omega_c^2 - \omega^2}$$  (12.6.3.)

to study metallic reflection in the 4,000 Å system of the dye 1,5 bis-(dimethylamino) pentamethinium. They introduced the constant $\zeta$ empirically to allow for the influence of higher transitions and this corresponds to our use of $\alpha$ (c.f. Hall, 1962). With $\zeta = \frac{4}{3}\pi\alpha$ and for frequencies near the resonance frequency $\omega_c$ the two formulae (12.6.2.) and (12.6.3.) are very similar.
Anex and Simpson find quite good agreement between (12.6.3.) and their experimental reflection curve when $G = 0.25$. This seems quite a reasonable order of magnitude value and agrees well with the value of $\alpha$ which can be obtained by taking the mean polarizability of Benzene. In any case since there seems to be no better estimate available we shall adopt this value for calculations on naphthalene and anthracene.

Using the value $\frac{4}{3} \pi \alpha = 0.25$ in (12.6.2.) we obtain

$$\omega_\mu = \omega_c + \frac{4}{3} \bar{\omega}$$

$$\omega_\nu = \omega_c - \frac{4}{3} \bar{\omega}$$

(12.6.4.)

so that the width of the reflection band will be $\frac{8}{3} \bar{\omega}$.

The reflection band widths corresponding to the strong transitions in naphthalene (at 2200 Å) and anthracene (at 2500 Å) have been calculated using the dipole-dipole sums reported by Craig and Hobbins (1955) and Craig and Walsh (1958) and the results are given in table 12.6.

There are two molecules per unit cell in the crystals of anthracene and naphthalene and so for each free molecule transition there will be two absorption frequencies and associated with each of these will be a reflection band. The two reflection bands for each molecular transition will, however, be very dissimilar as can be seen from the table. The one which arises from the crystal
transition polarized in the $\mathbf{P}_a - \mathbf{P}_b$ direction is quite narrow but the other band is very wide and in this respect is similar to the reflection bands which occur with strong transitions in dye films (Weigl, 1956). There have been no experimental studies on the reflection spectra of naphthalene and anthracene crystals to compare with the results in table 12.6

<table>
<thead>
<tr>
<th>Width of bands (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direction of crystal transition</td>
</tr>
<tr>
<td>Naphthalene 2200 Å system</td>
</tr>
<tr>
<td>Anthracene 2500 Å system</td>
</tr>
</tbody>
</table>

Table 12.6 Width of reflection bands in naphthalene and anthracene.

12.7 Absorption and Reflection

According to equation (12.6.1.) $\mathbf{u}^2$ is negative in the region $\omega_L < \omega < \omega_H$ so that the refractive index is complex. Therefore, the reflective power $R$ which is defined by:

$$R = \left| \frac{n-1}{n+1} \right|^2 \quad (12.7.1.)$$

will be unity everywhere in the region. This implies that the reflection should be perfect there whereas in practice this does not happen. Hall (1962) has explained
that the theory can be modified to show this if the finite lifetime $\tau/\gamma$ of the excitation is allowed for.

When this is done the equation (12.6.1.) becomes

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi\alpha}{3} + \frac{\bar{\omega}}{\omega_c - \omega - \frac{1}{2}i\gamma} \quad (12.7.2.)$$

where $n$ is now the complex refractive index $\nu + i\kappa$ with $\kappa$ the extinction coefficient. Using equation (12.7.2.), absorption and reflection curves for any given crystal transition can be obtained by plotting $\kappa^2$ and $R$ against $\omega$ and the shape of these curves is indicated in fig. 12.7.

![Fig. 12.7 Absorption and Reflection Curves.](image)

Dotted line: $\gamma = 0$  \hspace{1cm} Full line: $\gamma \neq 0$

A: Absorption curve $\kappa^2$ versus $\omega$

R: Reflection curve $R$ versus $\omega$
Also included in fig. 12.7 is the reflection curve for the case when \( \gamma = 0 \) i.e. corresponding to equation (12.6.1.). The figure shows how the introduction of \( \gamma \) reduces \( R \) to a value less than unity in the reflective region and the resulting curve is similar to the experimental curves of Anex and Simpson and Weigl (op.cit.). Even though equation (12.6.1.) is not suitable for describing reflection throughout the region \( \omega_L < \omega < \omega_H \), fig. 12.7 shows that it is quite satisfactory at the boundaries \( \omega_L \) and \( \omega_H \). Thus the introduction of \( \gamma \) will not change very significantly the results given in table 12.6.

If the absorption curve is now examined it shows that the maximum value of \( \kappa^2 \) is close to the low frequency boundary. This is a rather important result since it shows that the absorption frequency is \( \omega_L \) and not \( \omega_c \) as is usually assumed and this will change the theoretical values of the Davydov splittings and shift terms as described in chapter 11. The effect for the strong transitions of naphthalene and anthracene is shown in table 12.7 which also includes the results by Craig and his collaborators who assumed that \( \omega_c \) was the absorption frequency.
Table 12.7 Energies of the crystal components of the strong transitions in naphthalene and anthracene.

As fig. 12.7 shows the absorption frequency will not be exactly at \( \omega_L \) but will in fact be at a somewhat higher frequency. In order to make the calculations for table 12.7, therefore, a rather arbitrary value of \( \omega_C - \bar{\omega} \) has been taken as the correct transition frequency. Table 12.7 shows that the energy values differ very much depending on whether \( \omega_C \) or \( \omega_C - \bar{\omega} \) is taken as the key value. The experimental results are not sufficient to show which is correct and in fact the only experimental data concerns the position of \( \bar{\omega} \) in anthracene. Craig and Hobbins have measured this to be \(-3000 \text{ cm}^{-1}\) so that this tends to confirm \( \omega_C \) as the absorption frequency. However, this is by no means conclusive since the experimental result is not very accurate and, moreover, the calculated values of \( \omega^+ \)
and $W$ cannot be very good since there are extra terms which were ignored in equation (11.3.1.) but whose effect is to change the absolute positions of the energy levels. The splittings will not be affected by this and the table shows that a fairly accurate measurement of these splittings and especially the splitting in naphthalene would suffice to distinguish between $\omega_c - \bar{\omega}$ and $\omega_c$

The basic reason for there being two conflicting choices for the absorption frequency is due to the assumptions made about the shape of the exciton. To obtain (12.3.3.) we assumed in effect that the exciton was infinite whereas Craig et al. assume that the excitation is spherical and this means that the term $\frac{4}{3} \pi P$ should not be included in (12.3.3.). It would be quite easy to repeat the analysis of this chapter for the case of an exciton bounded by a sphere. If this were done the transition energy would turn out to be $\omega_c$ but at the same time the width of the reflection band would be considerably reduced. Thus experiments on the reflectivity of naphthalene and anthracene could also resolve the problem as to which of $\omega_c$ and $\omega_c - \bar{\omega}$ is the correct absorption frequency and, at the same time, they would give information about the size and shape of the exciton packet.
Let $S$ be a rectangular matrix of order $a \times b$ and of rank $a$, where $a < b$. The product $S^+S$ has order $b \times b$ and is Hermitian and positive definite. It can be diagonalized, therefore, by a unitary matrix whose columns are eigencolumns and these columns can be so ordered that the eigenvalues are in decreasing order. If $V$ is this matrix then

$$ (S^+S)V = VD $$

where $D$ is the diagonal matrix of eigenvalues.

From this equation, by multiplication with $S$, it follows that

$$ (SS^+)(SV) = (SV)V^+ $$

This is also an eigenvalue equation with the same eigenvalues and with the columns of $SV$ as eigencolumns of $SS^+$. Since $S$ has rank $a$, $SV$ has also rank $a$ and, therefore $a$ independent columns. Its remaining $(b-a)$ columns could repeat eigencolumns or could be zeros. But

$$ (SV)^+SV = D $$

so that all the $a$ columns are orthogonal and repetitions are excluded. The extra $(b-a)$ columns are then zeros and so have zero length. Thus from (A.3) they correspond to zero eigenvalues in $D$ and therefore to the
last \((b-a)\) columns.

The first \(\alpha\) eigencolumns may not be normalized but, when they are made normal, they will form a unitary matrix since \(S S^+\) also is Hermitian. The matrix \(S V\), therefore, must have the form

\[
S V = U^T
\]

where \(U\) is unitary and \(T\) has non-zero elements only on the diagonal. Thus the rectangular matrix \(S\) is brought into diagonal form \(T\) by the pair of unitary matrices \(U\) and \(V\) so that

\[
U^T S V = T
\]

This theorem can also be applied to an antisymmetric wave function of arbitrary form. The wave function can be expanded into the form

\[
\Psi = \sum_{rs} S_{rs} \phi_r(1) \Phi_s(2...N)
\]

where the functions \(\phi_r(1)\) are orthonormal and also the functions \(\Phi_s(2...N)\). The first-order density matrix is then

\[
\gamma(1|2) = N \sum_{rs} S_{rs} S_{rs}^* \phi_r(1) \phi_r(2)
\]

while the \((N-1)\)st order density matrix is

\[
\tau(a'|N'|2...N) = n \sum_{rs} S_{rs}^* S_{rs} \Phi_s(a'|N') \Phi_s(2...N)
\]
According to the theorem the matrix $U$ defines the natural spin orbitals $\gamma_{\tau}$ by diagonalizing $S S^\dagger$ and giving
\begin{equation}
\gamma(1\mid 2) = \sum_{\tau} d_{\tau} \gamma_{\tau}^*(1) \eta_{\tau}(2) \tag{A.9}
\end{equation}
where the occupation numbers $d_{\tau}$ are the diagonal elements of $D$. Similarly $V$ defines the natural spin function $F_{\tau}$ for which
\begin{equation}
\Gamma(2\ldots n\mid 2\ldots N) = \sum_{\tau} d_{\tau} \frac{F_{\tau}^*(2\ldots n'\mid 2\ldots N)} {F_{\tau}(2\ldots N)} \tag{A.10}
\end{equation}
The well-known equality of the occupation numbers $d_{\tau}$ follows from the theorem. The theorem also shows that the wave function itself reduces to the form
\begin{equation}
\Psi = \sum_{\tau} t_{\tau} \gamma_{\tau}(1) F_{\tau}(2\ldots N) \tag{A.11}
\end{equation}
where $t_{\tau}$ are the diagonal elements of $T$ and $t_{\tau}^2 = d_{\tau}$
These results are readily extended to a factorization into natural spin functions of order $s$ and ones of order $(n-s)$
REFERENCES

Coulson and Daudel, 1957. "Dictionary of Values of Molecular Constants (Wave Mechanical Methods)". (Published Privately).


Hochstrasser, 1961 preprint.


Wheland, 1942. J.Amer.Chem.Soc. 64, 900.