AN SCF PERTURBATION APPROACH TO MOLECULAR CRYSTALS

A SELF CONSISTENT FIELD PERTURBATION APPROACH
TO THE
ELECTRONIC PROPERTIES OF MOLECULAR CRYSTALS

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SCOPE AND CONTENTS:

Molecular orbital theory in general and the Complete Neglect of Differential Overlap approximation are reviewed. The Self Consistent Field perturbation theory for molecular crystals is discussed in some detail and used to study the binding energy and charge distribution of a number of real crystals which were chosen to represent a wide range of bonding situations. A discussion of intermolecular charge transfer and its possible effect on the vibrational spectra is given.

A method of obtaining the electronic band structure, and hence the density of electronic states, by a suitable transformation of the crystal orbitals obtained from the self consistent field perturbation method is presented. This transformation is used to study the band structure and density of electronic states of formamide, formic acid and urea and the band structure of naphthalene and ethylene. The effect of the crystal interactions on the molecular electronic levels is discussed.

A molecular orbital theory of the electronic states of molecular crystals is given and the resultant equations are compared to those of Davydov's valence bond approach. Some of the limitations of the neglect of differential overlap are discussed and the method is applied to the lowest singlet states of naphthalene and formamide crystals.

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INTRODUCTION

The single distinguishable geometrical characteristic of molecular crystals is that intramolecular bonded distances are significantly smaller than intermolecular nonbonded distances [1]. For example, in hydrocarbon crystals the carbon hydrogen bonds are about 1 Å whereas the intermolecular hydrogen contacts are at least 2.2 Å. The carbon carbon bonded distances are 1.2 to 1.5 Å while the corresponding intermolecular spacings are at least 3.3 Å. Hydrogen bonded crystals, in which an electron deficient hydrogen atom forms a weak intermolecular bond with a lone pair of electrons or a region of high electron density on an adjacent molecule [2], are an exception to the above generalization. Although the intermolecular hydrogen bonds may be as short as 1.6 Å, they are still classified as molecular in nature.

This single property has had a profound influence on the manner in which the theory of molecular crystals has been developed. In general, they are classified according to the nature of the intermolecular forces thought to be of greatest importance in the binding of their lattices. Hence, theoretical studies of these systems are usually based on a priori assumptions concerning the type of interactions to be included and as to the pairwise additivity of these interactions. Little effort has been made in assessing the relative importance of various types of intermolecular forces or pairwise additivity by treating molecular crystals with a unified approach.

The usual method of calculating the lattice energy is to take the difference in energy of molecular pairs and the isolated molecules summed over the lattice. The intermolecular interaction is most often calculated by a perturbation method [3,4] in which the wavefunction on each molecule is expanded as a summation of excited free molecule functions, Ψ^i,

$$\Psi_a = \Psi_a^0 + \sum_i a_i \Psi_a^i \, , \qquad (1.1)$$

where the summation is over all functions that involve the excitation of a single electron. Neglecting overlap of the electronic distributions between the molecules, the wavefunction for the pair is written as a simple product and the resulting energy, up to second order in the molecular potential, V_{ab}, is:

$$\langle\Psi_a^0 \; \Psi_b^0|V_{ab}|\Psi_a^0 \; \Psi_b^0\rangle + \sum_{i\neq 0} \frac{\langle\Psi_a^0 \; \Psi_b^0|V_{ab}|\Psi_a^i \; \Psi_b^0\rangle^2}{E_a^0 - E_a^i} + \sum_{j\neq 0} \frac{\langle\Psi_a^0 \; \Psi_b^0|V_{ab}|\Psi_a^0 \; \Psi_b^j\rangle^2}{E_b^0 - E_b^j}$$

$$+ \sum_{i\neq 0} \; \sum_{j\neq 0} \frac{\langle\Psi_a^0 \; \Psi_b^0|V_{ab}|\Psi_a^i \; \Psi_b^j\rangle^2}{E_a^0 + E_b^0 - E_a^i - E_b^j} \qquad (1.2)$$

The most important feature of this result is that the energy appears as four distinct terms: the first is the interaction between the ground state charge distribution of the molecules and the remaining terms are the dispersive contributions to the intermolecular energy. The last term is the one usually associated with the van der Waals interaction between molecules which have zero or small moments of charge distribution. Because of the form of the dispersive term it is the lowest excited states that contribute the most to the van der

Waals interaction. The potential V_{ab} is usually expanded about the centres of the two interacting molecules in a series of terms which are the interactions between the various moments of the static and transition charge distributions of the molecules. The integrals are then evaluated using experimental moments of the static distribution and molecular or bond polarizabilities by terminating this series at the first term that is not zero.

Buckingham[5] has suggested that "the structures of molecular crystals are normally determined by the leading multipole moments" and Nagi and Nakamura[6] have confirmed that for N_2, N_2O, CO_2 and CO the quadrupole quadrupole interaction has its minimum near the actual orientation of the molecules in the lattice. However, Mason and others [3,7,8] have shown that the major orientational effect is the short ranged repulsions between nonbonded atoms due to the overlapping of their charge distributions not included in equation (1.2) and that although the dispersive term may contribute the largest amount to the binding energy its variation with orientation within the crystal lattice is small. When all the terms of (1.2) are included, the predicted values of the lattice energy, lattice constants and molecular orientations are within a few percent of the experimental values [3,7-11]. However, the evaluation of the repulsion energy between nonbonded atoms often requires the use of an empirically determined parameter which may offset any inadequacies in treating the other terms.

A method that has been useful in the study of hydrocarbon crystals is the method of atom atom potentials [4,12-14]. In this method the entire interaction is taken between nonbonded atoms and is of the simple form

$$Ar^{-6} + B\exp(Cr)\ , \qquad (1.3)$$

with the constants fitted empirically from the equilibrium structures of crystals.

Recently, a method of calculating the intermolecular forces by treating the dimer system as one molecule and using the difference between this system and that of monomeric molecules has been used by Hasimoto and Isobe [15,16] to calculate the lattice energy of N_2, CO_2, C_2H_2, N_2O, CO, HCN and F_2 crystals with some degree of success. However, as this is a single determinantal method, it cannot include any dispersive effects[3] and its good agreement with experiment should be questioned. This type of calculation for the dimer has been most often applied to the hydrogen bond [17-23] but it has not as yet been applied to extended hydrogen bonded networks.

The spectra of molecular crystals exhibit several interesting features. The absorption bands in a molecular crystal are generally displaced from the free molecule energy and split into a number of components equal to the number of molecules in the unit cell. The spectrum of the crystal also exhibits a strong variation with the direction of polarization of the incident light, transitions forbidden in the vapour may appear, molecular vibrations change slightly and lattice vibrations appear.

In order to explain the number and polarization of the crystal excited states Davydov applied Frenkel's theory of "excitation waves" [24], excitons, to molecular crystals [25]. In doing so Davydov considered only excitons in which the electron and hole were tightly bound, that is spread over only one molecule at any particular time as they travel throughout the lattice. The main result is that the excitation energies can be written

$$\Delta W = \Delta E + D + \sum_{i} \sum_{l} {\sum_{j}}' \omega_{\lambda i}\omega_{\lambda l} M_{ij,\ell m} \quad , \qquad (1.4)$$

where ΔE is the excitation energy of the isolated molecule, D is the change in the Coulomb interaction of a molecule with the lattice upon excitation, $M_{ij,\ell m}$ is the energy corresponding to the transfer of the exciton from the molecule at site ℓ in unit cell m to the molecule at site i in cell j and the $\omega_{\lambda i}$ are coefficients that are determined by the crystal factor group. The matrix elements $M_{ij,\ell m}$ for different sites, $i \neq \ell$, determine the splitting between the components that arise from one electronic band in the vapour and the elements for which $i = \ell$ contribute to the shift of the centre of the band from the vapour spectrum. The required matrix elements are usually evaluated by expanding the interaction potential in a series of multipole-multipole terms. For strong transitions, the leading dipole-dipole term is often used. This method has been used by Davydov [25] and others [26-30] for the study of strong transitions in various aromatic hydrocarbons.

For weak transitions the transition dipole moments become small and if the intermolecular interaction is represented by the dipole-dipole term alone the splittings are too small and the polarizations different from the experimental values. Craig [31-32] has suggested that a crystal induced mixing of the upper state of one transition with the upper state of another, called second order mixing, takes place and as a result the intensity of the weak transition is increased and the polarization ratio changed. Craig also showed that the inclusion of higher multipoles in the evaluation of the integrals can account for the larger observed splittings. Jortner, Rice and Silbey [30,33-35] have shown that the inclusion of charge transfer states increases the splitting but does not affect the polarization ratio significantly. Both the theoretical and experimental aspects of the spectra of the crystals have extensive literatures that have been reviewed by several authors [36].

Although many of these methods satisfactorily predict some properties of molecular crystals, for instance structure and lattice dynamics or the spectrum of the excited states, there is no one single theory which makes predictions of lattice energy and crystal spectrum. A theory of the electronic properties of molecular crystals should predict the relative importance of the various forces responsible for the binding of the lattice as well as the charge distributions and electronic spectra. The overall objective here is to investigate the development of a theory of the electronic properties of molecular crystals which makes no a priori assumptions concerning the type of interactions to be included or of pairwise additivity which can be used to study many aspects of this type of system.

In order to accomplish this end a perturbation theory for the total crystal energy and molecular charge distributions for crystals of strongly interacting molecules is presented in chapter one. In order to assess its applicability to different crystal types it is applied to a series of crystals in chapter two; in chapter three a method of obtaining the crystal orbitals and hence the band structure and density of electronic states is presented and in chapter four a theory of the excited states of strongly interacting crystal molecules is given.

CHAPTER 1

Basic Theory

§ 1.1 Molecular Orbital Theory

The foundation of the molecular orbital method[37] is the approximation of a many-electron wavefunction for a system of several electrons by a product of single-electron functions called molecular orbitals. The electronic description of the ground state of an n electron system is obtained by the occupation of the n molecular orbitals of lowest energy according to the aufbau principle.

As for all quantum mechanical calculations for stationary states, the starting point is the time independent Schroedinger equation,

$$H\Psi = E\Psi \; , \qquad (1.1)$$

where H is the quantum mechanical Hamiltonian operator for the system and Ψ is its wavefunction in the stationary state with total energy E. Neglecting relativistic and magnetic effects, the Hamiltonian for a system of nuclei (labelled by A and B) and electrons (labelled by i and j) can be written

$$H = -\sum_A \frac{\hbar^2 \nabla_A^2}{2M_A} - \sum_i \frac{\hbar^2 \nabla_i^2}{2m_e} - \sum_A \sum_i \frac{e^2 Z_A}{r_{Ai}} + \sum_{A<B}\sum \frac{e^2 Z_A Z_B}{R_{AB}} + \sum_{i<j}\sum \frac{e^2}{r_{ij}} \qquad (1.2)$$

or

$$H = T_N + T_E + V_{EN} + V_{NN} + V_{EE} \tag{1.3}$$

where

$T_N = -\sum_A \frac{\hbar^2 \nabla_A^2}{2M_A}$ is the total kinetic energy of the nuclei each of mass M_A, (1.4)

$T_E = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m_e}$ is the total kinetic energy of the electrons, (1.5)

$V_{EN} = -\sum_A \sum_i \frac{e^2 Z_A}{r_{Ai}}$ is the interaction energy of the electrons and nuclei each of charge eZ_A, (1.6)

$V_{NN} = \sum\sum_{A<B} \frac{e^2 Z_A Z_B}{R_{AB}}$ is the electrostatic repulsion energy among the nuclei, (1.7)

and

$V_{EE} = \sum\sum_{i<j} \frac{e^2}{r_{ij}}$ is the electrostatic repulsion energy among the electrons. (1.8)

In terms of atomic units, where

$$\frac{e^2}{a_o} = 1 \ , \quad a_o = 1 \ , \quad m_e = 1 \ , \quad \text{and} \quad \hbar = 1 \ , \tag{1.9}$$

the Hamiltonian becomes

$$H = -\sum_A \frac{\nabla_A^2}{2M_A} - \sum_i \frac{\nabla_i^2}{2} - \sum_A \sum_i \frac{Z_A}{r_{Ai}} + \sum\sum_{A<B} \frac{Z_A Z_B}{R_{AB}} + \sum\sum_{i<j} \frac{1}{r_{ij}} \ . \tag{1.10}$$

Since the motions of all the electrons and nuclei are coupled through the interaction terms of (1.10), the Schroedinger equation is exactly soluble only for two particles. However, the Born-Oppenheimer [38] approximation allows for the approximate separation of the electronic and nuclear motions. When the nuclei are in fixed positions ($T_N = 0$ and V_{NN} = a constant), it is assumed that there is a set of electronic functions, Φ_e, that satisfy an approximate electronic Schroedinger equation

$$H_e\Phi_e = E_e\Phi_e \qquad (1.11)$$

where

$$H_e = T_E + V_{EN} + V_{EE} \qquad (1.12)$$

and E_e is the total electronic energy of the system. If Φ_e varies slowly as a function of the nuclear coordinates, then the electronic energy just provides part of the potential for the nuclei and the equation for the nuclear motion is:

$$(T_N + V_{NN} + E_e)\Phi_n = E\Phi_n \ . \qquad (1.13)$$

Here, E is the total energy of the system and Φ_n is a set of nuclear wavefunctions. Neglecting small cross terms, the total wavefunction under the Born-Oppenheimer approximation is the product function

$$\Psi = \Phi_e\Phi_n \qquad (1.14)$$

and the motions of the electrons and nuclei are effectively separated. As a result of this separation the electronic problem can be solved for fixed nuclei and then the nuclear energy added to obtain the total energy.

It is the solution of (1.11), the Schroedinger equation for the electrons moving in the potential of the fixed nuclei of a molecule, which is usually of central concern to chemists. But, because the motions of the electrons are correlated, accurate solutions have only been obtained for systems of up to four electrons [39]. However, the variational method [40] allows the approximation of the ground state energy and the molecular orbitals for the system without solving the Schroedinger equation. It can be shown that the expectation value of an approximate wavefunction, Ψ_t, with the Hamiltonian, H, provides an upper bound on the exact ground state energy, E_0. That is,

$$\frac{\int \Psi_t^* H \Psi_t d\tau}{\int \Psi_t^* \Psi_t d\tau} = E_t \geq E_0 \ . \qquad (1.15)$$

This provides a simple means to approximate the exact Φ_e by the adoption of a trial function which depends on some set of parameters; the best such function is the one which minimizes the energy E_t with respect to variations in those parameters.

The trial function may be taken as the simple product of one-electron functions known as the Hartree product [41]. However, since electrons have a spin of ½, they obey Fermi-Dirac statistics and their wavefunctions must be antisymmetric with respect to the interchange of electrons [37]. Therefore, to properly account for electron spin, linear combinations of Hartree products must be taken. A convenient way of expressing these combinations is the Slater determinant [42]. For a 2n electron system this determinantal trial function is expressed as

$$\Psi_t = \{(2n)!\}^{-\frac{1}{2}} |\phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) \cdot \cdot \cdot \phi_n(2n-1)\bar{\phi}_n(2n)| \qquad (1.16)$$

For the closed shell ground state, the electrons are assigned in pairs to molecular orbitals, ϕ_i, which are one-electron functions of the spatial coordinates of the assigned electron, the two possible spin states of the electron, α and β, being denoted by an unbarred ϕ and a barred ϕ respectively. This determinantal form of wavefunction is one which is properly antisymmetric with respect to interchange of electrons. Thus, it accounts for the Pauli principle [43] which arises from Fermi electron correlation.

Lennard-Jones [44] has shown that under an orthogonal transformation of the molecular orbitals the wavefunction Ψ_t remains essentially unchanged (to within a multiplicative constant). This makes it possible to transform the molecular orbitals to an orthonormal set without any loss of generality. Hence, for the sake of simplicity, it may be assumed that the molecular orbitals form such a set.

Using (1.16), the expectation value of the Hamiltonian (1.12), under the assumption that the molecular orbitals are orthonormal, is

$$\bar{E}_e = \sum_{i=1}^{n} \{2H_{ii} + \sum_{j=1}^{n} (2J_{ij} - K_{ij})\} \qquad (1.17)$$

where

$$H_{ii} = \langle\phi_i(1)|-\tfrac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}}|\phi_i(1)\rangle \ , \qquad (1.18)$$

$$J_{ij} = \langle\phi_i(1)\phi_j(2)|\frac{1}{r_{12}}|\phi_j(2)\phi_i(1)\rangle, \qquad (1.19)$$

$$K_{ij} = \langle\phi_i(1)\phi_j(2)|\frac{1}{r_{12}}|\phi_j(1)\phi_i(2)\rangle, \qquad (1.20)$$

and the labels i and j refer to the molecular orbitals. The one-electron integral H_{ii} represents the energy of an electron in molecular orbital ϕ_i in the field of the bare nuclei. J_{ij} is the Coulomb integral and is the electrostatic interaction between the charge distributions $\phi_i^*(1)\phi_i(1)$ and $\phi_j^*(2)\phi_j(2)$. K_{ij} is the exchange integral which represents the reduction in energy due to the Fermi correlation between electrons in orbitals ϕ_i and ϕ_j. Under the Born-Oppenheimer approximation, the total energy is now given by

$$E = \bar{E}_e + \sum_{A<B}\sum \frac{Z_A Z_B}{R_{AB}} \qquad (1.21)$$

The Hartree-Fock orbitals[45] are the best possible ϕ_i determined by the variational theorem subject to the orthonormality constraints

$$\langle\phi_i|\phi_j\rangle = \delta_{ij} \qquad (1.22)$$

Using the method of Lagrangian undetermined multipliers [40], the Hartree-Fock orbitals are found by applying variations in the ϕ_i to the functional

$$E' = \bar{E}_e - \tfrac{1}{2} \sum_{i<j}^{n} \sum^{n} \varepsilon_{ij} (\langle\phi_i|\phi_j\rangle + \langle\phi_j|\phi_i\rangle) \tag{1.23}$$

and setting the result equal to zero. The ε_{ij} are the undetermined multipliers. The resulting conditions for $\delta E' = 0$ determine the molecular orbitals and are given by

$$\{H_c + \sum_j^n (2J_j - K_j)\}|\phi_i\rangle = \sum_j^n |\phi_j\rangle\varepsilon_{ji} \tag{1.24}$$

and

$$\langle\phi_i|\{H_c^* + \sum_j^n (2J_j^* - K_j^*)\} = \sum_j^n \langle\phi_j|\varepsilon_{ij} \; . \tag{1.25}$$

The operators H_c, J_j and K_j are defined as

$$H_c|\phi_i(1)\rangle = \{-\tfrac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{1A}}\}|\phi_i(1)\rangle \; , \tag{1.26}$$

$$J_j|\phi_i(1)\rangle = \langle\phi_j(2)|\frac{1}{r_{12}}|\phi_j(2)\rangle|\phi_i(1)\rangle \tag{1.27}$$

and

$$K_j|\phi_i(1)\rangle = \langle\phi_j(2)|\frac{1}{r_{12}}|\phi_i(2)\rangle|\phi_j(1)\rangle \tag{1.28}$$

Since, for the closed shell ground state, the ε_{ij} form a hermitian matrix [45], the two conditions for $\delta E' = 0$ are equivalent (each others complex conjugate), and there is a unitary transformation such that the right hand sides of (1.24) and (1.25) are diagonal. The canonical

Hartree-Fock equations are then

$$(H_c + \sum_{j}^{n} (2J_j - K_j))|\phi_i(1)\rangle = \epsilon_{ii}|\phi_i(1)\rangle \tag{1.29}$$

or

$$F|\phi_i(1)\rangle = \epsilon_{ii}|\phi_i(1)\rangle \tag{1.30}$$

where F is the Fock operator defined by the above. The ϵ_{ii} (often written as ϵ_i) are the orbital energies and are minus the vertical ionization energies of the electrons in orbitals ϕ_i[46]. The total energy is not just the sum of the orbital energies but is modified by the Coulomb and exchange interactions as shown in (1.31).

$$\bar{E}_e = \sum_{i=1}^{n} \{2\epsilon_{ii} - \sum_{j=1}^{n} (2J_{ij} - K_{ij})\}. \tag{1.31}$$

The molecular orbitals, in principle, can be determined by solving equation (1.30). However, except for the simplest molecules, this is computationally out of the question and approximations to the Hartree-Fock molecular orbitals must be used. Commonly, the molecular orbitals are expanded in some set of basis functions and the variational theorem applied to the expansion coefficients. In the LCAO (Linear Combination of Atomic Orbitals) method, the basis functions are a set of m atomic orbitals, χ_ν, on the atoms of the molecule and

$$\phi_i = \sum_{\nu=1}^{m} c_{\nu i}\chi_\nu \tag{1.32}$$

where the $C_{\nu i}$ are the expansion coefficients. This method has an added advantage as for many molecular problems it is convenient to relate the molecular orbitals to the atomic orbitals on the atoms of the molecule. The conditions for a minimum in E' ($\delta E' = 0$) become a set of equations for the expansion coefficients known as the Roothaan equations [45].

$$\sum_{\nu=1}^{m} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) C_{\nu i} = 0 \qquad \mu = 1,2, \cdots, m \tag{1.33}$$

or in matrix notation

$$\underline{F}\underline{C} = \underline{S}\underline{C}\underline{E} \tag{1.34}$$

In (1.33) $S_{\mu\nu}$ is the overlap integral between atomic orbitals χ_μ and χ_ν and

$$F_{\mu\nu} = \langle\chi_\mu|H_c|\chi_\nu\rangle + \sum_{j=1}^{n}\sum_{\lambda=1}^{m}\sum_{\sigma=1}^{m} C^*_{\lambda j} C_{\sigma j} \{2\langle\chi_\mu(1)\chi_\lambda(2)|\frac{1}{r_{12}}|\chi_\sigma(2)\chi_\nu(1)\rangle - \langle\chi_\mu(1)\chi_\lambda(2)|\frac{1}{r_{12}}|\chi_\nu(2)\chi_\sigma(1)\rangle\} \tag{1.35}$$

or

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{j=1}^{n}\sum_{\lambda=1}^{m}\sum_{\sigma=1}^{m} C^*_{\lambda j} C_{\sigma j} \{2J_{\mu\nu\lambda\sigma} - K_{\mu\nu\lambda\sigma}\}. \tag{1.36}$$

Where the core Hamiltonian, Coulomb and exchange integrals in the atomic basis, $H_{\mu\nu}$, $J_{\mu\nu\lambda\sigma}$ and $K_{\mu\nu\lambda\sigma}$, respectively are defined by the above. Under the LCAO approximation, the electronic energy can be written

$$\bar{E}_e = \tfrac{1}{2} \sum_{\mu=1}^{m} \sum_{\nu=1}^{m} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) \ , \qquad (1.37)$$

where

$$P_{\mu\nu} = 2 \sum_{j=1}^{n} C^*_{\mu j} C_{\nu j} \qquad (1.38)$$

is the population matrix and the sum in (1.38) is over the n doubly occupied molecular orbitals.

The Roothaan equations (1.33) are algebraic and hence less difficult to solve than the differential Hartree-Fock equations (1.29). Even so, they have to be solved iteratively since the elements of the Fock matrix, the $F_{\mu\nu}$, required to construct the equations depend on the solutions of the equations themselves, the $C_{\mu i}$. The usual method of solving equations (1.33) is as follows: Assuming a set of expansion coefficients the approximate Fock and overlap matrices are calculated. Equations (1.33) are then solved by diagonalizing the Fock matrix and the resulting coefficients are compared with the assumed set. If their difference is less than a given amount the self consistent solution has been found, if not, the new coefficients are used to construct a new Fock matrix and the diagonalization is repeated. Because of the self consistent field procedure used to solve the Roothaan equations, the molecular orbitals obtained by this method are known as the LCAOSCF (Linear Combination of Atomic Orbitals Self Consistent Field) molecular orbitals.

§ 1.2 The CNDO Approximate Method [47-51]

The theory presented to this point involves the evaluation of a number of integrals and an algebraic self-consistent procedure to determine the molecular orbitals. Unfortunately, this method is not readily adaptable to molecules of large size because of the numerous Coulomb and exchange integrals that must be evaluated. In this section an approximate method that avoids much of this computational effort for large systems is presented.

The CNDO (Complete Neglect of Differential Overlap) theory of Pople, Santry and Segal [47] is based on the LCAOSCF procedure and retains the essential features of electron repulsion but avoids the calculation of many of the integrals and approximates others using experimental data. The large saving in computation arises from the neglect of integrals that involve the overlap distribution $\chi_\mu(1)\chi_\nu(1)$, with $\mu \neq \nu$, in the integrals

$$J_{\mu\nu\lambda\sigma} = \langle\chi_\mu(1)\chi_\lambda(2)|\frac{1}{r_{12}}|\chi_\sigma(2)\chi_\nu(1)\rangle \tag{1.39}$$

$$= (\mu\nu|\lambda\sigma)$$

and

$$K_{\mu\nu\lambda\sigma} = \langle\chi_\mu(1)\chi_\lambda(2)|\frac{1}{r_{12}}|\chi_\nu(2)\chi_\sigma(1)\rangle \tag{1.40}$$

$$(\mu\sigma|\lambda\nu)$$

The round bracket notation illustrates this overlap more clearly than the Dirac notation used previously. A further reduction in computation is achieved by treating only the valence electrons explicitly, the inner shells acting to modify the nuclear potential, Z_A, in the Hamiltonian. In order to take advantage of the neglect of differential overlap and the inner shell electrons, Pople, Santry and Segal [47] make the following assumptions.

Approximation 1:

The χ_ν are treated as if they form an orthonormal set. That is, the overlap integrals, $S_{\mu\nu}$, in equation (1.33) satisfy

$$S_{\mu\nu} = \delta_{\mu\nu} \ . \tag{1.41}$$

For orbitals on the same atom $S_{\mu\nu}$ is already zero. For orbitals on different atoms (1.41) is not quantitatively accurate but simplifies the subsequent analysis considerably. The coefficients in equation (1.32) then form an orthogonal matrix and the orthogonality condition on the ϕ_i becomes

$$\sum_\mu C_{\mu i} C_{\mu j} = \delta_{ij} \ . \tag{1.42}$$

Under this approximation, the diagonal elements of the bond order matrix, $P_{\mu\mu}$, are the electron populations of the atomic orbitals and

$$\sum_\mu P_{\mu\mu} = 2n \ . \tag{1.43}$$

Approximation 2:

All two electron integrals that depend on the overlapping of charge distributions of different basis orbitals are neglected. That is,

$$(\mu\nu|\lambda\sigma) = (\mu\mu|\lambda\lambda)\delta_{\mu\nu}\delta_{\lambda\sigma} \tag{1.44}$$

$$= \gamma_{\mu\lambda}\delta_{\mu\nu}\delta_{\lambda\sigma}$$

This approximation can be partially justified by approximation 1, as $S_{\mu\nu}$ is the magnitude of the overlap distribution $\chi_\mu(1)\chi_\nu(1)$ and has already been neglected.

With approximations 1 and 2 the theory is not invariant under transformations that mix any atomic basis orbitals on the same atom or the rotation of local axes. In order to restore this invariance approximation 3 is made.

Approximation 3:

The electronic interaction integrals, $\gamma_{\mu\nu}$, are assumed to depend only on the atoms to which χ_μ and χ_ν belong and not on the actual type of orbital. The $\gamma_{\mu\nu}$ reduce to a set of electron-interaction integrals, γ_{AB}, that measure the average repulsion between a valence electron on atom A and one on atom B.

Under approximations 1 and 2 the matrix elements $F_{\mu\nu}$ are

$$F_{\mu\mu} = H_{\mu\mu} + \tfrac{1}{2}P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\sigma\neq\mu} P_{\sigma\sigma}\gamma_{\mu\sigma} \tag{1.45}$$

$$F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} . \tag{1.46}$$

After approximation 3, they are

$$F_{\mu\mu} = H_{\mu\mu} - \tfrac{1}{2}P_{\mu\mu}\gamma_{AA} + \sum_{B} P_{BB}\gamma_{AB} \tag{1.47}$$

$$F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{AB} \qquad (\chi_\mu \text{ on A, } \chi_\nu \text{ on B}) \tag{1.48}$$

Where P_{BB} is the valence electron density on atom B,

$$P_{BB} = \sum_{\nu}^{B} P_{\nu\nu} \tag{1.49}$$

and the summation is over all atomic orbitals on atom B.

The matrix elements $H_{\mu\nu}$ of the core Hamiltonian H_c, defined by equation (1.26), are next developed. The diagonal elements, $H_{\mu\mu}$, can be written as one and two centre terms

$$\begin{aligned} H_{\mu\mu} &= (\mu|-\tfrac{1}{2}\nabla_1^2 - V_A|\mu) - \sum_{B\neq A}(\mu|V_B|\mu) \\ &= U_{\mu\mu} - \sum_{B\neq A}(\mu|V_B|\mu) \qquad (\mu \text{ on atom A}) \end{aligned} \tag{1.50}$$

where $$V_A = \frac{Z_A}{r_{1A}} \tag{1.51}$$

and Z_A is the core charge of atom A (the nuclear charge plus the charge of the core electrons). The $U_{\mu\mu}$ are essentially atomic parameters and are chosen from experimental data. Discussion of the numerical values will be left to later. Similarly, the off diagonal elements can be written

$$H_{\mu\nu} = U_{\mu\nu} - \sum_{B\neq A}(\mu|V_B|\nu) \qquad (\mu \text{ and } \nu \text{ on atom A}) \tag{1.52}$$

where $U_{\mu\nu}$ is a one electron matrix element that is zero by symmetry if χ_μ and χ_ν are s, p or d type functions. The remaining terms are the interaction of $\chi_\mu\chi_\nu$ with the cores of other atoms. Since differential overlap is neglected, it is necessary to make approximation 4.

Approximation 4:

Integrals of the type $(\mu|V_B|\nu)$ where μ and ν belong to atom A satisfy

$$(\mu|V_B|\nu) = \delta_{\mu\nu}V_{AB} \tag{1.53}$$

and V_{AB} is the same for all valence orbitals.

Then,

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B\neq A} V_{AB} \qquad (\mu \text{ on atom A}) \tag{1.54}$$

and

$$H_{\mu\nu} = 0 \qquad (\mu \neq \nu \text{ but both on the same atom}). \tag{1.55}$$

The remaining matrix elements $H_{\mu\nu}$ where μ and ν are on different atoms are taken to depend only on the local environment between the atoms and not on any interactions with distant cores.

Approximation 5:

The off-diagonal core matrix elements between atomic orbitals on different atoms are written

$$H_{\mu\nu} = \beta_{\mu\nu} = \beta^{o}_{AB}S_{\mu\nu} \tag{1.56}$$

where $S_{\mu\nu}$ is the overlap integral and β^{o}_{AB} is a parameter that depends only on atoms A and B. The method of choosing the β^{o}_{AB}'s is given in the next section. The $F_{\mu\nu}$ matrix elements then become

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \tfrac{1}{2}P_{\mu\mu})\gamma_{AA} + \sum_{B\neq A}(P_{BB}\gamma_{AB} - V_{AB}) \tag{1.57}$$

$$F_{\mu\nu} = \beta^{o}_{AB}\, S_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{AB} \tag{1.58}$$

Equation (1.58) applies even when μ and ν are on the same atom, when $S_{\mu\nu} = 0$ and $\gamma_{AB} = \gamma_{AA}$.

Under these approximations the total energy can be written as a sum of one and two atom terms

$$E = \sum_{A} E_A + \sum_{A<B}\sum E_{AB} \tag{1.59}$$

where

$$E_A = \sum_{\mu}^{A} P_{\mu\mu}U_{\mu\mu} + \tfrac{1}{2}\sum_{\mu}^{A}\sum_{\nu}^{A} (P_{\mu\mu}P_{\nu\nu} - \tfrac{1}{2}P^2_{\mu\nu})\gamma_{AA} \tag{1.60}$$

and

$$E_{AB} = \sum_{\mu}^{A}\sum_{\nu}^{B} (2P_{\mu\nu}\beta_{\mu\nu} - \tfrac{1}{2}P^2_{\mu\nu}\gamma_{AB}) + (Z_A Z_B R^{-1} - P_{AA}V_{AB} - P_{BB}V_{BA} + P_{AA}P_{BB}\gamma_{AB}) \tag{1.61}$$

For large interatomic separations, the integrals V_{AB}, V_{BA} and γ_{AB} all approach R^{-1} so that the last group of terms in (1.61) becomes $Q_A Q_B R^{-1}_{AB}$, where Q_A is the net charge on atom A. This illustrates that the theory takes proper account of the interaction of charged atoms in a molecule.

The CNDO/2 Parameterization [49]

In order to specify a CNDO calculation, values for the overlap integrals, $S_{\mu\nu}$, the core Hamiltonian elements, $U_{\mu\mu}$ and V_{AB}, the electron repulsion integrals, γ_{AB}, and the bonding parameters, β^{o}_{AB}, are required.

The overlap integrals are calculated explicitly using formulae given by Mulliken, Rieke, Orloff and Orloff [52] for Slater atomic orbitals. The electron repulsion integrals are calculated from the two centre Coulomb integrals for s type functions given by Roothaan [53]. The parameter V_{AB}, which represents the interaction of a valence electron on atom A with the core of B, is taken as

$$V_{AB} = Z_A\gamma_{AB} \tag{1.62}$$

The significance of this choice can be seen if (1.57) is rewritten as

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \tfrac{1}{2}P_{\mu\mu})\gamma_{AA} + \sum_{B\neq A}(-Q_B\gamma_{AB} + (Z_B\gamma_{AB} - V_{AB})), \tag{1.63}$$

where Q_B is the net charge on atom B,

$$Q_B = Z_B - P_{BB} \tag{1.64}$$

The choice of V_{AB} makes the penetration integral [54], $(Z_B\gamma_{AB} - V_{AB})$, zero. This neglect of penetration partially offsets the effects of the neglect of differential overlap [49].

The one electron local core matrix elements, $U_{\mu\mu}$, are computed from observed atomic spectra. Under the CNDO approximation the electronic energy for a configuration $2s^m 2p^n$ for an atom or ion A is given by

$$E(A, 2s^m 2p^n) = m\, U_{2s2s} + n\, U_{2p2p} + \tfrac{1}{2}(m + n)(m + n - 1)\gamma_{AA} \qquad (1.65)$$

Since several states arise from each of these configurations, the energy is taken as an appropriately weighted average of the experimental energies. The core integrals can be estimated from ionization potentials and electron affinities, calculated from the energies of the average states, by using the relations,

$$-\tfrac{1}{2}(I_{2s} + A_{2s}) = U_{2s2s} + (Z_A - \tfrac{1}{2})\gamma_{AA} \qquad (1.66)$$

$$-\tfrac{1}{2}(I_{2p} + A_{2p}) = U_{2s2s} + (Z_A - \tfrac{1}{2})\gamma_{AA} \qquad (1.67)$$

The ionization potentials, I, can be calculated using spectral data. However, sufficient data for the accurate determination of the electron affinities, A, for most elements is not available so that Pople and Segal [48] based their evaluation on the affinity of lithium for an s electron and carbon and fluorine for a p electron. Using these electron affinities obtained by Edlen [55] and spectroscopic data of Moore [56], the values of $(I_{2s} + A_{2s})$ and $(I_{2p} + A_{2p})$ were calculated for lithium, carbon and flourine and were obtained by quadratic interpolation for the rest of the first row elements. For hydrogen, the observed value of 13.605 eV was used for I and the calculated value of .747 eV for the electron affinity. Tables of these values are given in reference[51].

In order to reduce the amount of empirical parameterization the remaining parameters, the β^o_{AB}, are taken to be of the form

$$\beta^o_{AB} = \tfrac{1}{2}(\beta^o_A + \beta^o_B) \tag{1.68}$$

with the β^o_A depending only on the nature of atom A, so that only a single parameter is chosen for each element. The values were selected to give the best overall fit of molecular orbitals and orbital energies with more detailed LCAOSCF calculations on diatomic molecules using a minimal basis set. The values of β^o_A obtained from the analysis are also given in reference [51].

The CNDO method is known to reproduce the geometries of molecules reasonably well. The bond lengths are usually calculated to within ten percent and the angles to within a few degrees [51]. The orbital energy differences for the occupied orbitals agree well with those from more detailed calculations, however, although the ordering of the unoccupied virtual orbitals is usually correct, their spacing, in general, is too large making the values of the excitation energies calculated too large [57]. Fortunately, the charge distributions produced by the CNDO method are in reasonable agreement with more detailed calculations [58-59].

§1.3 The SCF Perturbation Theory for Molecular Crystals [60-65]†

The SCF perturbation theory for molecular crystals was first proposed by Bacon and Santry [60,61] for the case in which the molecules in the unit cell are symmetry related. Later, Crowe and Santry [62,63] extended the theory to crystals in which the unit cell molecules are not necessarily related. The non-empirical version of the theory has recently been given by O'Shea and Santry [64].

In order to develop the perturbation equations, the SCF matrix equation for the crystal under the neglect of overlap is written

$$\underset{\sim}{F}\underset{\sim}{C} = \underset{\sim}{C}\underset{\sim}{E} . \tag{1.69}$$

Where the matrices $\underset{\sim}{F}$ and $\underset{\sim}{C}$ are now referred to a basis set of atomic orbitals centered on all the atoms on all the molecules of the crystal. In order to aid in the explanation and facilitate the solution of the matrix equation, the basis set is assumed to be ordered so that all of the atomic orbitals associated with a given molecule are collected together as a group.

In their treatment, Bacon and Santry consider all the interactions between all the molecules in a crystal as a single perturbation through the solution of the SCF perturbation equations. These equations are derived by expanding the matrices $\underset{\sim}{F}$, $\underset{\sim}{C}$ and $\underset{\sim}{E}$ in the various orders of the perturbation as follows:

$$\underset{\sim}{F} = \underset{\sim}{F}^{(0)} + \lambda\underset{\sim}{F}^{(1)} + \lambda^2\underset{\sim}{F}^{(2)} + \lambda^3\underset{\sim}{F}^{(3)} \cdot \cdot \cdot , \tag{1.70}$$

---

†The correspondence between this work and that of McWeeny for the density matrix is given in appendix 3.

$$\underset{\sim}{C} = \underset{\sim}{C}^{(0)} + \lambda\underset{\sim}{C}^{(1)} + \lambda^2\underset{\sim}{C}^{(2)} + \lambda^3\underset{\sim}{C}^{(3)} \cdots, \qquad (1.71)$$

$$\underset{\sim}{E} = \underset{\sim}{E}^{(0)} + \lambda\underset{\sim}{E}^{(1)} + \lambda^2\underset{\sim}{E}^{(2)} + \lambda^3\underset{\sim}{E}^{(3)} \cdots, \qquad (1.72)$$

Substituting these expansions in the matrix equation (1.69) and equating the coefficients of like powers in λ yields the perturbation equations which can be summarised as

$$\sum_{m=0}^{n} \underset{\sim}{F}^{(m)}\underset{\sim}{C}^{(n-m)} = \sum_{m=0}^{n} \underset{\sim}{C}^{(n-m)}\underset{\sim}{E}^{(m)} \qquad (1.73)$$

for the $n^{\underline{th}}$ order perturbation.

Because of the molecular character of the crystals under consideration, the zero order solution of (1.69) is chosen as the molecular orbitals of a hypothetically non-interacting lattice, i.e. an oriented gas. These orbitals satisfy the zero order equation

$$\underset{\sim}{F}^{(0)}\underset{\sim}{C}^{(0)} = \underset{\sim}{C}^{(0)}\underset{\sim}{E}^{(0)}, \qquad (1.74)$$

where $\underset{\sim}{F}^{(0)}$ and $\underset{\sim}{C}^{(0)}$ are assumed to be block diagonal because of the basis set ordering. The diagonal blocks are the Fock and molecular orbital matrices for the isolated molecules. With the above choice, since the crystal is made up of identical molecules, the zero order solutions are highly degenerate and reducible under the crystal space group symmetry. Since the inclusion of any intermolecular interaction requires that the crystal orbitals transform irreducibly under the crystal space group, a zero order transformation of the $\underset{\sim}{C}^{(0)}$'s should be undertaken. Fortunately, this transformation is unitary and therefore does not affect the bond order matrix or the crystal binding energy [44] and may be neglected in the calculation of these quantities. Hence; equation (1.69) is solved directly for the bond order matrix in preference to the orbital coefficient matrix $\underline{C}$. With the neglect of this transformation the orbital energy matrix cannot be calculated directly; however, it will be shown in chapter 3 that the transformation can be applied, after the completion of the perturbation calculation, to calculate the elements of $\underline{E}$.

The orthonormality of the $\underline{C}$'s,

$$\tilde{\underline{C}}\underline{C} = 1, \qquad (1.75)$$

is used as a constraint in solving the perturbation equations and since the zero order solutions are already normalized,

$$\sum_{m=0}^{n} (\tilde{\underline{C}}^{(m)}\underline{C}^{(n-m)} + \tilde{\underline{C}}^{(n-m)}\underline{C}^{(m)}) = 0, \quad \text{for all } n > 0. \qquad (1.76)$$

The $n^{\underline{th}}$ order change in the bond order matrix is obtained by expanding $\underline{P}$ in the same manner in which $\underline{F}$, $\underline{C}$ and $\underline{E}$ were expanded, substituting (1.71) into the expression for the bond order (1.38) and equating the coefficients of like powers in λ. The net result is

$$P^{(n)}_{\mu\nu} = 2 \sum_{i}^{occ} \sum_{m=0}^{n} C^{(m)}_{\mu i} C^{(n-m)}_{\nu i} , \qquad n > 0, \qquad (1.77)$$

where μ and ν label atomic orbitals and the summation over i includes all occupied molecular orbitals.

The first order equation is solved by expanding the perturbed molecular orbitals in terms of the zero order orbitals, $\underline{C}^{(0)}$. That is,

$$\underline{C}^{(1)} = \underline{C}^{(0)}\underline{A} \qquad (1.78)$$

where $\underline{A}$ is a matrix of mixing coefficients. Substituting (1.78) into the orthonormality constraint (1.76) for the first order gives

$$A_{ij} = -A_{ji} \qquad (1.79)$$

and, therefore,

$$A_{ii} = 0. \qquad (1.80)$$

Substituting into the perturbation equation (1.73) shows

$$A_{ij} = \underline{C}_i^{(0)}\underline{F}^{(1)}\underline{C}_j^{(0)}/(\varepsilon_j^{(0)} - \varepsilon_i^{(0)}) = F_{ij}^{(1)}/(\varepsilon_j^{(0)} - \varepsilon_i^{(0)}), \qquad (1.81)$$

where $\underline{C}_i^{(0)}$ is the zero order molecular orbital and $\varepsilon_i^{(0)}$ is the corresonding orbital energy. Explicitly,

$$F_{ij}^{(1)} = \sum_{\mu}\sum_{\nu} C_{\mu i}^{(0)}F_{\mu\nu}^{(1)}C_{\nu j}^{(0)}. \qquad (1.82)$$

The corresponding first order change in the bond order matrix is given by

$$P_{\mu\nu}^{(1)} = 2\sum_{i}^{occ}\sum_{\ell}^{all}(C_{\mu i}^{(0)}C_{\nu\ell}^{(0)} + C_{\mu\ell}^{(0)}C_{\nu i}^{(0)})A_{\ell i}. \qquad (1.83)$$

As the crystal molecules are identical, the zero order solutions are degenerate and the denominators of the $A_{\ell i}$ in equation (1.83) will be zero for many of the terms in the occ-occ part of the sums over i and ℓ. Hence, the expression for $\underline{P}^{(1)}$ appears singular but it can be reduced to a nonsingular form. Using the skew symmetry of $\underline{A}$, equation (1.83) can be reduced to [†]

$$P_{\mu\nu}^{(1)} = 2\sum_{i}^{occ}\sum_{\ell}^{vac}(C_{\mu i}^{(0)}C_{\nu\ell}^{(0)} + C_{\mu\ell}^{(0)}C_{\nu i}^{(0)})A_{\ell i}, \tag{1.84}$$

which is non-singular. This reduction also reduces the computation required to calculate the bond order which must be done iteratively as $\underline{F}^{(1)}$ depends on $\underline{A}$ through $\underline{P}^{(1)}$.

Proceeding in a manner similar to that for the first order solution, $\underline{C}^{(2)}$ is expanded in terms of the zero order molecular orbitals,

$$\underline{C}^{(2)} = \underline{C}^{(0)}(\underline{B} + \underline{b}) \tag{1.85}$$

The matrix $\underline{B}$ is skew symmetric and analogous to the first order matrix $\underline{A}$. Substitution into equation (1.73) yields

$$B_{ij} = -B_{ji}, \tag{1.86}$$

$$B_{ii} = 0, \tag{1.87}$$

and

$$B_{ij} = \underline{C}_i^{(0)}\underline{F}^{(2)}\underline{C}_j^{(0)}/(\varepsilon_j^{(0)} - \varepsilon_i^{(0)}) = F_{ij}^{(2)}/(\varepsilon_j^{(0)} - \varepsilon_i^{(0)}). \tag{1.88}$$

[†] This reduction can be avoided. See appendix 3.

The second component $\underline{b}$ has no counterpart in the first order theory and is neither symmetric nor skew symmetric. It is a second order quantity that arises from the summation of pairs of first order quantities. Equation (1.76) gives

$$b_{ij} + b_{ji} = -\sum_{\ell}^{\text{all}} A_{\ell i}A_{\ell j}. \tag{1.89}$$

Substitution into the second order perturbation equation yields

$$b_{ij} = \{\sum_{\ell}^{\text{all}} F^{(1)}_{i\ell}A_{\ell j} - A_{ij}\varepsilon^{(1)}_{j}\}/(\varepsilon^{(0)}_{j} - \varepsilon^{(0)}_{i}). \tag{1.90}$$

Using (1.85) and (1.77), the second order change in the bond order matrix is given by

$$P^{(2)}_{\mu\nu} = 2\sum_{i}^{\text{occ}}\sum_{k}^{\text{all}}\sum_{\ell}^{\text{all}} A_{ki}A_{\ell i}C^{(0)}_{\mu k}C^{(0)}_{\nu\ell}$$

$$+ 2\sum_{i}^{\text{occ}}\sum_{k}^{\text{all}} (B_{ki} + b_{ki})(C^{(0)}_{\mu i}C^{(0)}_{\nu k} + C^{(0)}_{\mu k}C^{(0)}_{\nu i}). \tag{1.91}$$

This expression for $P^{(2)}$ is singular and must therefore be reduced to a non-singular form. The contribution from the skew symmetric component B_{ki} can be simplified in the same way as equation (1.83) but the remaining terms present a more difficult problem. Using (1.89), the b_{ki} contribution to (1.91) can be written,

$$2\sum_{i}^{occ}\sum_{k}^{vac}(C_{\mu i}^{(0)}C_{\nu k}^{(0)} + C_{\mu k}^{(0)}C_{\nu i}^{(0)})b_{ki} - 2\sum_{i}^{occ}\sum_{k}^{occ}\sum_{\ell}^{vac}C_{\mu i}^{(0)}C_{\nu k}^{(0)}A_{\ell i}A_{\ell k}$$

$$- 2\sum_{i}^{occ}\sum_{k}^{occ}\sum_{\ell}^{occ}C_{\mu i}^{(0)}C_{\nu k}^{(0)}A_{\ell i}A_{\ell k}. \qquad (1.92)$$

The last term of (1.92) cancells part of the first term of (1.91). Thus,

$$P_{\mu\nu}^{(2)} = 2\{\sum_{i}^{occ}\sum_{k}^{vac}\sum_{\ell}^{vac}C_{\mu k}^{(0)}C_{\nu\ell}^{(0)}A_{ki}A_{\ell i} + \sum_{i}^{occ}\sum_{k}^{vac}(C_{\mu i}^{(0)}C_{\nu k}^{(0)} + C_{\mu k}^{(0)}C_{\nu i}^{(0)})B_{ki}$$

$$- \sum_{i}^{occ}\sum_{k}^{occ}\sum_{\ell}^{vac}C_{\mu i}^{(0)}C_{\nu k}^{(0)}A_{\ell i}A_{\ell k} + \sum_{i}^{occ}\sum_{k}^{vac}(C_{\mu i}^{(0)}C_{\nu k}^{(0)} + C_{\mu k}^{(0)}C_{\nu i}^{(0)})b_{ki}$$

$$+ \sum_{i}^{occ}\sum_{k}^{vac}\sum_{\ell}^{occ}(C_{\mu i}^{(0)}C_{\nu k}^{(0)} + C_{\mu k}^{(0)}C_{\nu i}^{(0)})A_{i\ell}A_{k\ell}\} \qquad (1.93)$$

Some of the singular terms in the second order bond order have been eliminated, but two, the fourth and fifth, still remain. On collecting these two terms together one has:

$$\sum_{i}^{occ}\sum_{k}^{vac}(C_{\mu i}^{(0)}C_{\nu k}^{(0)} + C_{\mu k}^{(0)}C_{\nu i}^{(0)})(b_{ki} + \sum_{\ell}^{occ}A_{k\ell}A_{\ell i}). \qquad (1.94)$$

Using (1.90) and

$$\varepsilon_{i}^{(1)} = F_{ii}^{(1)} \qquad (1.95)$$

the second part of (1.94) can be expanded,

$$(b_{ki} + \sum_{\ell}^{occ} A_{k\ell}A_{\ell i}) = \sum_{\ell}^{all} F_{k\ell}^{(1)} A_{\ell i}/(\epsilon_i^{(0)} - \epsilon_k^{(0)}) + \sum_{\ell}^{occ} A_{k\ell}A_{\ell i}$$

$$- F_{ii}^{(1)} A_{ki}/(\epsilon_i^{(0)} - \epsilon_k^{(0)}). \qquad (1.96)$$

By making use of (1.80) and (1.81), the right hand side of equation (1.96) simplifies to

$$\sum_{\ell}^{vac} F_{k\ell}^{(1)} A_{\ell i}/(\epsilon_i^{(0)} - \epsilon_k^{(0)}) + \sum_{\ell}^{occ} A_{\ell k}F_{\ell i}^{(1)}/(\epsilon_i^{(0)} - \epsilon_k^{(0)}) \qquad (1.97)$$

Thus, the second order bond order is given by

$$P_{\mu\nu}^{(2)} = 2\Big(\sum_{i}^{occ} \sum_{k}^{vac} \sum_{\ell}^{vac} C_{\mu k}^{(0)} C_{\nu\ell}^{(0)} A_{ki}A_{\ell i}$$

$$+ \sum_{i}^{occ} \sum_{k}^{vac} (C_{\mu i}^{(0)} C_{\nu k}^{(0)} + C_{\mu k}^{(0)} C_{\nu i}^{(0)})\{ \sum_{\ell}^{vac} F_{k\ell}^{(1)} A_{\ell i}/(\epsilon_i^{(0)} - \epsilon_k^{(0)})$$

$$+ \sum_{\ell}^{occ} A_{\ell k}F_{\ell i}^{(1)}/(\epsilon_i^{(0)} - \epsilon_k^{(0)}) + B_{ki}\}$$

$$-\tfrac{1}{2} \sum_{i}^{occ} \sum_{k}^{occ} \sum_{\ell}^{vac} (C_{\mu i}^{(0)} C_{\nu k}^{(0)} + C_{\mu k}^{(0)} C_{\nu i}^{(0)}) A_{\ell i}A_{\ell k}\Big). \qquad (1.98)$$

Equation (1.98) has no singular terms and may be used when the zero order solutions are degenerate. It is useful to introduce the following notation

$$P_{\mu\nu}^{(2)} = 2\Big(\sum_{i}^{occ} \sum_{k}^{vac} \sum_{\ell}^{vac} C_{\mu k}^{(0)} C_{\nu\ell}^{(0)} A_{ki}A_{\ell i} + \sum_{i}^{occ} \sum_{k}^{all} (C_{\mu i}^{(0)} C_{\nu k}^{(0)} + C_{\mu k}^{(0)} C_{\nu i}^{(0)}) B_{ki}\Big)$$

$$(1.99)$$

where, if i and k label occupied and vacant orbitals, respectively

$$\mathcal{B}_{ki} = \{ \sum_{\ell}^{\mathrm{vac}} F^{(1)}_{k\ell} A_{\ell i} + \sum_{\ell}^{\mathrm{occ}} A_{\ell k} F^{(1)}_{\ell i} + F^{(2)}_{ki} \} / (\varepsilon_i^{(0)} - \varepsilon_k^{(0)}), \qquad (1.100)$$

and, if i and k both label occupied orbitals

$$\mathcal{B}_{ki} = -\tfrac{1}{2} \sum_{\ell}^{\mathrm{vac}} A_{\ell k} A_{\ell i} . \qquad (1.101)$$

The terms collected under $\mathcal{B}$ are also useful in the calculation of the third order bond order matrix. The second order bond order may be separated into two parts, iterative and non-iterative. The only iterative part is the $\underline{F}^{(2)}$ contribution which depends on $\underline{B}$ through $\underline{P}^{(2)}$. The non-iterative component arises from products of $\underline{A}$ and $\underline{F}^{(1)}$ and need be calculated only once, on the completion of the first order calculation.

A non-singular expression for the third order bond order may be obtained in a manner similar to that used for the second order bond order. This bond order also has iterative and non-iterative terms and the non-iterative parts depend only on the first and second order solutions. Thus, if they are solved consecutively starting from the zeroth order, the perturbation equations for the various orders are independent. Each order contributes to all higher orders and is simply added on as constants.

The basic approach to the solution of the infinite bond order matrix equations is to break them down into infinite sets of finite sub-matrix equations by means of the special ordering of the basis set. The crystal bond order matrix is then built up from these sub-matrices.

The numerous sub-matrices that appear in the theory are labelled according to the lattice molecules involved, by the unit cell they occupy, R, and the site within that cell, u. All the crystal matrices, except the $\underline{C}^{(n)}$'s, are partitioned into intra- and intermolecular sub-matrices,

$$ {}^{RuSy}\underline{M} \;, \qquad (1.102)$$

where the sub-matrix ${}^{RuSy}\underline{M}$ has elements between the atomic orbitals on the $Ru^{\underline{th}}$ and $Sy^{\underline{th}}$ molecules. Generally, the sub-matrices ${}^{RuSy}\underline{M}$ are not square unless the $Ru^{\underline{th}}$ and $Sy^{\underline{th}}$ molecules are of the same chemical species. The diagonal sub-matrices, where R = S and u = y, are the intramolecular submatrices and the off diagonal sub-matrices are intermolecular sub-matrices.

Expressions for the crystal bond order sub-matrices are obtained by partitioning and partially multiplying out the equations for the corresponding bond orders making use of the block diagonal form of $C^{(0)}$. From (1.83)

$$ {}^{RuSy}P_{\mu\nu}(1) = 2 \sum_{i}^{occ_{Ru}} \sum_{k}^{vac_{Sy}} {}^{u}C_{\mu i}(0)\; {}^{y}C_{\nu k}(0)\; {}^{SyRu}A_{ki} + 2 \sum_{i}^{occ_{Sy}} \sum_{k}^{vac_{Ru}} {}^{u}C_{\mu k}(0)\; {}^{y}C_{\nu i}(0)\; {}^{RuSy}A_{ki} , \qquad (1.103)$$

where $\sum_{i}^{occ_{Ru}}$ sums over all occupied orbitals on the $Ru^{\underline{th}}$ molecule, ${}^{u}C_{\mu i}(0)$ is the $i^{\underline{th}}$ zero order molecular orbital coefficient for the

μ^{th} atomic orbital on the Ru^{th} molecule and

$$ {}^{SyRu}A_{ki} = \sum_{\mu}^{Sy} \sum_{\nu}^{Ru} {}^{y}C^{(0)}_{\mu k}\ {}^{SyRu}F^{(1)}_{\mu\nu}\ {}^{u}C^{(0)}_{\nu i} / (\varepsilon_i^{(0)} - \varepsilon_k^{(0)}). \qquad (1.104) $$

Hence, the matrix equation for $\underline{P}^{(1)}$ has been broken down into an infinite number of finite matrix equations that are coupled through the corresponding Fock matrices but can be more or less decoupled by means of the lattice symmetry. Similarly,

$$ {}^{RuSy}P^{(2)}_{\mu\nu} = 2 \sum_{T} \sum_{w} \sum_{i}^{occ\,Tw} \sum_{k}^{vac\,Ru} \sum_{\ell}^{vac\,Sy}\ {}^{RuTw}A_{ki}\ {}^{SyTw}A_{\ell i}\ {}^{u}C^{(0)}_{\mu k}\ {}^{y}C^{(0)}_{\nu\ell} $$

$$ + 2 \sum_{i}^{occ\,Ru} \sum_{k}^{all\,Sy}\ {}^{SyRu}\mathcal{B}_{ki}\ {}^{u}C^{(0)}_{\mu i}\ {}^{y}C^{(0)}_{\nu k} + 2 \sum_{i}^{occ\,Sy} \sum_{k}^{all\,Ru}\ {}^{RuSy}\mathcal{B}_{ki}\ {}^{u}C^{(0)}_{\mu k}\ {}^{y}C^{(0)}_{\nu i}, \qquad (1.105) $$

where the summations over T and w include all the molecules in the crystal. Fortunately, this series is strongly convergent so that few terms need be included. This second order contribution explicitly includes three molecule interactions; that is the interaction of two molecules modified by their interaction with a third.

The corresponding expressions for the third order sub-matrices may be derived in a similar manner and include four molecule interactions.

Explicit expressions for the Fock sub-matrices necessary for the calculation of the bond orders are give below. Although these expressions are presented in terms of the CNDO approximate method, the theory is independent of this approximation [22].

(I) Zero Order Fock Sub-Matrices, ${}^{RuSy}\underline{F}^{(0)}$

Since the zero order solution of the perturbation equations is chosen as the molecular orbitals of a hypothetically non-interacting lattice, all of the zero order Fock sub-matrices are intramolecular in character ~~and~~, under the CNDO approximation in a notation that reflects the crystal problem, are given by

$$
\begin{aligned}
{}^{RuRu}F^{(0)}_{\mu\mu} = {}^{RuRu}U_{\mu\mu} &+ \sum_{\beta} \left({}^{Ru}Q^{(0)}_{\beta} - {}^{Ru}Z_{\beta}\right)\gamma^{RuRu}_{\alpha\beta} \\
&+ \left({}^{Ru}Q^{(0)}_{\alpha} - \tfrac{1}{2}\,{}^{RuRu}P^{(0)}_{\mu\mu}\right)\gamma^{RuRu}_{\alpha\alpha} \qquad (1.106)
\end{aligned}
$$

$$
{}^{RuRu}F^{(0)}_{\mu\nu} = -\tfrac{1}{2}\,{}^{RuRu}P^{(0)}_{\mu\nu}\,\gamma^{RuRu}_{\alpha\beta} \qquad (1.107)
$$

where μ and ν label atomic orbitals on the α and β atoms of the $Ru^{\underline{th}}$ molecule. ${}^{Ru}Q^{(0)}_{\beta}$ and ${}^{Ru}Z_{\beta}$ are the zero order charge density and effective nuclear charge for the $\beta^{\underline{th}}$ atom of the $Ru^{\underline{th}}$ molecule, $\gamma^{RuRu}_{\alpha\beta}$ is the CNDO electron repulsion integral between the $\alpha^{\underline{th}}$ and $\beta^{\underline{th}}$ atoms of the $Ru^{\underline{th}}$ molecule and ${}^{RuRu}U_{\mu\mu}$ is the one electron CNDO matrix element.

(II) Intramolecular Sub-Matrices, ${}^{RuRu}\underline{F}^{(n)}$, for $n > 0$:

For $n > 0$, the elements of the $n^{\underline{th}}$ order intramolecular Fock sub-matrices, under the CNDO approximation, are given by

$$
\begin{aligned}
{}^{RuRu}F^{(n)}_{\mu\mu} = &\left(\sum_{S}{}'\sum_{y}{}'\sum_{\beta}\left({}^{Sy}Q^{(0)}_{\beta} - {}^{Sy}Z_{\beta}\right)\gamma^{RuSy}_{\alpha\beta}\right)\delta_{1n} + \sum_{S}\sum_{y}\sum_{\beta} {}^{Sy}Q^{(n)}_{\beta}\,\gamma^{RuSy}_{\alpha\beta} \\
&-\tfrac{1}{2}\,{}^{RuRu}P^{(n)}_{\mu\mu}\,\gamma^{RuRu}_{\alpha\alpha}, \qquad (1.108)
\end{aligned}
$$

$$ {}^{RuRu}F^{(n)}_{\mu\nu} = -\tfrac{1}{2}\,{}^{RuRu}P^{(n)}_{\mu\nu}\,\gamma^{RuRu}_{\alpha\beta}\,, \qquad (1.109) $$

where ${}^{Sy}Q^{(n)}_{\beta}$ and ${}^{Sy}Z_{\beta}$ are, respectively, the n^{th} order change in the total electron density and the effective nuclear charge for the β^{th} atom of the Sy^{th} molecule and $\gamma^{RuSy}_{\alpha\beta}$ is the CNDO electron repulsion integral between the α^{th} and β^{th} atoms on the Ru^{th} and Sy^{th} molecules. The primes on the summations over S and y, which label unit cells and sites respectively, are to exclude the Ru^{th} molecule. δ_{1n} is the Kronecker delta, which is zero unless $n = 1$. All of the intramolecular Fock sub-matrix equations are coupled through the charge densities which appear in their diagonal elements. That is, the charge densities and hence the bond orders for all the molecules in the lattice are required to calculate each ${}^{RuRu}F^{(n)}$ sub-matrix, so that all the equations for the intramolecular Fock matrices are interdependent. This coupling is easily removed for regions of perfect lattice symmetry by noting that translationally equivalent molecules are identical and hence, their bond order sub-matrices, total charge densities and effective nuclear charges are equal. Thus, the unit cell label on both $Q^{(n)}$ and Z is redundant and can be omitted. By making use of this and rearranging the summations the diagonal elements of the intramolecular Fock sub-matrices can be simplified to

$$ {}^{RuRu}F^{(n)}_{\mu\mu} = \Big(\sum_{y}\sum_{\beta}({}^{y}Q^{(0)}_{\beta} - {}^{y}Z_{\beta})\Gamma^{uy}_{\alpha\beta}\Big)\delta_{1n} + \sum_{y}\sum_{\beta}{}^{y}Q^{(n)}_{\beta}\Gamma^{uy}_{\alpha\beta} + \sum_{\beta}{}^{u}Q^{(n)}_{\beta}\gamma^{RuRu}_{\alpha\beta} $$

$$ -\tfrac{1}{2}\,{}^{RuRu}P^{(n)}_{\mu\mu}\,\gamma^{RuRu}_{\alpha\beta}\,, \qquad (1.110) $$

where $\Gamma^{uy}_{\alpha\beta}$ is a lattice sum of CNDO Coulomb integrals

$$\Gamma^{uy}_{\alpha\beta} = \sum_{S}{}' \gamma^{RuSy}_{\alpha\beta} . \tag{1.111}$$

The prime omits the origin cell, S = R, if u = y. The intramolecular sub-matrix equations for translationally equivalent molecules are no longer coupled through the Fock sub-matrices. However, the equations between unit cell molecules are still coupled since the factor group symmetry was not used in deriving (1.110).

(iii) Intermolecular $n^{\underline{th}}$ order Sub-Matrices, ${}^{RuSy}\underline{F}^{(n)}$

$${}^{RuSy}F^{(n)}_{\mu\nu} = {}^{RuSy}H^{(1)}_{\mu\nu}\delta_{1n} - \tfrac{1}{2}\,{}^{RuSy}P^{(n)}_{\mu\nu}\,\gamma^{RuSy}_{\alpha\beta} , \tag{1.112}$$

where ${}^{RuSy}H^{(1)}_{\mu\nu}$ is an element of the intermolecular core Hamiltonian sub-matrix, and is given by a product of a resonance parameter and the corresponding overlap integral.

The lattice energy, W', can be calculated from the energy expression equation (1.37) by substituting the perturbation series for $\underline{H}$, $\underline{P}$ and $\underline{F}$. The result to third order is

$$W = \tfrac{1}{4} \sum_{n=0}^{3} \sum_{m=0}^{n} \sum_{\mu} \sum_{\nu} \{P^{(m)}_{\mu\nu}(H^{(n-m)}_{\mu\nu} + F^{(n-m)}_{\mu\nu}) + P^{(n-m)}_{\mu\nu}(H^{(m)}_{\mu\nu} + F^{(m)}_{\mu\nu})\}$$

$$+ \text{ nuclear repulsion} \tag{1.113}$$

On partitioning the $\underline{P}$,$\underline{H}$ and $\underline{F}$ matrices into sub-matrices and summing over translationally equivalent molecules for a lattice of N unit cells

$$W' = \tfrac{1}{2}N \sum_{S}\sum_{u}\sum_{y}\Big(\sum_{n=0}^{3}\sum_{m=0}^{n}\sum_{\mu}\sum_{\nu}\{{}^{RuSy}P_{\mu\nu}^{(m)}({}^{RuSy}H_{\mu\nu}^{(n-m)} + {}^{RuSy}F_{\mu\nu}^{(n-m)})\}$$

$$+ \sum_{\alpha}\sum_{\beta} {}^{Ru}Z_{\alpha}\,{}^{Sy}Z_{\beta}/\,\mathrm{Rad}_{\alpha\beta}\Big), \qquad (1.114)$$

where $\mathrm{Rad}_{\alpha\beta}$ is the interatomic distance between atoms α and β on the Ruth and Syth molecules. The energy per unit cell, W, is obtained by dividing (1.114) through by N. When there is intermolecular charge transfer between lattice molecules the energy per molecule is not a well defined quantity.

The energy expression can be resolved into the sum of five contributions termed $W_{molecular}$, $W_{electrostatic}$, $W_{polarization}$, $W_{intermolecular}$ and $W_{intramolecular}$. This organization of the energy equation into five terms is partly to take advantage of the interpretive potential of the perturbation approach and partly for computational convenience.

$W_{molecular}$ is the zero order molecular energy, including nuclear repulsion, for the hypothetically independent lattice molecules.

$W_{electrostatic}$ includes all terms involving zero order charge densities and the Coulomb lattice sums. It represents the electrostatic interaction in the crystal. Under the CNDO approximation $^{9-13}$, this is modified by the neglect of penetration so that it also includes the overlap dependent closed shell repulsion energy.

$W_{polarization}$ includes all the contributions involving the product of perturbed charge densities with the Coulomb lattice sums. It is the polarization energy of the lattice subject to the neglect of penetration.

$W_{\text{intermolecular}}$ includes all contributions involving the intermolecular bond order sub-matrices.

$W_{\text{intramolecular}}$ includes all the remaining terms. That is, terms that involve the perturbed intramolecular sub-matrices. It is the increase in molecular energy resulting from the crystal induced polarization of the molecular charge distribution.

The corresponding expressions for these energies are;

$$W_{\text{molecular}} = \tfrac{1}{2} \sum_{u} \sum_{\mu} \sum_{\nu} {}^{RuRu}P^{(0)}_{\mu\nu} \left({}^{RuRu}H^{(0)}_{\mu\nu} \quad {}^{RuRu}F^{(0)}_{\mu\nu} \right)$$

$$+ \text{ nuclear repulsion}, \qquad (1.115)$$

$$W_{\text{electrostatic}} = \tfrac{1}{2} \sum_{u} \sum_{y} \sum_{\alpha} \sum_{\beta} {}^{u}Q^{(0)}_{\alpha} \left({}^{y}Q^{(0)}_{\beta} - 2\,{}^{y}Z_{\beta} \right) \Gamma^{uy}_{\alpha\beta}$$

$$+ \text{ nuclear repulsion}, \qquad (1.116)$$

$$W_{\text{polarization}} = \tfrac{1}{2} \sum_{u} \sum_{y} \sum_{\alpha} \sum_{\beta} {}^{u}Q^{(0)}_{\alpha}\ {}^{y}Q^{(1)}_{\beta} + {}^{u}Q^{(1)}_{\alpha}\ {}^{y}Q^{(1)}_{\beta} + {}^{u}Q^{(0)}_{\alpha}\ {}^{y}Q^{(2)}_{\beta}$$

$$+ {}^{u}Q^{(0)}_{\alpha}\ {}^{y}Q^{(3)}_{\beta} + {}^{u}Q^{(1)}_{\alpha}\ {}^{y}Q^{(2)}_{\beta} + {}^{u}Q^{(2)}_{\alpha}\ {}^{y}Q^{(1)}_{\beta}$$

$$+ \left({}^{u}Q^{(1)}_{\alpha} + {}^{u}Q^{(2)}_{\alpha} \right) \left({}^{y}Q^{(0)}_{\beta} - 2\,{}^{y}Z_{\beta} \right) \Gamma^{uy}_{\alpha\beta}, \qquad (1.117)$$

$$W_{\text{intermolecular}} = \tfrac{1}{2} \sum_{S} \sum_{u} {\sum_{y}}' \sum_{\mu} \sum_{\nu} \left({}^{RuSy}P^{(1)}_{\mu\nu} + {}^{RuSy}P^{(2)}_{\mu\nu} \right) \left(2\,{}^{RuSy}H^{(1)}_{\mu\nu} \right.$$

$$\left. - \tfrac{1}{2}\,{}^{RuSy}P^{(1)}_{\mu\nu}\,\gamma^{RuSy}_{\alpha\beta} \right). \qquad (1.118)$$

The primed sum over unit cells, S, excludes the reference cell S = R, when u = y as this corresponds to an intramolecular contribution.

The intramolecular term is not so straightforward since there is a significant level of cancellation. Specifically, it can be shown that the first order intramolecular energy is zero so that all intramolecular terms are of second or third order.

$$
\begin{aligned}
W_{\text{intramolecular}} = \tfrac{1}{2} \sum_{u} \sum_{\alpha} \sum_{\beta} \{ & {}^{u}Q_{\alpha}^{(2)}\, {}^{u}Q_{\beta}^{(0)} + {}^{u}Q_{\alpha}^{(1)}\, {}^{u}Q_{\beta}^{(1)} + {}^{u}Q_{\alpha}^{(0)}\, {}^{u}Q_{\beta}^{(2)} \\
& + {}^{u}Q_{\alpha}^{(0)}\, {}^{u}Q_{\beta}^{(3)} + {}^{u}Q_{\alpha}^{(1)}\, {}^{u}Q_{\beta}^{(2)} + {}^{u}Q_{\alpha}^{(2)}\, {}^{u}Q_{\beta}^{(1)} + {}^{u}Q_{\alpha}^{(3)}\, {}^{u}Q_{\beta}^{(0)} \} \gamma_{\alpha\beta}^{RuRu} \\
& + \sum_{\mu} \sum_{\nu} \{ {}^{RuRu}P_{\mu\nu}^{(2)} (2\, {}^{RuRu}H_{\mu\nu}^{(0)} - {}^{RuRu}P_{\mu\nu}^{(0)} \gamma_{\alpha\beta}^{RuRu}) \\
& - \tfrac{1}{2}\, {}^{RuRu}P_{\mu\nu}^{(1)}\, {}^{RuRu}P_{\mu\nu}^{(1)} \gamma_{\alpha\beta}^{RuRu} + 2\, {}^{RuRu}P_{\mu\nu}^{(3)}\, {}^{RuRu}H_{\mu\nu}^{(0)} \\
& - ({}^{RuRu}P_{\mu\nu}^{(3)}\, {}^{RuRu}P_{\mu\nu}^{(0)} + {}^{RuRu}P_{\mu\nu}^{(2)}\, {}^{RuRu}P_{\mu\nu}^{(1)}) \gamma_{\alpha\beta}^{RuRu} \}.
\end{aligned}
\tag{1.119}
$$

The SCF perturbation method for molecular crystals has been successfully applied to solid hydrogen fluoride [61], the two forms of oxalic acid dihydrate crystals [62], cubic and hexagonal ices [62-63] and ice-II [65]. The predicted structural parameters are comparable to the experimental values for hydrogen fluoride, hexagonal ice and ice-II with the molecular parameters in considerably better agreement than those for the unit cell. The relative binding energies for the three ice structure studied are in the correct order but the relative intervals are calculated rather much larger than the experimental values. The change in dipole moment for water molecules in hexagonal ice on crystallization calculated by this method is much smaller than the value predicted by two other calculations [66-67]. Although these calculations are superior in some respects, both are based on essentially electrostatic models that cannot adequately describe hydrogen bonding interactions. In general, the SCF perturbation method appears to predict structural parameters, binding energies and charge distributions for hydrogen bonded crystals nearly as well as the CNDO method for molecules.

CHAPTER 2

Theoretical Lattice Energies and Charge Distributions of Molecular Crystals

§ 2.1 Introduction

The SCF perturbation method appears to predict structural parameters, binding energies and charge distributions very well for the case of small molecules bound together predominantly by hydrogen bonds [61-63,65]. In order to assess its applicability in a general sense, it is of interest to study a range of crystal types using this method. However, it must be noted that as it is a single determinantal method, Coulomb electron correlation which is responsible for the dispersive forces is not included [4]. Nevertheless, the non-dispersive hydrogen bonding and electrostatic multipole interactions are included explicitly. Also, Fermi electron correlation, intermolecular exchange, overlap dependent closed shell repulsion and electron delocalization are included at an approximate level.

In this chapter this method is used to calculate the binding energy and charge distributions for a series of crystals in order to estimate the importance of the perturbation contribution to the energy in each type and to assess its applicability to different types. Included in the series are some weakly bound dispersive crystals, some in which the electrostatic multipoles are usually assumed to be largely responsible for the binding energy, hydrogen bonded crystals and two ionic crystals. Among the crystals studied are three, triazine, melamine and cyanuric acid, whose molecules have a common ring structure.

§2.2 Computational Details

The unit cell parameters, number of molecules per unit cell and space group for each of the crystals studied are given in table 2.1. The atomic coordinates of the reference molecule in each crystal used in the calculations are given in the various sections of appendix 1 to the six decimal places assumed by the program used. An asterisk is used to indicate the hydrogen, in a hydrogen bonded crystal, which makes the shortest intermolecular contact. These coordinates, with the exception of those of the formic acid protons, were taken directly from references [68-84]. The formic acid proton coordinates, which were not listed with the experimental crystal structure, were calculated using assumed bond lengths of 1.086 Å and 0.96 Å for the C-H and O-H bonds respectively.

The SCF perturbation calculations for the crystals were carried out using a version of the program CRYDEN [85]. The Coulomb or exterior lattice sums were evaluated by summing over all molecules within a sphere of radius 35 Å for all crystals studied except cyanuric acid for which 30 Å was used. The molecules included in the perturbation or interior scans were restricted to those which make an intermolecular atomic contact of less than 5.5 Å for nitrogen, 3.0 Å for melamine, SF_3BF_4 and $NH_4^+BF_4$ and 3.5 Å for the rest.

A Saunder's level shifting technique [86] was used in order to obtain convergence of the TCNE and TCNEO zero order calculations. Convergence of the first and higher orders for these two crystal calculations was achieved by setting the net atomic electron densities at each site equal to those of the reference molecule.

Table 2.1 Lattice parameters and space groups of the crystals studied

	a_o	b_o	c_o	β	Z	space group
Nitrogen[68]	5.644	5.644	5.644	90.	4	Pa3
S-triazine[69]	9.647	9.647	7.281	120.*	4	$R\bar{3}c$
Naphthalene[70]	8.266	5.968	8.669	122.92	2	$P2_1/a$
Benzene[71]	7.39	9.42	6.81	90.	4	Pbca
Hydrogen cyanide[72]	7.80	9.16	8.20	90.	2	Imm2
Carbon dioxide[73]	5.575	5.575	5.575	90.	4	Pa3
Sulphur dioxide[74]	6.07	5.94	6.14	90.	4	Aba
Diborane[75]	5.72	6.50	4.40	105.1	2	$P2_1/n$
Tetracyanoethylene[76] oxide(TCNEO)	9.718	6.141	12.162	110.28	4	$P2_1/c$
Tetracyanoethylene[77] (TCNE)	9.736	9.736	9.736	90.	6	Im3
Formic acid[78]	10.23	3.64	5.34	90.	4	$Pna2_1$
Melamine[79]	10.606	7.495	7.295	112.26	4	$P2_1/a$
Formamide[80]	3.69	9.18	6.87	98.	4	$P2_1/n$
Urea[81]	5.582	5.582	4.686	90.	2	$P\bar{4}2_1m$
Cyanuric acid[82]	7.749	6.736	11.912	130.69	4	C2/n
SF_3BF_4[83]	9.599	5.755	8.974	90.	4**	Pnma
NH_4BF_4[84]	9.077	5.679	7.279	90.	4**	Pnma

* This is the hexagonal angle γ.

** Each of these molecules is composed of two oppositely charged ions.

The SF_3BF_4 and NH_4BF_4 crystals are particularly interesting since they are thought to be almost ionic in character. Accordingly, they represent a special problem since the intermolecular interactions are rather strong. In order to circumvent this difficulty the compound molecule approach was introduced. That is, these crystals were treated as being composed of neutral molecules compounded from nearest neighbour oppositely charged ions.

§ 2.3 The Calculated Lattice Energies

The theoretical contributions to the lattice energies along with the experimental values, where available, are given in table 2.2. The experimental values are the heat of sublimation at $0^{\circ}K$ either as given in the reference cited or calculated by the method of Rae [11] using the value at a higher temperature or data given in the reference. The calculations for carbon dioxide and sulphur dioxide were carried out with and without the inclusion of interactions between molecules as modified by the presence of a third (three centre interactions) in order to determine their importance in the binding of these two crystals. The electrostatic, polarization, intramolecular and intermolecular contributions to the lattice energy are as defined in chapter 1.

With the exception of ionic crystals, the calculated lattice energy is largely the result of the partial cancellation of a binding intermolecular energy by the destabilizing intramolecular energy, whilst the electrostatic term is considerably smaller than either and may tend to increase or decrease the binding energy. The polarization energy makes the smallest contribution in all cases. As one would

Table 2.2 Contributions to the lattice energies in kcal per mole

	Nitrogen	S-triazine	Naphthalene	Benzene	HCN	Carbon dioxide (no 3 centre)	Carbon dioxide
Electrostatic†	.0103	.8346	2.3320	2.0845	1.7896	-1.2823	-1.2823
Polarization	.0000	-.0321	-.0019	.0015	.0015	-.1426	-.1426
Intramolecular	.0735	1.8946	4.7773	4.5679	4.9503	2.9788	2.9361
Intermolecular	-.1385	-3.5049	-8.9503	-8.6056	-9.0279	-5.3715	-5.3104
Total	-.0547	-.8078	-1.8409	-1.9499	-2.2865	-3.8176	-3.8602
Experimental	-1.65[87]	-11.3[10]	-19.82[88]	-12.9[9]	-9.086[11]	-6.6[91]	-6.6[91]

	Sulphur dioxide (no 3 centre)	Sulphur dioxide	Diborane	TCNEO	TCNE	Formic acid	Formamide
Electrostatic†	-1.8593	-1.8593	.8586	-.5634	-.8162	8.5785	5.1852
Polarization	-.2510	-.2148	-.0212	-.4465	-.3978	-1.2205	-2.6752
Intramolecular	2.8474	3.2486	5.9335	5.2129	5.1665	27.0041	30.7076
Intermolecular	-4.9191	-5.7293	-11.2292	-9.2460	-9.2262	-46.2777	-51.4242
Total	-4.1820	-4.5188	-4.4583	-5.0430	-5.2737	-11.9156	-18.2066
Experimental					-20.4[88]	-14.4[139]	-17.0[139]

Table 2.2 continued

	Melamine	Urea	Cyanuric acid	SF_3BF_4	NH_4BF_4
Electrostatic[†]	7.8744	4.1596	9.4130	-42.4965	-96.7661
Polarization	-.9052	-2.6699	-2.8778	-6.4584	-10.3191
Intramolecular	32.8060	30.8521	47.6487	2.1912	7.8896
Intermolecular	-58.7402	-52.8944	-81.5023	-15.6257	-6.9072
Total	-18.3650	-20.5526	-27.3184	-58.0932	-106.1026
Experimental	-29.5 [89]	-21.93 [90]			

[†] Under the CNDO approximation the electrostatic energy includes the overlap dependent closed shell repulsion energy.

expect the binding energy of the ionic crystals is extensively determined by the electrostatic interaction.

The overall agreement between the experimental and calculated lattice energies ranges from good for the strongly hydrogen bonded crystals to especially poor for the crystals such as nitrogen and s-triazine. This poor agreement is likely due to the neglect of dispersive interactions in the perturbation method and a poor representation of the quadrupole and higher moments in the CNDO approximation.

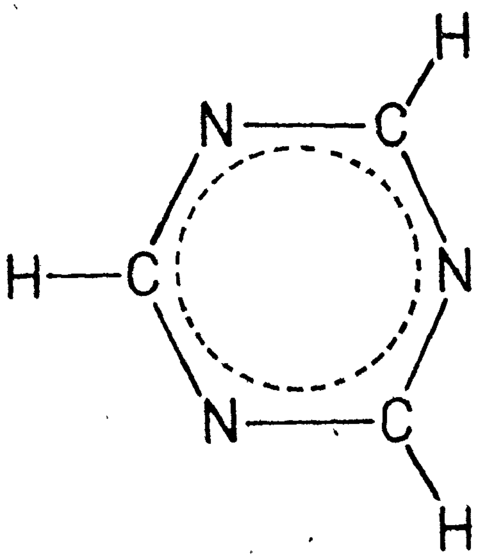
For formic acid, formamide, and urea which are hydrogen bonded crystals in which the leading molecular moment is the dipole, the agreement with experiment is relatively good. For this particular class of crystals, the main contribution to the lattice energy not included is the dispersive term. Hence, the difference between the calculated and experimental energies may give some indication of the relative importance of this kind of interaction. Thus, the dispersive forces may make a small but significant contribution, about 14% in formic acid, to the energy.

For the dispersive crystals and crystals in which the higher multipole moments are important, the agreement with experiment is poor. However, the sum of the intermolecular and intramolecular contributions to the energy can be used to determine the contribution to the lattice energy due to the perturbing effect of the molecules on each other. For instance, the perturbation makes a contribution of about 30% in the case of benzene and though carbon dioxide and sulphur dioxide are most often described in terms of the quadrupole quadrupole interactions, it appears at least in the case of carbon dioxide, that the perturbation interaction may make a significant contribution to the lattice energy.

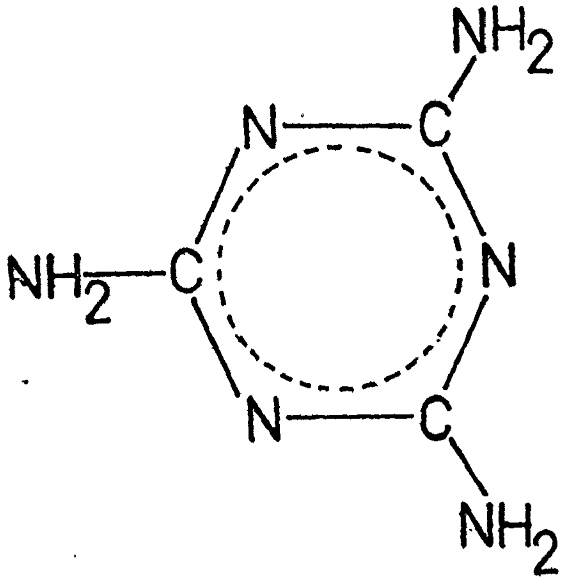
As shown in figure 2.1, the s-triazine, melamine and cyanuric acid molecules have a similar ring structure, aromatic for the first two and saturated for cyanuric acid. Because of this similarity in structure, they are an interesting set for comparison. S-triazine and melamine both have aromatic rings and have quite similar probable contributions from dispersive interactions and higher multipoles, 10.5 and 11.2 kcal per mole respectively, whilst their experimental lattice energies are quite different. Unfortunately, the experimental lattice energy for cyanuric acid is not available so that its dispersive contribution cannot be estimated but it may be smaller than that of s-triazine or melamine since the low energy $\pi \to \pi^*$ excitations that contribute to the dispersive term in equation (1.2) for the aromatic molecules are absent.

The main contribution to the deviation from the pairwise additivity of intermolecular forces is the three body interaction. That is, the modification of the interaction between pairs of molecules by the presence of a third molecule is the main effect responsible for the non pairwise additive part of the intermolecular interactions. The net stabilization energy arising from these three centre interactions in the carbon dioxide and sulphur dioxide crystals was obtained by subtraction of the total binding energies from the calculations with and without their inclusion. The results are .0426 and .3386 kcal per mole for carbon dioxide and sulphur dioxide respectively, and are small when compared to the total binding energies. The result for carbon dioxide is much less than that of Hashimoto and Isobe [16]. However, their single determinantal method seems to be rather unreliable as,

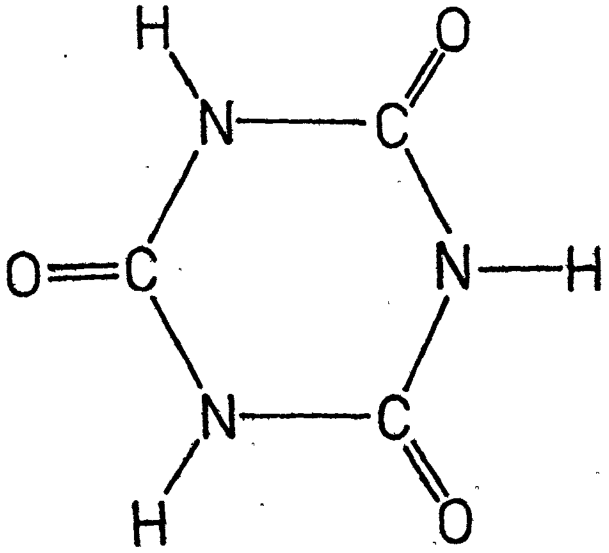
Figure 2.1 The structure of the s-triazine, melamine and cyanuric acid molecules.



s-triazine



melamine



cyanuric acid

although it cannot acount for dispersive interactions [4], it closely reproduces the experimental lattice energies of crystals for which these forces are important. Since three centre interactions, at least in the case of hydrogen, are highly orientation dependent [92], the large difference in the calculated three centre interaction energy for the carbon dioxide and sulphur dioxide crystals may be due to favourable orientations in the latter.

Although the above arguments are based on the assumption that the SCF perturbation calculations reproduce virtually all of the perturbation energy, the results for the series of crystals taken together indicate that this assumption is likely valid and the method can be used to estimate the perturbation contribution to the energy for a wide range of crystal types, and the lattice energy for hydrogen bonded crystals.

§ 2.4 Charge Distributions in Molecular Crystals:

Intermolecular Charge Transfer [101]

The experimental determination of electronic charge distributions for molecules within crystals has been made possible, in principle at least, by recent improvements in the accuracy of X-ray and neutron diffraction methods [94-96]. These molecular charge distributions may provide a unique opportunity for the comparison of theoretical results with detailed experimental data.

The discussion presented here is relevant to the comparison of experimental and theoretical results since it is clearly necessary to estimate the gross effect of the crystal environment on the charge distribution before evaluating the agreement between theory and experiment.

It will be shown that the first order intermolecular transfer of charge is zero; that is, intermolecular charge transfer is a second and higher order effect.

Following the notation used in chapter 1, the $\mu^{\underline{th}}$ diagonal element of the intramolecular bond order submatrix for the $Ru^{\underline{th}}$ molecule, ${}^{RuRu}P^{(1)}_{\mu\mu}$, is given by equation (1.103). With a slight rearrangement (1.103) becomes

$$ {}^{RuRu}P^{(1)}_{\mu\mu} = 4 \sum_{i}^{occ_u} \sum_{k}^{vac_u} {}^{RuRu}A_{ki} \; {}^{u}C^{(0)}_{\mu k} \; {}^{u}C^{(0)}_{\mu i} \tag{2.1} $$

where the summations are over the occupied and vacant molecular orbitals of a molecule occupying the $u^{\underline{th}}$ site in the crystal lattice. It is unnecessary to identify the unit cell in this instance since the molecular orbitals of translationally equivalent molecules are the same. ${}^{u}C^{(0)}_{\mu k}$ is the molecular orbital coefficient for the $\mu^{\underline{th}}$ atomic orbital in the $k^{\underline{th}}$ molecular orbital localized on a molecule occupying the $u^{\underline{th}}$ site and ${}^{RuRu}A_{ki}$ is the molecular orbital mixing coefficient defined by equation (1.104).

The total first order change in the electron population of the $u^{\underline{th}}$ molecule, ${}^{u}Q^{(1)}$, is given by the trace of ${}^{RuRu}\underline{P}^{(1)}$.

$$ {}^{u}Q^{(1)} = 4 \sum_{\mu}^{u} \sum_{i}^{occ_u} \sum_{k}^{vac_u} {}^{RuRu}A_{ki} \; {}^{u}C^{(0)}_{\mu k} \; {}^{u}C^{(0)}_{\mu i} \tag{2.2} $$

$$ = 4 \sum_{i}^{occ_u} \sum_{k}^{vac_u} {}^{RuRu}A_{ki} \sum_{\mu}^{u} {}^{u}C^{(0)}_{\mu k} \; {}^{u}C^{(0)}_{\mu i} = 0 \tag{2.3} $$

Thus, the first order intermolecular charge transfer is zero.

However, the second order charge transfer between inequivalent molecules is not zero. Once again following chapter 1, the diagonal elements of the second order intramolecular bond order are given by (1.105) which, with a slight rearrangement, becomes:

$$ {}^{RuRu}P_{\mu\mu}^{(2)} = 2 \sum_{T}^{u.c.} \sum_{y}^{sites} \sum_{i}^{occ_y} \sum_{k}^{vac_u} \sum_{\ell}^{vac_u} {}^{RuTy}A_{ki} \; {}^{RuTy}A_{\ell i} \; {}^{u}C_{\mu k}^{(0)} \; {}^{u}C_{\mu \ell}^{(0)} $$

$$ + 4 \sum_{i}^{occ_u} \sum_{k}^{all_u} {}^{RuRu}\mathcal{B}_{ki} \; {}^{u}C_{\mu k}^{(0)} \; {}^{u}C_{\mu i}^{(0)} \qquad (2.4) $$

where $\sum_T \sum_y$ is a lattice summation over unit cells and sites respectively. If k labels a vacant and i an occupied molecular orbital, then ${}^{RuRu}\mathcal{B}_{ki}$ is given by

$$ {}^{RuRu}\mathcal{B}_{ki} = \sum_{T}^{u.c.} \sum_{y}^{sites} \Big(\sum_{\ell}^{vac_y} {}^{RuTy}F_{k\ell}^{(1)} \; {}^{TyRu}A_{\ell i} + \sum_{\ell}^{occ_y} {}^{TyRu}A_{\ell k} \; {}^{TyRu}F_{\ell i}^{(1)} \Big) $$

$$ /({}^{u}\varepsilon_{i}^{(0)} - {}^{u}\varepsilon_{k}^{(0)}) \quad + \quad {}^{RuRu}F_{ki}^{(2)} / ({}^{u}\varepsilon_{i}^{(0)} - {}^{u}\varepsilon_{k}^{(0)}) \qquad (2.5) $$

and if both k and i label occupied orbitals

$$ {}^{RuRu}\mathcal{B}_{ki} = -\tfrac{1}{2} \sum_{T}^{u.c.} \sum_{y}^{sites} \sum_{\ell}^{vac_y} {}^{TyRu}A_{\ell i} \; {}^{TyRu}A_{\ell k}. \qquad (2.6) $$

The second order charge in the charge distribution of the u^{th} molecule is obtained by summing equation (2.4) over μ. Hence,

$$ {}^{u}Q^{(2)} = 2 \sum_{T} \sum_{y} \sum_{i}^{occ_y} \sum_{k}^{vac_u} \{ {}^{RuTy}A_{ki} \}^2 + 4 \sum_{i}^{occ_u} {}^{RuRu}\mathcal{B}_{ii} \qquad (2.7) $$

On expanding ${}^{RuRu}\mathcal{B}_{ii}$ using equation (2.6), equation (2.7) becomes

$$ {}^{u}Q^{(2)} = 2 \sum_{T} \sum_{y} {\sum_{i}^{occ}}^{y} {\sum_{k}^{vac}}^{u} \{ {}^{RuTy}A_{ki} \}^2 \; - \; 2 \sum_{T} \sum_{y} {\sum_{i}^{occ}}^{u} {\sum_{k}^{vac}}^{y} \{ {}^{TyRu}A_{ki} \}^2 \qquad (2.8) $$

$$ = 2 \sum_{T} \sum_{y} \left({\sum_{i}^{occ}}^{y} {\sum_{k}^{vac}}^{u} \{ {}^{RuTy}A_{ki} \}^2 \; - \; {\sum_{i}^{occ}}^{u} {\sum_{k}^{vac}}^{y} \{ {}^{TyRu}A_{ki} \}^2 \right) \qquad (2.9) $$

Since only diagonal terms of ${}^{RuRu}\mathcal{B}_{ki}$ occur, equation (2.5) does not contribute to ${}^{u}Q^{(2)}$; hence the first contribution to the electron population Q from $\underline{F}^{(2)}$ is in the third order.

If all the unit cell molecules are symmetry related the two terms in equation (2.9) become equivalent when summed over the lattice and ${}^{u}Q^{(2)}$ will vanish for all u, as it should. If the unit cell molecules are not all crystallographically equivalent, the two terms of (2.9) do not cancel and ${}^{u}Q^{(2)}$ is non-zero. It is interesting to note that even here the intramolecular terms, Ty = Ru, in equation (2.9) cancel. Thus, the leading contribution to intermolecular charge transfer arises from intermolecular interactions.

The conservation of charge requires that

$$ \sum_{u}^{sites} {}^{u}Q^{(n)} = 0 \qquad \text{all } n > 0 \qquad (2.10) $$

It can easily be shown by summing equation (2.9) over all u, that this is satisfied in the case of ${}^{u}Q^{(2)}$.

The above results give important insights into the convergence of the SCF perturbation series for the bond order matrix. The first order term in this expansion does not include any contribution from intermolecular charge transfer and may, therefore, be smaller than the second order term where this process is allowed. Clearly, the perturbation expansion must be taken to at least the second order. Even at this level the quantity of charge transferred is not calculated self-consistently since $u_Q^{(2)}$ originates from the constant, non-iterative, component of $\underline{P}^{(2)}$ [63]. The first self-consistent correction to the quantity of charge transferred is made at the third order through $\underline{P}^{(3)}$. The expansion of the density matrix should thus be taken to the third order for crystals which contain crystallographically independent molecules where charge transfer is expected. However, for the majority of simple hydrogen bonded crystals, $\underline{P}^{(3)}$ is negligible for most purposes. Typical results supporting this conclusion are given in Table 1 of Reference 63.

The necessary condition for the transfer of electron density between molecules in crystals is that they be crystallographically independent. There are three distinct ways in which this condition can be met and it is of interest to compare the levels of charge transfer in each of them.

The most obvious way for a crystal to satisfy the above condition is for it to be composed of two or more different species. Examples of this are provided by the two forms, α and β, of the oxalic acid dihydrate crystal. Both crystallise with two oxalic acid molecules plus four water molecules in their unit cells [97]. Despite the strong intermolecular hydrogen bonding, the calculated transfer of electron density [62], taken to the third order, is only about .04e and .03e for the α and β structures respectively; the water molecules carry positive charges in both cases.

Charge transfer is allowed between molecules of the same species as long as they are not related through any element of the crystal's space group. An example of such a crystal is ice-II, where the twelve unit cell molecules fall into two crystallographically independent sets of six molecules [98]. As might be expected, the level of charge transfer calculated [65] for this system, 10^{-3} e, is very small. Thus, for many purposes, the water molecules in ice-II can be considered as being effectively neutral.

The equivalence of unit cell molecules can be broken by a structural distortion of the type produced by either an inter- or intramolecular asymmetric vibration of equivalent molecules. Accordingly, such vibrations should be accompanied by a measure of intermolecular charge transfer.

The magnitude of this effect for the C-O stretching and molecular oscillatory motions of the formamide molecules within the crystal lattice has been estimated in the following manner. The formamide crystal [80] has four equivalent molecules per unit cell which are related in pairs by centres of inversion. The symmetry of this arrangement and the molecular equivalence was broken by subjecting opposite molecules in each pair to opposing distortions which produce two pairs of inequivalent molecules within the unit cell. The calculated quantity of charge transferred for each of the four motions is given in Table 2.3.

Thus, to take C-O stretching as an example, Table 2.3 shows that the 0.05 Å distortion produces two molecules carrying a charge of $+8.9 \times 10^{-3}$e and two with a charge of -8.9×10^{-3}e in each unit cell.

Table 2.3 Net molecular charges for formamide molecules in the distorted unit cell.

DISTORTION	ΔQ
C-O stretch of .05 Å	8.9×10^{-3} e
x	0.2×10^{-3} e
Rotation about y by 5°	3.2×10^{-3} e
z	18.7×10^{-3} e

The first distortion corresponds to the alternate extension and compression of the C-O bonds in the four formamide molecules by .05 Å. The three rotations correspond to alternate rotations of 5° about the principal axes of inertia.

Of course, the total unit cell charge must remain zero. Although the quantities of charge in Table 2.3 are small, the resultant changes in unit cell dipole moments are appreciable because the separations between the oppositely charged molecules, 3.7 Å, is quite large. Thus, $\partial\mu/\partial Q$ for the C-O stretch is of the order of .8D/Å per pair of molecules. Comparison of this with the theoretical and experimental data collected in reference 99 shows it would make a significant contribution to the spectral intensity for this vibration. Similar conclusions follow for the other three motions under discussion here. These results suggest that intermolecular charge transfer may have a marked effect on the spectral intensity of inter- and intramolecular vibrations in hydrogen bonded molecular crystals.

The above results closely parallel those of Dreyfus and Pullman[99] for hydrogen bonding between formamide dimers. However, the approach outlined here has the advantage of being applicable to real, physically realizable, systems. The theory, for example, could be applied to the calculation of crystal field effects on the frequencies and spectral intensities of molecular vibrations. The resultant data would be directly comparable to the corresponding frequencies and intensities derived from the crystal's infrared spectrum.

In summary, the quantity of charge transferred between inequivalent molecules in a crystal lattice tends to be small. This is in agreement with McConnell's [100] suggestion that molecular crystals tend to be either strongly ionic or non-ionic in character. Nonetheless, it may have an effect on the intensities of lattice vibrations since the separation between slightly charged molecules is relatively large.

§ 2.5 The Calculated Net Charge Distributions

The contributions to the calculated net charge distributions of the crystals listed in table 2.1 are given in table 2.4. The numbering of the atoms is the same as in Appendix 1 and any atoms not included in the table are symmetry related to others in the unit cell. Since their unit cells contain only equivalent molecules, there is no net intermolecular charge transfer in any of the crystals studied This is true even for the SF_3BF_4 and NH_4BF_4 crystals since they were treated as being composed of neutral molecules compounded from the ions. The nitrogen crystal is not included as all nitrogen atoms in the unit cell are symmetry related and hence no polarization of the nitrogen nitrogen bond can occur. As can be seen from the table, the charge distributions have converged satisfactorily by the third order and even in the worst cases, those of SF_3BF_4 and NH_4BF_4, the third order contributions are only a few per cent of the final charge densities.

In all cases the effect of the crystal field is small when compared to the net charge on the atom. Broadly, the crystal field tends to slightly increase the charge of atoms over that of the isolated molecule. There are, of course, some exceptions, the most notable of which is that of the hydrogen atom in a carbon hydrogen bond. In all the cases studied, irregardless of the charge of the hydrogen in the isolated molecule, electronic charge is transferred from the hydrogen atom to the rest of the molecule under the influence of the crystal field; that is the hydrogen atom, in a carbon hydrogen bond, becomes relatively more positively charged in the crystal.

For the hydrogen bonded crystals, the crystal induced polarizations

Table 2.4 The calculated net atomic charges for the reference molecule of each crystal. CIP refers to the crystal induced polarization; a positive CIP indicates an increase in relative positive charge. An asterisk indicates the hydrogen atom that makes the shortest intermolecular contact.

a) S-triazine

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
H_1	-.0220	.0033	.0012	.0000	-.0175	.0045
C_1	.2250	-.0005	-.0013	.0000	.2232	-.0018
N_1	-.2030	-.0028	.0001	.0000	-.2057	-.0027

b) Naphthalene

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
H_1	-.0088	.0033	.0012	.0000	-.0073	.0015
H_2	-.0088	-.0033	.0003	.0000	-.0088	.0000
H_3	-.0062	.0000	.0010	.0000	-.0052	.0010
H_4	-.0060	-.0023	.0025	.0000	-.0055	.0005
C_1	.0075	.0007	-.0010	.0000	.0072	-.0003
C_2	.0075	.0005	-.0005	.0000	.0075	.0000
C_3	-.0061	.0004	-.0016	.0000	-.0073	-.0012
C_4	-.0063	.0000	-.0023	.0000	-.0086	-.0023
C_5	.0273	.0006	.0001	.0000	.0280	.0007

Table 2.4 continued

c) Benzene

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
H_1	-.0097	-.0004	.0009	.0000	-.0092	.0005
H_2	-.0066	-.0007	.0019	.0000	-.0054	.0012
H_3	-.0046	-.0002	.0017	.0000	-.0031	.0015
C_1	.0093	.0005	-.0006	.0000	.0092	-.0001
C_2	.0064	.0004	-.0022	.0000	.0046	-.0018
C_3	.0052	.0004	-.0017	.0000	.0039	-.0013

d) Hydrogen cyanide

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
H	.0706	-.0006	.0063	.0000	.0763	.0057
C	.0306	-.0004	-.0068	.0000	.0234	-.0072
N	-.1012	.0010	.0015	.0000	-.0997	.0015

e) Carbon dioxide

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
C	.5363	.0220	.0015	.0000	.5598	.0235
O	-.2681	-.0110	-.0008	.0000	-.2799	-.0118

Table 2.4 continued

f) Sulphur dioxide

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
S	.7447	.0299	.0018	.0000	.7764	.0317
O	-.3723	-.0149	-.0009	.0000	-.3881	-.0158

g) Diborane

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
H_1	-.0540	-.0030	-.0010	.0000	-.0580	-.0040
H_2	-.0519	-.0015	-.0012	.0001	-.0545	-.0026
H_5	.1480	.0021	-.0029	.0002	.1472	-.0006
B	-.0421	.0024	.0051	-.0003	-.0349	.0072

Table 2.4 continued

h) Tetracyanoethylene oxide

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
C_1	.0781	.0135	.0008	.0000	.0924	.0143
C_2	.0775	.0126	.0007	.0000	.0908	.0133
C_3	.0756	.0188	.0003	.0000	.0947	.0191
C_4	.0757	.0082	.0005	.0000	.0844	.0087
C_5	.1680	.0036	-.0004	.0000	.1712	.0032
C_6	.1742	.0012	.0000	.0000	.1754	.0012
N_1	-.1170	-.0149	-.0001	.0000	-.1320	-.0150
N_2	-.1179	-.0111	-.0003	.0000	-.1293	-.0114
N_3	-.1162	-.0266	-.0003	.0000	-.1431	-.0269
N_4	-.1186	-.0073	-.0006	.0000	-.1265	-.0079
O	-.1796	.0021	-.0006	.0000	-.1781	.0015

Table 2.4 continued

i) Tetracyanoethylene

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
C_1	.0661	.0038	-.0004	.0000	.0695	.0034
C_3	.0934	.0136	.0006	.0000	.1076	.0142
N	-.1264	-.0155	-.0004	.0000	-.1423	-.0159

j) Formic acid

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
H_1	-.0315	.0114	-.0017	.0002	-.0216	.0099
H_2^*	.1901	.0237	.0236	-.0012	.2362	.0461
C	.4019	.0143	.0110	-.0110	.4251	.0242
O_1	-.2374	-.0085	-.0301	.0013	-.2747	-.0373
O_2	-.3231	-.0408	-.0027	.0008	-.3658	-.0427

Table 2.4 continued

k) Melamine

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
H_1	.1039	.0138	.0090	-.0002	.1260	.0221
H_2	.1045	.0030	.0023	.0000	.1078	.0053
H_3^*	.1186	.0173	.0105	-.0003	.1462	.0276
H_4	.1180	.0015	.0004	.0000	.1199	.0019
H_5	.1182	.0019	.0059	-.0002	.1358	.0176
H_6	.1199	.0135	.0079	-.0002	.1411	.0212
N_1	-.3684	-.0135	.0001	.0001	-.3817	-.0133
N_2	-.3673	-.0177	.0011	.0001	-.3838	-.0165
N_3	-.3658	-.0137	.0002	.0001	-.3792	-.0134
N_4	-.2318	-.0108	-.0124	.0002	-.2548	-.0230
N_5	-.2403	-.0068	-.0140	.0003	-.2602	-.0199
N_6	-.2429	-.0093	-.0143	.0006	-.2709	-.0280
C_1	.3747	.0036	.0028	-.0001	.3810	.0063
C_2	.3811	.0034	.0024	-.0002	.3867	.0056
C_3	.3776	.0037	.0030	-.0002	.3841	.0065

Table 2.4 continued

l) Formamide

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
H_1^*	.1313	.0383	.0018	-.0009	.1805	.0492
H_2	.1601	.0201	.0108	-.0006	.1904	.0303
H_3	-.0458	.0042	-.0023	.0002	-.0437	.0021
C	.3440	.0171	.0109	-.0024	.3596	.0256
N	-.2307	-.0168	-.0322	.0024	-.2773	-.0466
O	-.3589	-.0630	.0010	.0012	-.4197	-.0608

m) Urea

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
H_1^*	.1355	.0179	.0096	-.0004	.1626	.0271
H_2	.1146	.0231	.0029	-.0001	.1405	.0259
N_1	-.2612	-.0148	-.0194	.0009	-.2945	-.0333
C	.4363	.0124	.0061	-.0017	.4731	.0168
O	-.4341	-.0646	.0077	.0009	-.4901	-.0560

Table 2.4 continued

n) Cyanuric acid

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
H_1^*	.1577	.0251	.0138	-.0007	.1959	.0382
H_2	.1570	.0204	.0155	-.0006	.1923	.0353
C_1	.4950	.0225	.0060	-.0005	.4870	.0280
C_2	.4567	.0191	.0068	-.0006	.4820	.0253
N_1	-.2511	-.0037	-.0168	.0006	-.2710	-.0199
N_2	-.2511	-.0044	-.0197	.0006	-.2742	-.0235
O_1	-.3616	-.0366	-.0040	.0006	-.4016	-.0400
O_2	-.3650	-.0388	-.0020	.0006	-.4052	-.0402

o) SF_3BF_4

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
B	.6067	.0041	.0068	-.0101	.6075	.0008
F_1	-.4250	.0173	.0147	-.0078	-.4008	.0242
F_2	-.4184	.0108	.0070	-.0077	-.4083	.0101
F_3	-.3669	-.0295	.0225	-.0270	-.4009	-.0340
F_5	-.1502	-.0087	-.0142	.0124	-.1607	-.0105
F_7	-.1862	.0231	-.0104	.0092	-.1643	.0219
S	1.4572	.0212	-.0347	.0455	1.4892	.0320

Table 2.4 continued

p) NH_4BF_4

Atom	Zero order charge	First order change	Second order change	Third order change	Total charge	CIP
H_1	.2559	.0093	-.0058	.0184	.2778	.0219
H_2	.2559	.0026	-.0056	.0179	.2708	.0149
H_3	.2751	-.0059	-.0064	.0189	.2817	.0066
N	-.0620	-.0001	-.0202	.0172	-.0651	-.0031
B	.6073	.0029	.0059	-.0096	.6065	-.0008
F_1	-.3846	.0018	.0062	-.0129	-.3895	-.0049
F_2	-.4179	.0164	.0109	-.0219	-.4125	.0054
F_3	-.4024	-.0105	.0107	-.0234	-.4256	-.0232

are relatively large. This accounts for the large intramolecular destabilization energies calculated for these crystals. Also, the hydrogen atom in a hydrogen bonded crystal that makes the shortest contact, hence the one likely involved in the strongest hydrogen bond, has the largest crystal induced increase in positive charge for the molecule. This increase in positive charge tends to increase the strength of the bond through an increase in the electrostatic attraction between the hydrogen atom and a region of negative charge on the other molecule whilst it tends to destabilize the molecule in which the hydrogen atom is located.

Of the three molecules with a similar ring structure cyanuric acid has a largely hydrogen bonded lattice, the s-triazine crystal is bound by dispersive forces and the melamine crystal has important contributions from both. For all three crystals, electronic charge is transferred from the hydrogen atoms to the ring with the amount transferred proportional to the strength of the hydrogen bonding in the crystal. That is s-triazine has the smallest polarization while cyanuric acid has the largest polarization due to the crystal interactions.

§ 2.6 Comparison of Theoretical and Experimental Charge Distributions

The diffraction of X-rays by a crystal, in principle, is capable of providing detailed information concerning the one electron density function. This may provide a method for the comparison of detailed experimental results with those from theoretical calculations. However, systematic errors occur in the standard X-ray diffraction approach which obscure the bond density features [93]. In order to overcome these difficulties, recent studies have been carried out using combined neutron and X-ray data [94-96]. Although the results may appear to be encouraging, the net charge distributions obtained vary with the particular model used to fit them to the experimental data [96]. Table 2.5 gives a comparison of typical experimental molecular charge distributions obtained by diffraction methods with those calculated in section 2.3 for s-triazine, melamine, cyanuric acid and TCNE. The charge distribution obtained from an alternate experimental method, ESCA [104], is included for TCNE.

As indicated in the table, the agreement between the calculated charge distributions and those from diffraction experiments is fair but may be poor for the hydrogen atom charges. This poor agreement in general may be due to uncertainties in the diffraction data and the fact that the centre of charge for a bonded hydrogen is not at the position of the proton [79,96]. The effect of this can be seen in the case of s-triazine. Although the agreement for the hydrogen and carbon charges is still poor, a great deal of improvement is obtained when the atomic coordinates are treated as variables, thus allowing for a shift in the position of the hydrogen atom of .13 Å. The agreement of the theoretical charge distributions with those from the ESCA experiments is much better than for diffraction experiments but these experiments could not detect any change in charge distribution on crystallization.

An alternate method of investigating the crystal induced change in charge distribution is to examine the change in dipole moment on crystallization. The changes in the components along three orthogonal directions in the molecule as well as the net change in magnitude of the dipole moments for HCN, urea, formamide and formic acid are given

Table 2.5 Theoretical and experimental net atomic charges for s-triazine, melamine, cyanuric acid and TCNE.

a) s-triazine

Atom	Theoretical	Experimental[96]	
H	-.02	.48*	.26**
C	.22	-.13	-.06
N	-.21	-.35	-.21

*Best agreement between the model charge distribution and the experimental data.

**Atomic coordinates treated as variables in the model of the charge distribution.

b) melamine

Atom	Theoretical	Experimental[72]
H_1	.13	.20
H_2	.11	.27
H_3	.15	.36
H_4	.12	.32
H_5	.13	.24
H_6	.14	.22
C_1	.38	.20
C_2	.37	.30
C_3	.38	.24

Atom	Theoretical	Experimental[72]
N_1	-.38	-.41
N_2	-.38	-.42
N_3	-.38	-.38
N_4	-.25	-.45
N_5	-.26	-.35
N_6	-.27	-.34

Table 2.5 Continued

c) cyanuric acid

Atom	Theoretical	Experimental [102]
H_1	.19	.33
H_2	.19	.24
C_1	.49	.30
C_2	.48	.15
N_1	-.27	-.61
N_2	-.27	-.54
O_1	-.40	-.08
O_2	-.41	.15

d) TCNE

Atom	Theoretical	Experimental [103] (diffraction)	Experimental [104] (ESCA)
C_1	.07	.20	.04
C_3	.11	-.04	.17
N	-.14	-.06	-.19

in table 2.6 along with the experimental values for HCN and urea. The net changes given in the table are a result only of the crystal field; no attempt has been made to assess the changes due to differences in molecular configuration which are assumed to be negligible. The agreement with experiment appears poor. However, the relative sign of the change is correct, an increase for urea and a decrease for HCN. The two experimental results for urea are quite different, the calculated value falling between them. The calculated change for HCN differs considerably from the 60% increase predicted by a recent calculation of Munn et al.[108]. This calculation was, however, based on a point dipole approximation which, since some intermolecular contacts in HCN, 2.12 Å, are less than the length of the molecule itself, 2.22 Å, cannot be expected to apply.

The most notable feature of the calculated changes in dipole moment is that they are not necessarily negligibly small as might be expected from the results of Crowe and Santry[62] for the lattice water molecules in α and β oxalic acid dihydrate and hexagonal and cubic ice. The dipole moment of a molecule, μ, in general can be written as the sum of two contributions[51]

$$\mu = \mu_{\text{charge}} + \mu_{\text{hybrid}} , \qquad (2.11)$$

where μ_{charge} is the dipole moment contribution from net atomic charges and μ_{hybrid} is proportional to the $P_{2s,2p}$ bond orders. For the lattice water[62] and HCN it is a cancellation of these two terms rather than the size of the terms themselves that leads to the small induced change in dipole moment. For urea, formamide and formic acid, the terms themselves

Table 2.6 Crystal field induced changes in the dipole moments of HCN, urea, formamide and formic acid.

Change in dipole moment (D)	HCN	urea	formamide	formic acid
$\Delta\mu_x$	0	0	-.1515	.1458
$\Delta\mu_y$	0	0	.4280	.1896
$\Delta\mu_z$	-.0240	-.3888	.2691	.0239
net change in magnitude	-.0240	.3888	.4768	.1866
experimental change	-.6 [105]	.98 [106] .10 [107]		
calculated zero order dipole moment	2.4636	4.9403	3.9712	1.2651
experimental free molecule dipole moment	2.95 [108]	4.56 [106]	3.71 [108]	1.35 [108]

A zero without a decimal point indicates a component that is zero by symmetry. The calculated zero order dipole moment corresponds to an isolated molecule with the geometry of the crystal molecule.

are large and the cancellation is less efficient so that the resultant changes can be relatively large.

In summary, the agreement between the theoretical and experimental charge distributions is only fair and until experiments are done that can detect the change in the charge distribution on crystallisation directly are done, any meaningful comparison between experimental results and the predictions of different theoretical calculations cannot be made. However, the calculated changes in the charge distribution are expected to be within reason as these changes are due to the intermolecular perturbation and the contribution to the energy of the crystals from this source are reasonable.

CHAPTER 3

A Self Consistent Field Perturbation Theory for Band Structures

§ 3.1 Introduction

Band structure calculations give an indication of the relative effect of intermolecular interactions on particular molecular levels in a crystal through the amount of dispersion of the bands derived from the levels. The greater the dispersion, the greater the effect of the interaction. Also, the density of states calculable from the band energies is directly comparable to the one obtained by the experimental technique ESCA. This comparison has been done recently for the ethylene polymer [116] and the extension of the theoretical portion of the approach to three dimensional hydrogen bonded crystals is given in section 3.5.

Bands in the electronic energy are a characteristic of any periodic structure [110] and the periodicity of the lattice is often used in order to simplify the calculation of these bands. For instance, in the conventional approach to band structure calculations, [111-115] the atomic basis functions are written in a symmetrized form characterized by a wave vector $\bar{k}$,

$$\psi_\mu(\bar{k}) = N^{-\frac{1}{2}} \sum_s \exp(2\pi i \bar{k}\cdot\bar{s})\chi_\mu(\bar{s}) \tag{3.1}$$

where N is the number of unit cells in the lattice, $\chi_\mu(\bar{s})$ is the $\mu^{\underline{th}}$ atomic orbital in the $s^{\underline{th}}$ unit cell and the summation is over all unit cells in the lattice. The crystal orbitals, $C_\ell(\bar{k})$, are the solutions of the wave vector dependent SCF matrix equations

$$\underline{F}(\bar{k})\underline{C}(\bar{k}) = \underline{S}(\bar{k})\underline{C}(\bar{k})\underline{E}(\bar{k}) , \qquad (3.2)$$

where the Fock matrix, $\underline{F}(\bar{k})$, the crystal orbital matrix $\underline{C}(\bar{k})$, the overlap matrix $\underline{S}(\bar{k})$ and the orbital energy matrix $\underline{E}(\bar{k})$ are referred to the basis of symmetrized atomic orbitals $\psi_\mu(\bar{k})$.

There are an infinite number of these equations, one for each value of $\bar{k}$. For most systems, however, only a finite set of these equations need be solved [111].

For one dimensional crystals and polymers, the scalar character of the wave vector simplifies the theory and limits the amount of computation necessary. However, for three dimensional systems, the vector character of $\bar{k}$ complicates the calculations to the point where even approximate studies of chemically and biologically significant systems become prohibitively time consuming. Furthermore, much of this computational effort is wasted in the case of molecular crystals. The first stage of such a calculation involves setting up delocalized orbitals, the $C_\ell(\bar{k})$, which then are localized to some extent by the solution of the coupled equations (3.2). An alternate approach is clearly required for these crystals in order to avoid the large amount of computational effort and to facilitate calculations for aggregates of complex molecules.

The SCF perturbation theory proposed by Bacon and Santry [60-65] avoids many of the disadvantages of the above approach by using a localized basis set for the crystal rather than a delocalized set of the form in equation (3.1). As this theory was specifically developed to provide a computational method which is independent of the wave vector concept, it does not yield crystal orbitals or band structures. The only quantities calculated are the crystal binding energy, bond order matrix and Fock matrix.

Nonetheless, the crystal band structure can, in principle, be calculated from the crystal Fock matrix by the introduction of wave vector dependent symmetry orbitals on completion of the SCF perturbation calculation. A significant advantage of this approach, besides the saving in computational effort, is that individual energy bands can be calculated independent of the rest of the levels as long as there is no crossing of bands.

§ 3.2 The Orbital Energies

The Fock matrix for the crystal, from equation (1.70), is given to the third order by

$$\underline{F} = \underline{F}^{(0)} + \underline{F}^{(1)} + \underline{F}^{(2)} + \underline{F}^{(3)}. \qquad (3.3)$$

Similarly, the corresponding orbital energy matrix is given to the third order by

$$\underline{E} = \underline{E}^{(0)} + \underline{E}^{(1)} + \underline{E}^{(2)} + \underline{E}^{(3)}. \qquad (3.4)$$

Expressions for the various $\underline{E}^{(n)}$'s can be readily derived from the corresponding perturbation equations (1.73) for the $\ell^{\underline{th}}$ band level. For the zeroth order, writing $\underline{Q}^{(0)}$ for the zeroth order crystal orbital, equation (1.73) yields

$$\underline{F}^{(0)}\underline{O}^{(0)} = \underline{O}^{(0)}\underline{E}^{(0)} \tag{3.5}$$

Multiplication on the left by $\underline{\check{O}}^{(0)}$[†], gives, after making use of the orthonormality of the zero order crystal orbitals,

$$\underline{\check{O}}^{(0)}\underline{F}^{(0)}\underline{O}^{(0)} = \underline{E}^{(0)}. \tag{3.6}$$

Hence, the zero order orbital energy for the ℓth band level is

$$E_{\ell\ell}^{(0)} = \check{O}_{\ell}^{(0)}\underline{F}^{(0)}O_{\ell}^{(0)} = F_{\ell\ell}^{(0)}. \tag{3.7}$$

The first order perturbation equation is

$$\underline{F}^{(1)}\underline{O}^{(0)} + \underline{F}^{(0)}\underline{O}^{(1)} = \underline{O}^{(1)}\underline{E}^{(0)} + \underline{O}^{(0)}\underline{E}^{(1)} \tag{3.8}$$

Multiplication on the left by $\underline{\check{O}}^{(0)}$ gives

$$\underline{\check{O}}^{(0)}\underline{F}^{(1)}\underline{O}^{(0)} + \underline{\check{O}}^{(0)}\underline{F}^{(0)}\underline{O}^{(1)} = \underline{\check{O}}^{(0)}\underline{O}^{(1)}\underline{E}^{(0)} + \underline{\check{O}}^{(0)}\underline{O}^{(0)}\underline{E}^{(1)} \tag{3.9}$$

Substituting the analogue of equation (1.78),

$$\underline{O}^{(1)} = \underline{O}^{(0)}\underline{A} \tag{3.10}$$

into (3.9) and making use of the orthonormality of the zero order crystal orbitals yields

$$\underline{\check{O}}^{(0)}\underline{F}^{(1)}\underline{O}^{(0)} + \underline{\check{O}}^{(0)}\underline{F}^{(0)}\underline{O}^{(0)}\underline{A} = \underline{A}\underline{E}^{(0)} + \underline{E}^{(1)}, \tag{3.11}$$

and for the ℓth band level

[†] Here, and in subsequent usage, $\underline{\check{O}}$ implies $\underline{O}$ complex conjugate transposed.

$$F_{\ell\ell}^{(1)} + \sum_m F_{\ell m}^{(0)} A_{m\ell} = \sum_m A_{\ell m} E_{m\ell}^{(0)} + E_{\ell\ell}^{(1)}, \tag{3.12}$$

where the summations are over all the crystal orbitals. Since $\underline{F}^{(0)}$ and $\underline{E}^{(0)}$ are diagonal and $A_{\ell\ell} = 0$, the net result for the first order correction to the energy of the $\ell^{\underline{th}}$ band is

$$E_{\ell\ell}^{(1)} = F_{\ell\ell}^{(1)}. \tag{3.13}$$

The second order contribution is obtained in much the same way as the first. After multiplication on the left by $\underline{O}^{\dagger(0)}$, the second order perturbation equation is

$$\underline{O}^{\dagger(0)}\underline{F}^{(2)}\underline{O}^{(0)} + \underline{O}^{\dagger(0)}\underline{F}^{(1)}\underline{O}^{(1)} + \underline{O}^{\dagger(0)}\underline{F}^{(0)}\underline{O}^{(2)}$$
$$= \underline{O}^{\dagger(0)}\underline{O}^{(2)}\underline{E}^{(0)} + \underline{O}^{\dagger(0)}\underline{O}^{(1)}\underline{E}^{(1)} + \underline{O}^{\dagger(0)}\underline{O}^{(0)}\underline{E}^{(2)}. \tag{3.14}$$

After substituting the crystal orbital analogue of equation (1.85) into the above and making use of the orthonormality of the zero order crystal orbitals, one obtains for the $\ell^{\underline{th}}$ band level,

$$F_{\ell\ell}^{(2)} + \sum_m F_{\ell m}^{(1)} A_{m\ell} + \sum_m F_{\ell m}^{(0)} (B_{m\ell} + b_{m\ell})$$
$$= \sum_m (B_{\ell m} + b_{\ell m}) E_{m\ell}^{(0)} + \sum_m A_{\ell m} E_{m\ell}^{(1)} + E_{\ell\ell}^{(2)}, \tag{3.15}$$

and since the diagonal elements of $\underline{A}$ and $\underline{b}$ are equal to zero and $\underline{F}^{(0)}$ and the $\underline{E}^{(n)}$ are all diagonal, with $F_{\ell\ell}^{(0)} = E_{\ell\ell}^{(0)}$,

$$E_{\ell\ell}^{(2)} = F_{\ell\ell}^{(2)} + \sum_m F_{\ell m}^{(1)} A_{m\ell}. \tag{3.16}$$

The summations in the above are over all crystal orbitals. Similarly the third order contribution is

$$E^{(3)}_{\ell\ell} = F^{(3)}_{\ell\ell} + \sum_{m}^{\text{crystal orbitals}} \{F^{(1)}_{\ell m}(B_{m\ell} + b_{m\ell}) + F^{(2)}_{\ell m} A_{m\ell}\}. \qquad (3.17)$$

§ 3.3 The Zero Order Crystal Orbitals [117]

The inclusion of intermolecular interactions into the crystal perturbation equations strictly requires that the solutions, to all orders, transform irreducibly under the crystal space group. Since the zero order solutions chosen for the perturbation calculations are the unperturbed molecular orbitals of the lattice molecules, they are localized and reducible under the crystal space group. Moreover, as they are degenerate, they cannot be used in equations (3.7), (3.13), (3.16) and (3.17) to calculate the crystal band structure. However, a zero order transformation of these localized molecular orbitals to crystal orbitals that have the required transformation properties may be undertaken. As this transformation is unitary, it does not affect the crystal bond order matrix or the lattice energy, in the same way as unitary transformations of molecular orbitals do not affect the calculation of molecular bond orders and total electronic energy [44], and may, therefore, be neglected for calculations of these quantities. It does, however, have a significant effect on the calculated crystal orbital energies and, in fact, leads to the appearance of the band structure in the present treatment of molecular crystals.

This transformation is undertaken in two steps. The zero order molecular orbitals from translationally equivalent molecules are first combined to give crystal orbitals that transform irreducibly under the translational sub-group of the crystal space group. Linear combinations of these orbitals are then taken over all the unit cell sites to yield, where possible, irreducible representations of the unit cell group.

The zero order single site functions that transform, according to Bloch's theorem [36a], irreducibly under the translational sub-group are given by

$$D^{(0)}_{t,\ell}(\bar{k}) = N^{-\frac{1}{2}} \sum_{\bar{R}}^{\text{crystal}} \exp\{2\pi i\bar{k}\cdot(\bar{R} + \bar{t})\}C^{(0)}_{\ell}(\bar{R},\bar{t}), \qquad (3.18)$$

where $D^{(0)}_{t,\ell}(\bar{k})$ is the delocalized crystal orbital corresponding to the $\ell^{\underline{th}}$ free molecular level associated with the $t^{\underline{th}}$ unit cell molecule: it is a column vector of the same dimension as the almost infinite Fock matrix, with the same ordering as the basis set. N is the number of unit cells, labelled by $\bar{R}$ and $\bar{k}$ is a wave vector with values limited by the Born-von-Karman cyclic boundary condition [118]. There is one single site function for a given $\bar{k}$ and ℓ, for each molecule in the unit cell. These functions are combined to yield the final zero order crystal orbitals, $O^{(0)}_{\lambda,\ell}(\bar{k})$:

$$O^{(0)}_{\lambda,\ell}(\bar{k}) = \sum_{t}^{\text{unit cell}} \omega^{\ell}_{\lambda,t}(\bar{k})D^{(0)}_{t,\ell}(\bar{k}) \qquad (3.19)$$

where the summation is over all molecules in the unit cell. The coefficients $\omega^{\ell}_{\lambda,t}(\bar{k})$ may be determined by symmetry except for the case of wavevectors which are not invariant under the crystal point group. The discussion of their evaluation will be presented later. There are as many combinations, labelled by λ, as there are molecules in the unit cell. The inclusion of the site vector, $\bar{t}$, in the phase factor in equation (3.18) is to ensure that the various lattice sums that appear in the theory will be real for most crystals.

Substituting $O^{(0)*}_{\lambda,\ell}(\bar{k})$ for $O^{(0)}_{\ell}$ in the equations for the contributions to the $\ell^{\underline{th}}$ band level and using the expansions for $\underline{A}$, $\underline{B}$ and $\underline{b}$, equations (1.81), (1.88) and (1.90), one has

$$E^{(0)}_{\ell,\lambda}(\bar{k}) = \tilde{O}^{(0)}_{\lambda,\ell}(\bar{k})\underline{F}^{(0)}O^{(0)}_{\lambda,\ell}(\bar{k}), \tag{3.20}$$

$$E^{(1)}_{\ell,\lambda}(\bar{k}) = \tilde{O}^{(0)}_{\lambda,\ell}(\bar{k})\underline{F}^{(1)}O^{(0)}_{\lambda,\ell}(\bar{k}), \tag{3.21}$$

$$\begin{aligned} E^{(2)}_{\ell,\lambda}(\bar{k}) &= \tilde{O}^{(0)}_{\lambda,\ell}(\bar{k})\underline{F}^{(2)}O^{(0)}_{\lambda,\ell}(\bar{k}) \\ &+ \sum_{m}^{\text{molecular levels}} \tilde{O}^{(0)}_{\lambda,\ell}(\bar{k})\underline{F}^{(1)}O^{(0)}_{\lambda,m}(\bar{k})\tilde{O}^{(0)}_{\lambda,m}(\bar{k})\underline{F}^{(1)}O^{(0)}_{\lambda,\ell}(\bar{k})/(\varepsilon^{(0)}_{\ell}-\varepsilon^{(0)}_{m}) \end{aligned} \tag{3.22}$$

$$\begin{aligned} E^{(3)}_{\ell,\lambda}(\bar{k}) &= \tilde{O}^{(0)}_{\lambda,\ell}(\bar{k})\underline{F}^{(3)}O^{(0)}_{\lambda,\ell}(\bar{k}) \\ &+ \sum_{m}^{\text{molecular levels}} \{\tilde{O}^{(0)}_{\lambda,\ell}(\bar{k})\underline{F}^{(1)}O^{(0)}_{\lambda,m}(\bar{k})\,(\tilde{O}^{(0)}_{\lambda,m}(\bar{k})\underline{F}^{(2)}O^{(0)}_{\lambda,\ell}(\bar{k}) \\ &+ \sum_{n}^{\text{molecular levels}} (\tilde{O}^{(0)}_{\lambda,m}(\bar{k})\underline{F}^{(1)}O^{(0)}_{\lambda,n}(\bar{k})\tilde{O}^{(0)}_{\lambda,n}(\bar{k})\underline{F}^{(1)}O^{(0)}_{\lambda,\ell}(\bar{k})/(\varepsilon^{(0)}_{\ell}-\varepsilon^{(0)}_{n})) \\ &- \tilde{O}^{(0)}_{\lambda,m}(\bar{k})\underline{F}^{(1)}O^{(0)}_{\lambda,\ell}(\bar{k})\tilde{O}^{(0)}_{\lambda,\ell}(\bar{k})\underline{F}^{(1)}O^{(0)}_{\lambda,\ell}(\bar{k})/(\varepsilon^{(0)}_{m}-\varepsilon^{(0)}_{\ell})) \\ &+ \tilde{O}^{(0)}_{\lambda,\ell}(\bar{k})\underline{F}^{(2)}O^{(0)}_{\lambda,m}(\bar{k})\tilde{O}^{(0)}_{\lambda,m}(\bar{k})\underline{F}^{(1)}O^{(0)}_{\lambda,\ell}(\bar{k})\}/(\varepsilon^{(0)}_{m}-\varepsilon^{(0)}_{\ell}), \end{aligned} \tag{3.23}$$

where use has been made of the equalities

$$\gamma^{(0)}_{\lambda,\ell}(\bar{k})\underline{F}^{(1)}O^{(0)}_{\lambda',m}(\bar{k}') = 0 \text{ unless } k=k' \text{ and } \lambda=\lambda', \tag{3.24}$$

$$\gamma^{(0)}_{\lambda,\ell}(\bar{k})\underline{F}^{(2)}O^{(0)}_{\lambda',m}(\bar{k}') = 0 \text{ unless } k=k' \text{ and } \lambda=\lambda', \tag{3.25}$$

to exclude the summations over k and λ in the summations over crystal orbitals. The above conditions hold exactly for wavevectors that are invariant with respect to the crystal space group as then $\bar{k}$ and λ label irreducible representations of this group. However, λ=λ' does not hold for the general wavevector since the ω's may not be symmetry determined. Nonetheless, it will be shown that this approximation does not significantly affect the resultant band structures except in the case of very strongly interacting crystal molecules.

It is necessary to distinguish two cases for the determination of the ω's according to the transformation properties of the wave vector $\bar{k}$ [119]. In the first, the wave vector is invariant to all the operations of the group of the unit cell. Under these circumstances, the ω's are determined by the symmetry of the unit cell and are thus independent of both ℓ and $|\bar{k}|$. In the second case, the application of the unit cell group operators generates a star of $\bar{k}$'s[36a] from the original $\bar{k}$. Each member of the star is invariant only to a sub-group of the unit cell group, called the group of $\bar{k}$. Only the group of $\bar{k}$ can be used to determine the ω's. This group is often sufficient for crystals of high symmetry to fix the ω's, but for crystals of low symmetry some independent method for calculating them may be required.

Consider first the case in which the wave vector $\bar{k}$ is invariant with respect to all unit cell operations and the unit cell group has no degenerate representations for $\bar{k}$=0. Under these circumstances, assuming the neglect of overlap, the $\omega^{\ell}_{\lambda,t}(\bar{k})$ form a unitary matrix with elements equal to $\pm Z^{-\frac{1}{2}}$, where Z is the number of molecules in the unit cell and the dependence on ℓ and k can be omitted. Hence, equation (3.19) can be written

$$O^{(0)}_{\lambda,\ell}(\bar{k}) = \sum_{t}^{\text{unit cell}} \omega_{\lambda,t} D^{(0)}_{t,\ell}(\bar{k}) \qquad (3.26)$$

In the case of the general wave vector, the crystal symmetry is usually insufficient to completely determine the ω's and it is necessary to use an alternate method for calculating them. In the present treatment [117], the ω's are calculated by requiring that the orbital energy matrix be diagonal. Thus, for a given $\bar{k}$ and ℓ

$$\begin{aligned} E_{\ell\lambda,\ell\lambda'}(\bar{k}) &= E^{(0)}_{\ell\lambda,\ell\lambda'}(\bar{k}) + E^{(1)}_{\ell\lambda,\ell\lambda'}(\bar{k}) + E^{(2)}_{\ell\lambda,\ell\lambda'}(\bar{k}) + E^{(3)}_{\ell\lambda,\ell\lambda'}(\bar{k}) \\ &= 0, \quad \lambda \neq \lambda'. \end{aligned} \qquad (3.27)$$

Expanding the zero order crystal orbitals in equation (3.20) gives, for the zero order contribution to the band energy,

$$\begin{aligned} E^{(0)}_{\ell\lambda,\ell\lambda'}(\bar{k}) = N^{-1} \sum_{t}^{\text{unit}} \sum_{v}^{\text{cell}} \omega^{\ell}_{\lambda,t}(\bar{k}) \omega^{\ell}_{\lambda',v}(\bar{k}) \sum_{R}^{\text{crystal}} \sum_{S} e^{2\pi i \bar{k}\cdot(\bar{S}+\bar{v}-\bar{R}-\bar{t})} \\ \cdot \tilde{C}^{(0)}_{\ell}(\bar{R},\bar{t}) \underline{F}^{(0)} C^{(0)}_{\ell}(\bar{S},\bar{v}). \end{aligned} \qquad (3.28)$$

Using the block diagonal property of $\underline{F}^{(0)}$,

$$E^{(0)}_{\ell\lambda,\ell\lambda'}(k) = N^{-1} \sum_{t}^{\text{unit cell}} \omega^{\ell}_{\lambda,t}(\bar{k}) \omega^{\ell}_{\lambda',t}(\bar{k}) \sum_{R}^{\text{crystal}} {}^{Rt,Rt}F^{(0)}_{\ell\ell}, \qquad (3.29)$$

and since the orbital energy matrix is diagonal to all orders, then $\lambda=\lambda'$, and

$$E^{(0)}_{\ell\lambda,\ell\lambda}(\bar{k}) = N^{-1}\sum_{t}^{\text{unit cell}}\{\omega^{\ell}_{\lambda,t}(\bar{k})\}^{2}\sum_{R}^{\text{crystal}}{}^{Rt,Rt}F^{(0)}_{\ell\ell}$$

$$= {}^{Rt,Rt}F^{(0)}_{\ell\ell} = \varepsilon^{(0)}_{\ell} \qquad (3.30)$$

Hence, the zero order term does not restrict the ω's at all. Similarly the first order contribution is given by

$$E^{(1)}_{\ell\lambda,\ell\lambda'}(\bar{k}) = N^{-1}\sum_{t}^{\text{unit cell}}\sum_{v}\omega^{\ell}_{\lambda,t}(\bar{k})\,\omega^{\ell}_{\lambda',v}(\bar{k})\sum_{R}^{\text{crystal}}\sum_{S} e^{2\pi i\bar{k}\cdot(\bar{S}+\bar{v}-\bar{R}-\bar{t})}$$

$$\cdot\, \mathcal{C}^{(0)}_{\ell}(\bar{R},\bar{t})\,\underline{F}^{(1)}\,C^{(0)}_{\ell}(\bar{S},\bar{v})$$

$$= \sum_{t}^{\text{unit cell}}\sum_{v}\omega^{\ell}_{\lambda,t}(\bar{k})\,\omega^{\ell}_{\lambda',v}(\bar{k})\sum_{S}^{\text{crystal}} e^{2\pi i\bar{k}\cdot(\bar{S}+\bar{v}-\bar{R}-\bar{t})}\;{}^{Rt,Sv}F^{(1)}_{\ell\ell}\,. \qquad (3.31)$$

This may be conveniently expressed as

$$E^{(1)}_{\ell\lambda,\ell\lambda'}(\bar{k}) = \sum_{t}^{\text{unit cell}}\sum_{v}\omega^{\ell}_{\lambda,t}(\bar{k})\,\omega^{\ell}_{\lambda',v}(\bar{k})\,G^{(1)}_{t\ell,v\ell}(\bar{k}) \qquad (3.32)$$

where $G^{(1)}_{t\ell,v\ell}(\bar{k})$ is the phase modulated sum based on $F^{(1)}_{\ell\ell}$ given by

$$G^{(1)}_{t\ell,v\ell}(\bar{k}) = \sum_{S}^{\text{crystal}} e^{2\pi i\bar{k}\cdot(\bar{S}+\bar{v}-\bar{R}-\bar{t})}\;{}^{Rt,Sv}F^{(1)}_{\ell\ell}\,. \qquad (3.33)$$

As the ω's are the coefficients for the single site functions, $\underline{D}$, in the crystal orbitals, the condition that the first order orbital energy matrix be diagonal is satisfied by the ω's that diagonalize the Z X Z matrix over single site functions,

$$\left(D^{(0)}_{t,\ell}(\bar{k})\underset{\sim}{F}^{(1)}D^{(0)}_{v,\ell}(\bar{k})\right) = \left(G^{(1)}_{t\ell,v\ell}(\bar{k})\right). \tag{3.34}$$

These ω's will differ from $\pm Z^{-\frac{1}{2}}$ if, for the particular $\bar{k}$ direction, the diagonal $\underset{\sim}{G}$ lattice sums are not equal. The generality of this condition can be illustrated by considering the hypothetical two dimensional crystal shown in figure 3.1. As there are two molecules per unit cell, the calculation of the ω's for a given ℓ and general $\bar{k}$ involves the diagonalization of the 2 X 2 matrix:

$$\begin{pmatrix} G^{(1)}_{I\ell,I\ell}(\bar{k}) & G^{(1)}_{I\ell,II\ell}(\bar{k}) \\ G^{(1)}_{II\ell,I\ell}(\bar{k}) & G^{(1)}_{II\ell,II\ell}(\bar{k}) \end{pmatrix} \tag{3.35}$$

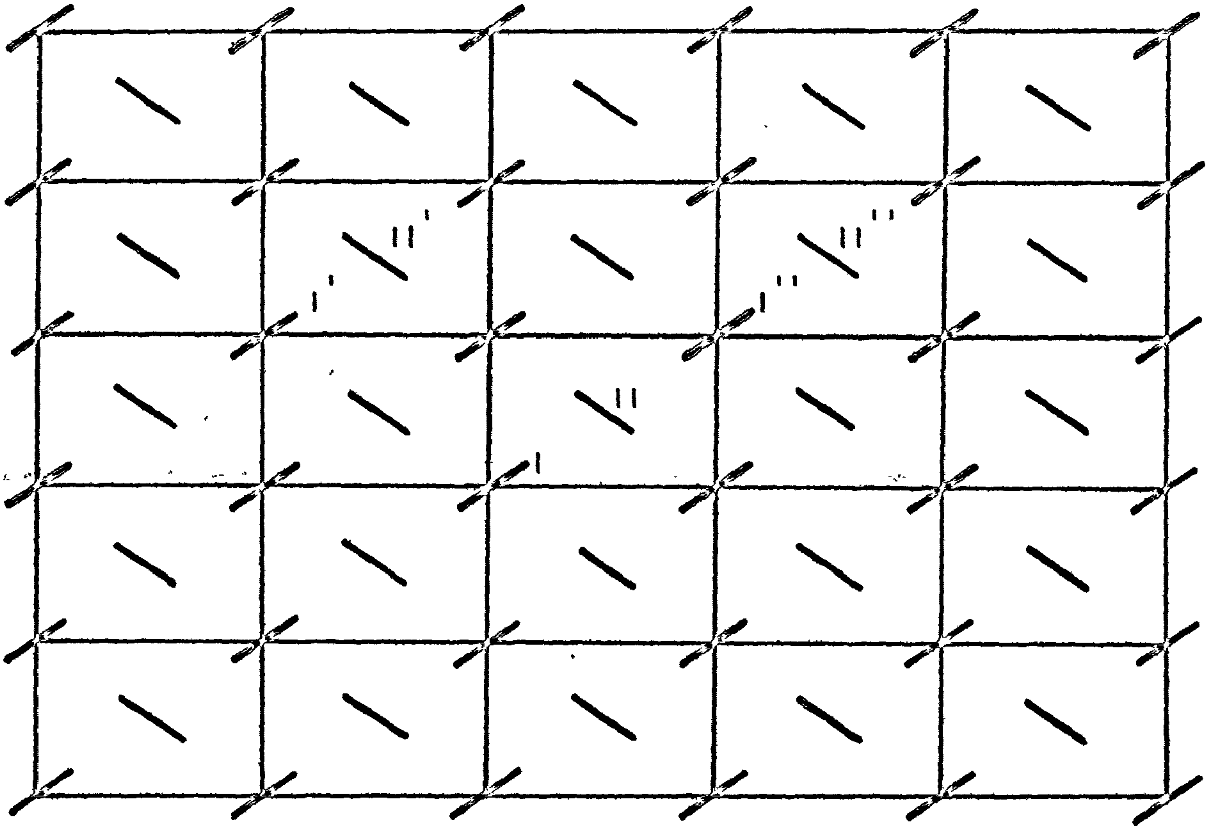
The eigenvalues will differ from $\pm 2^{-\frac{1}{2}}$ if

$$G^{(1)}_{I\ell,I\ell}(\bar{k}) \neq G^{(1)}_{II\ell,II\ell}(\bar{k}). \tag{3.36}$$

In the calculation of the I-I lattice sum all interactions between molecules I and I$'$ are included and the corresponding II-II$'$ interactions are included for the II-II sum. For each I-I$'$ interaction there is an equal II-II$'$ interaction but with a different direction for the vector $\bar{R}$. Thus, although the same interactions are found in both sums, they are included with different phase factors.

From the figure it can be seen that it is the fairly long range

Figure 3.1



The hypothetical two dimensional crystal with two molecules per unit cell.

interactions that are responsible for the inequality of the diagonal lattice sums. Fortunately, the unit cell dimensions and intermolecular interactions for the crystals studied in section 3.4, are such that only nearest neighbours contribute significantly to the diagonal $\underline{G}$ lattice sums so that the differences between these sums are negligible, and the corresponding ω's can be approximated by $\pm Z^{-\frac{1}{2}}$. To illustrate this the $\underline{G}^{(1)}$ and $\underline{G}^{(2)}$ lattice sums for the lowest occupied molecular level of formamide are given in tables 3.1 and 3.2. From these tables it can be seen that the diagonal sums do not differ significantly and the approximation for the ω's is valid.

In general, then, if the discussion is limited to those crystals for which the unit cell group has no degenerate irreducible representations and all the unit cell molecules are symmetry related, the ω's may be taken as the characters for the $\lambda^{\underline{th}}$ representation of this group times an appropriate normalization factor. This is a common approximation in the theory of excitons and is known as the restricted Frenkel limit [120].

Equation (3.32) may be written, neglecting the dependence of ω on k and ℓ,

$$E^{(1)}_{\ell\lambda,\ell\lambda}(\bar{k}) = \sum_{t}^{\text{unit cell}} \sum_{v} \omega_{\lambda,t}\omega_{\lambda,v}G^{(1)}_{t\ell,v\ell}(\bar{k}). \qquad (3.37)$$

Similarly, the second and third order contributions to the band energy may be expressed as

Table 3.1 The first order lattice sums, $G^{(1)}_{t\ell,v\ell}(\bar{k})$, for the lowest occupied level of formamide and k = (.2, .4, .8).

	1	2	3	4
1	.000457	.000470	.001053	-.001138
2	.000470	.000457	.001415	-.008349
3	.001053	.001425	.000456	-.001232
4	-.001138	-.008349	-.001232	.000456

Table 3.2 The second order lattice sums, $G^{(2)}_{t\ell,v\ell}(\bar{k})$, for the lowest occupied level of formamide and k = (.2, .4, .8).

	1	2	3	4
1	.006583	.000000	.000119	-.000041
2	.000000	.006583	.000048	-.000162
3	.000119	.000048	.006582	-.000000
4	-.000041	-.000162	-.000000	.006582

$$E^{(2)}_{\ell\lambda,\ell\lambda}(\bar{k}) = \sum_{t}^{\text{unit cell}} \sum_{v} \omega_{\lambda,t}\,\omega_{\lambda,v}\,G^{(2)}_{t\ell,v\ell}(\bar{k})$$

$$+ \sum_{t}^{\text{unit cell}} \sum_{u} \sum_{v} \sum_{w} \omega_{\lambda,t}\,\omega_{\lambda,u}\,\omega_{\lambda,v}\,\omega_{\lambda,w} \sum_{m}^{\text{mls.}} G^{(1)}_{t\ell,um}(\bar{k})\,G^{(1)}_{vm,w\ell}(\bar{k})/(\varepsilon^{(0)}_{\ell}-\varepsilon^{(0)}_{m})$$

$$(3.38)$$

and

$$E^{(3)}_{\ell\lambda,\ell\lambda}(\bar{k}) = \sum_{t}^{\text{unit cell}} \sum_{v} \omega_{\lambda,t}\,\omega_{\lambda,v}\,G^{(3)}_{t\ell,v\ell}(\bar{k})$$

$$+ \sum_{t}^{\text{unit cell}} \sum_{u} \sum_{v} \sum_{w} \omega_{\lambda,t}\,\omega_{\lambda,u}\,\omega_{\lambda,v}\,\omega_{\lambda,w} \sum_{m}^{\text{mls.}} G^{(1)}_{t\ell,um}(\bar{k})\,G^{(2)}_{vm,w\ell}(\bar{k}) + G^{(2)}_{t\ell,um}(\bar{k})\,G^{(1)}_{vm,w\ell}(\bar{k})$$

$$- \sum_{t}^{\text{unit cell}} \sum_{u} \sum_{v} \sum_{w} \sum_{x} \sum_{y} \omega_{\lambda,t}\,\omega_{\lambda,u}\,\omega_{\lambda,v}\,\omega_{\lambda,w}\,\omega_{\lambda,x}\,\omega_{\lambda,y}$$

$$\cdot \sum_{m}^{\text{mls.}} \left(\frac{G^{(1)}_{tm,u\ell}(\bar{k})\,G^{(1)}_{v\ell,w\ell}(\bar{k})\,G^{(1)}_{x\ell,ym}(\bar{k})}{(\varepsilon^{(0)}_{\ell} - \varepsilon^{(0)}_{m})(\varepsilon^{(0)}_{\ell} - \varepsilon^{(0)}_{m})} - \sum_{n}^{\text{mls.}} \left\{ \frac{G^{(1)}_{t\ell,um}(\bar{k})\,G^{(1)}_{vm,wn}(\bar{k})\,G^{(1)}_{xn,y\ell}(\bar{k})}{(\varepsilon^{(0)}_{\ell} - \varepsilon^{(0)}_{m})(\varepsilon^{(0)}_{\ell} - \varepsilon^{(0)}_{n})} \right\} \right)$$

$$(3.39)$$

In the above, mls. indicates the summation over molecular levels.

Upon the completion of an SCF perturbation calculation for a particular crystal, equations (3.30), (3.37), (3.38), and (3.39) can be used to calculate the band energies as a function of wave vector up to third order. From these equations, it can be seen that the energy of each level is independent of the rest if crossing of the levels is ignored. The only crossing that is not allowed is that of levels of the same symmetry. However, if such crossing does occur, it can be simply treated by degenerate perturbation theory.

Unfortunately, the theory in its present form cannot be used to study crystals in which there are molecules that have degenerate zero order molecular orbitals. For these crystals, the denominators in the second and third order contributions to the band energies will be zero for some of the terms in the sum over molecular levels. However, if a degenerate perturbation calculation on the molecular levels or a very small distortion of the molecular structure removes this degeneracy, then the theory could be applied.

§ 3.4 Band Structure Calculations for Ethylene, Naphthalene, Formamide, Formic Acid and Urea.

A. Symmetries of the Valence Set Orbitals

The ethylene crystal is classified under the space group Pnnm(D_{2h}^{12}) of the orthorhombic system and has two molecules per unit cell. These two molecules occupy sites of C_{2h} symmetry hence the crystal molecules are of lower symmetry than the free molecule which has D_{2h} symmetry. The unit cell molecules are related by two fold screw rotations about the $\bar{a}$ and $\bar{b}$ crystal axes, C_2^a and C_2^b, and two glide planes perpendicular to the rotational axes, σ^n and $\sigma^{n'}$. Under the operations that relate the unit cell molecules, the single site functions combine into eight sets of crystal orbitals of symmetries A_g, A_u, B_{1g}, B_{2g}, B_{3g}, B_{1u}, B_{2u} and B_{3u}. A group character analysis of these combinations is given in table 3.3. Any of the four possible choices for the relationships between the single site functions can be used to determine the ω's, the only difference between these choices is in the aribtrary subscripts 1,2 and 3 in the B symmetry labels. Table 3.4 gives the symmetries of the combinations based on the C_2^a operation and hence, the appropriate ω's.

Table 3.3 Group character analysis of the ethylene single site functions under D_{2h}^{12}

Single site function symmetry	$D_1 = ED_1$	$D_2 = C_2^a D_1$	$D_2 = C_2^b D_1$	$D_2 = \sigma^n D_1$	$D_2 = \sigma^{n'} D_1$	crystal orbital symmetry
A_g	+1	+1	+1	+1	+1	A_g
A_g	+1	-1	-1	-1	-1	B_{3g}
A_u	+1	+1	+1	-1	-1	A_u
A_u	+1	-1	-1	+1	+1	B_{3u}
B_g	+1	+1	-1	+1	-1	B_{2g}
B_g	+1	-1	+1	-1	+1	B_{1g}
B_u	+1	+1	-1	-1	+1	B_{2u}
B_u	+1	-1	+1	+1	-1	B_{1u}

Table 3.4 Symmetries of the combinations of ethylene single site functions under the C_2^a operation

Combination of single site functions D_1		D_2	Crystal orbital symmetry
A_g	+	A_g	A_g
A_g	-	A_g	B_{3g}
A_u	+	A_u	A_u
A_u	-	A_u	B_{3u}
B_g	+	B_g	B_{2g}
B_g	-	B_g	B_{1g}
B_u	+	B_u	B_{2u}
B_u	-	B_u	B_{1u}

The naphthalene crystal is monoclinic with space group $P2_1/a(C_{2h}^5)$ and has two molecules per unit cell related by a two fold screw axis, C_2^b, and a glide plane, σ^a. These molecules occupy sites of C_i symmetry which is much lower than the D_{2h} symmetry of the free molecule. Under the operations of the C_i point group, the naphthalene molecular orbitals are classified as of either a_g or a_u symmetry. Hence, the two sets of single site functions have either A_g or A_u symmetry. Under the operations that relate the two molecules in the unit cell, the single site functions combine into four sets of crystal orbitals with symmetries A_g, A_u, B_g, and B_u. A group character analysis of the four combinations and the symmetries of the combinations based on the glide plane operation are given in tables 3.5 and 3.6 respectively. Although Kopelman [121] has shown that the choice of the glide plane, rather than the screw axis, to relate the two molecules in the unit cell introduces a left handed coordinate system at the second molecule, it is retained because of its heavy usage [36b].

The formamide crystal is classified under the space group $P2_1/n(C_{2h}^5)$ of the monoclinic system and has four molecules per unit cell. Each of the unit cell molecules occupies a site of the same symmetry as the free molecule, C_1. Under the operations of this space group all of the formamide molecular orbitals are classified as of symmetry type a. Thus the four sets of single site functions are of A symmetry. These single site functions combine into four sets of crystal orbitals of A_g, A_u, B_g and B_u symmetries under the two fold screw axis, the glide plane and centre of symmetry that relate any one of the unit cell molecules to the three others. An analysis of the

Table 3.5 Group character analysis of the naphthalene single site functions under C_{2h}^5

Single site function symmetry	$D_1=ED_1$	$D_2=C_2^bD_1$	$D_2=\sigma^aD_1$	Crystal orbital symmetry
A_g	+1	+1	+1	A_g
A_g	+1	-1	-1	B_g
A_u	+1	+1	-1	A_u
A_u	+1	-1	+1	B_u

Table 3.6 Symmetries of the combinations of the naphthalene single site functions under the σ^a operation

Combination of single site functions D_1		D_2	Crystal orbital symmetry
A_g	+	A_g	A_g
A_g	-	A_g	B_g
A_u	+	A_u	B_u
A_u	-	A_u	A_u

relations between the single site functions and the symmetries of the appropriate combinations, and hence the ω's, are given in tables 3.7 and 3.8 respectively.

Crystalline formic acid is orthorhombic with space group $Pna2_1(C_{2v}^9)$ and four molecules per unit cell. Each of these molecules occupies a site of the same symmetry as the free molecule, C_1 and is related to the three others by a two fold screw axis, C_2^c, and two glide plane operations σ^a and σ^n. All the molecular orbitals are of symmetry type a. Hence the four sets of single functions are of A symmetry. These four sets of single functions combine into crystal orbitals of A_1, A_2, B_1 and B_2 symmetries, the analysis of which is given in tables 3.9 and 3.10.

The urea crystal is tetragonal with space group $P\bar{4}2_1m(D_{2d}^3)$ and has two molecules per unit cell. These two molecules occupy sites of C_{2v} symmetry which is the same as the free molecule's. Following the procedure outlined above, the valence orbitals of urea are classified as of a_1, a_2, b_1 or b_2 symmetry and hence the single site functions are of A_1, A_2, B_1 or B_2 symmetries. These functions combine into crystal orbitals of A_1, A_2, B_1, B_2 and E symmetries. An analysis of these combinations and the appropriate symmetry combinations under the C_2 operation are given in tables 3.11 and 3.12.

The symmetries of the combinations given in the tables are strictly only meaningful for the invariant wave vectors; they are retained, however, for the convenience of identifying particular bands. In the more general case the orbitals should be labelled according to the ± combinations rather than symmetry.

Table 3.7 Group character analysis of the formamide single site functions under C_{2h}^5

Single site function symmetry	$D_1=ED_1$	$D_2=\sigma D_1$	$D_3=iD_1$	$D_4=C_2D_1$	Crystal orbital symmetry
A	+1	+1	+1	+1	A_g
A	+1	-1	+1	-1	B_g
A	+1	-1	-1	+1	A_u
A	+1	+1	-1	-1	A_g

Table 3.8 Symmetries of the combinations of formamide single site functions under the operations of C_{2h}^5

Combination of single site functions							Crystal orbital symmetry
D_1		D_2		D_3		D_4	
A	+	A	+	A	+	A	A_g
A	-	A	+	A	-	A	B_g
A	-	A	-	A	+	A	A_u
A	+	A	-	A	-	A	B_u

Table 3.9 Group character analysis of the formic acid single site functions under C_{2v}^{9}

Single site function symmetry	$D_1 = ED_1$	$D_2 = C_2^c D_1$	$D_3 = {}^{n}D_1$	$D_4 = {}^{a}D_1$	Crystal orbital symmetry
A	+1	+1	+1	+1	A_1
A	+1	+1	-1	+1	A_2
A	+1	-1	-1	-1	B_1
A	+1	-1	+1	-1	B_2

Table 3.10 Symmetries of the combinations of formic acid single site functions under the operations of C_{2v}

Combination of single site functions D_1		D_2		D_3		D_4	Crystal orbital symmetry
A	+	A	+	A	+	A	A_1
A	+	A	-	A	-	A	A_2
A	-	A	-	A	+	A	B_1
A	-	A	+	A	-	A	B_2

Table 3.11 Group character analysis of the urea single site functions under D_{2d}^3

Single site function symmetry	$D_1=ED_1$	$D_2=C_2D_1$	$D_2=S_4D_1$	Crystal orbital symmetry
A_1	+1	+1	+1	A_1
A_1	+1	-1	-1	B_2
A_2	+1	+1	+1	A_2
A_2	+1	-1	-1	B_1
B_1	+1	+1	+1	E
B_1	+1	-1	-1	E
B_2	+1	+1	-1	E
B_2	+1	-1	+1	E

Table 3.12 Symmetries of the combinations of urea single site functions under the C_2 operation

Combination of single site functions D_1		D_2	Crystal orbital symmetry
A_1	+	A_1	A_1
A_1	-	A_1	B_2
A_2	+	A_2	A_2
A_2	-	A_2	B_1
B_1	+	B_1	E
B_1	-	B_1	E
B_2	+	B_2	E
B_2	-	B_2	E

B. The Band Structures

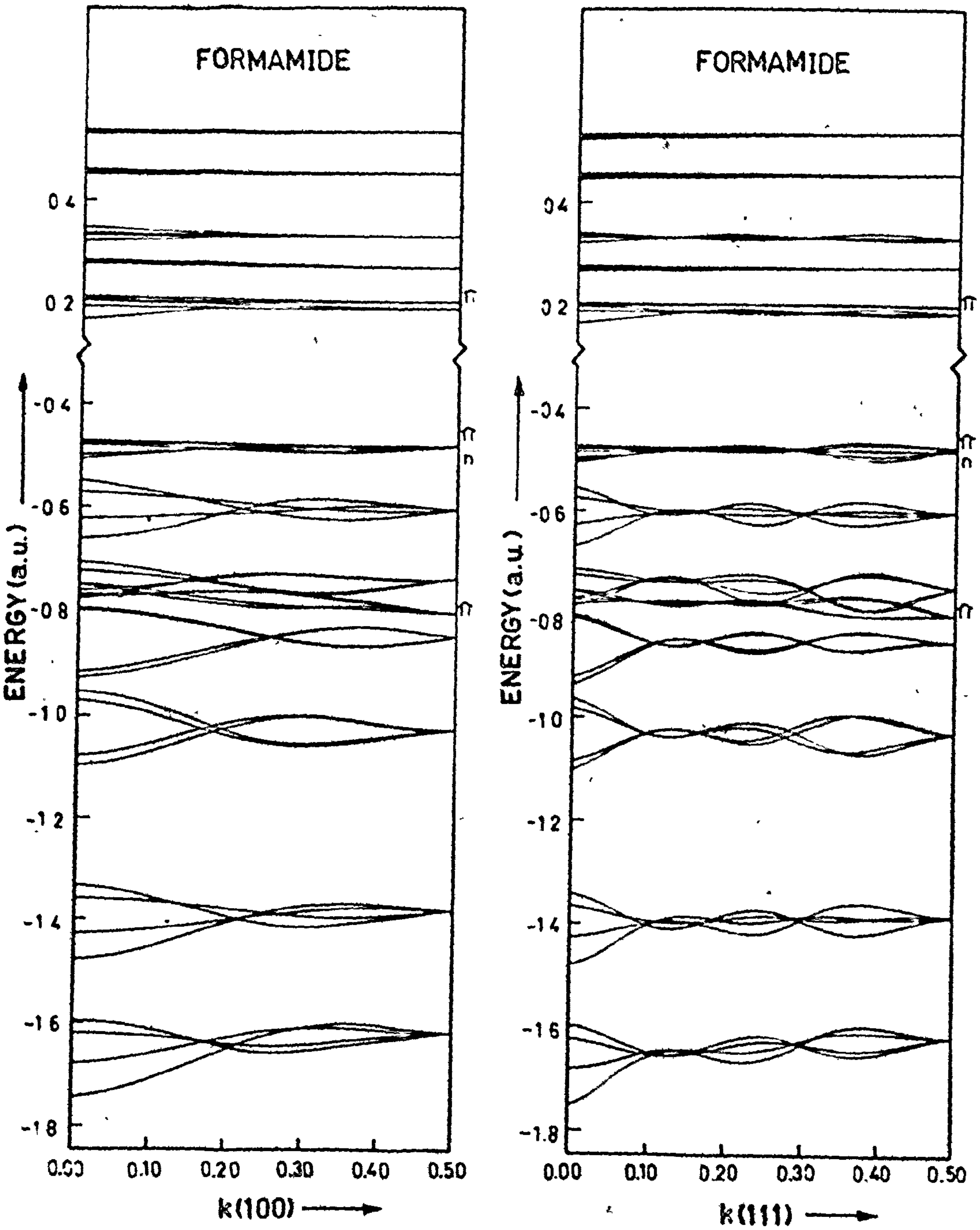
Sections of the band structures for the crystals under consideration were calculated using the $\underline{F}$ and $\underline{A}$ matrices and zero order molecular orbitals from the crystal perturbation calculations reported in reference 117 for ethylene and in chapter 2 for naphthalene, formamide, formic acid and urea. As an example of the convergence properties of this type of calculation, the first, second and third order contributions to the energies of the bands derived from the lowest occupied molecular orbital of the fairly strongly interacting crystalline formamide molecule are given in table 3.13, for three values of the wave vector along the 100 direction. From this table it can be seen that even in the case of strongly interacting crystal molecules, the band energy has sufficiently converged by the third order and that each successive order of correction is at least one order of magnitude smaller than the previous order. This suggests that for weakly interacting molecules second order calculations would likely be sufficient.

The band structures along the 100 and 111 directions, calculated to the third order, for all the valence levels of formamide, formic acid and urea are given in figures 3.2, 3.3 and 3.4 respectively. The corresponding plots for second order calculations for all the valence levels of ethylene and all the occupied and lowest vacant pi levels of naphthalene are in figures 3.5 and 3.6. The wave vector, $\bar{k}$, along the 100 direction in ethylene, naphthalene and urea lie along axes of symmetry; the $\bar{k}$'s along the 100 direction of formamide and formic acid and the 111 direction of all the crystals studied belong to stars. For the figures, crossing of levels of the same symmetry has been ignored as the gaps between the

Table 3.13 Contributions to the band levels derived from the lowest occupied level of formamide for the wave vectors (0., 0., 0.), (.25, 0., 0.) and (.5, 0., 0.). The zero order contribution is -1.647781 a.u.

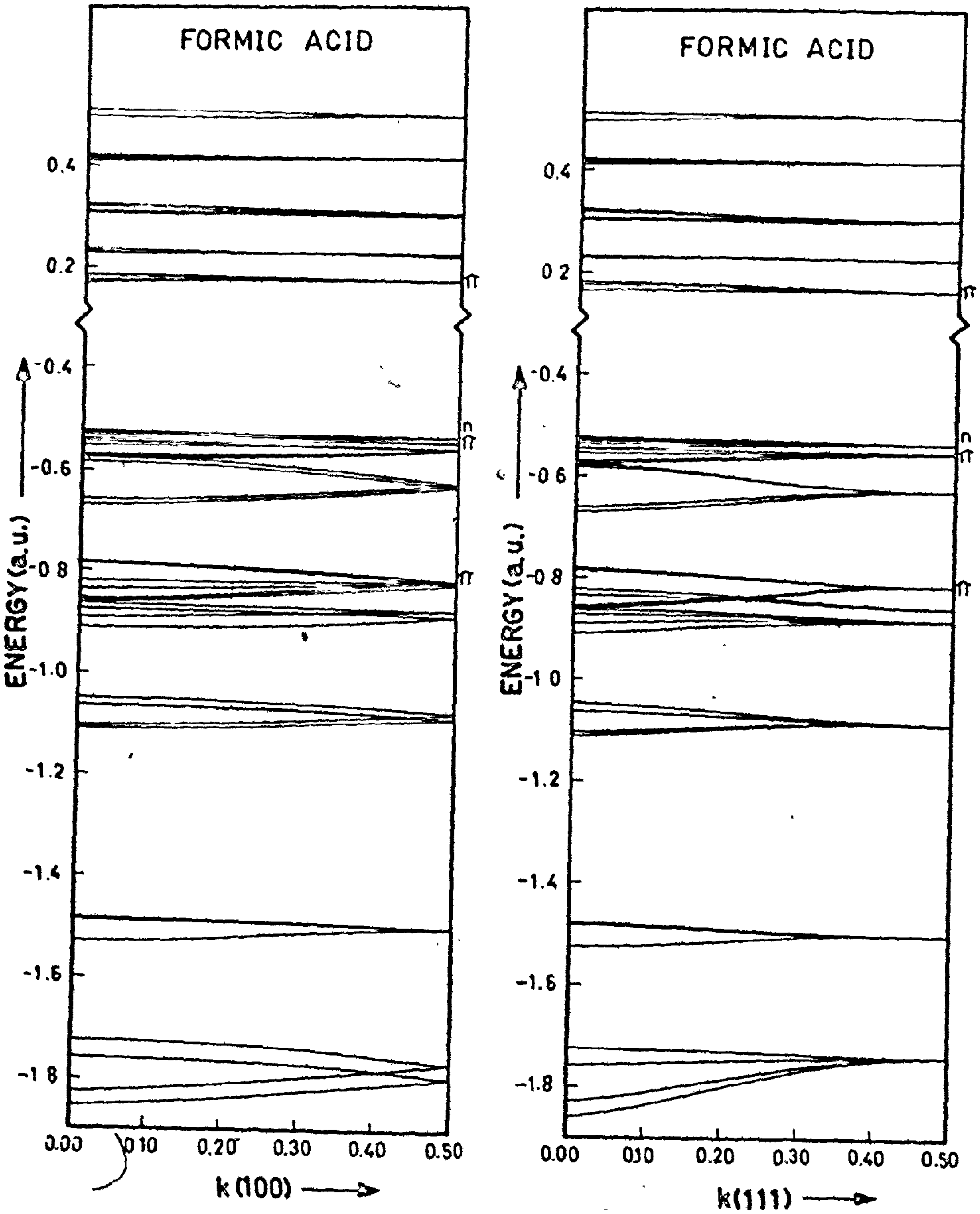
	(0., 0., 0.)	(.25, 0., 0.)	(.5, 0., 0.)
First order	-.099199	.020356	.025005
	.052332	-.015710	.025005
	.028036	-.005606	.025005
	-.029782	.026434	.025005
Second order	.002360	.001536	.002537
	.000166	.001570	.002537
	-.001326	.000871	.002537
	-.001226	.001562	.002537
Third order	.000017	-.000271	-.000338
	-.000620	-.000165	-.000338
	-.000379	-.000260	-.000338
	-.000570	-.000423	-.000338

Figure 3.2



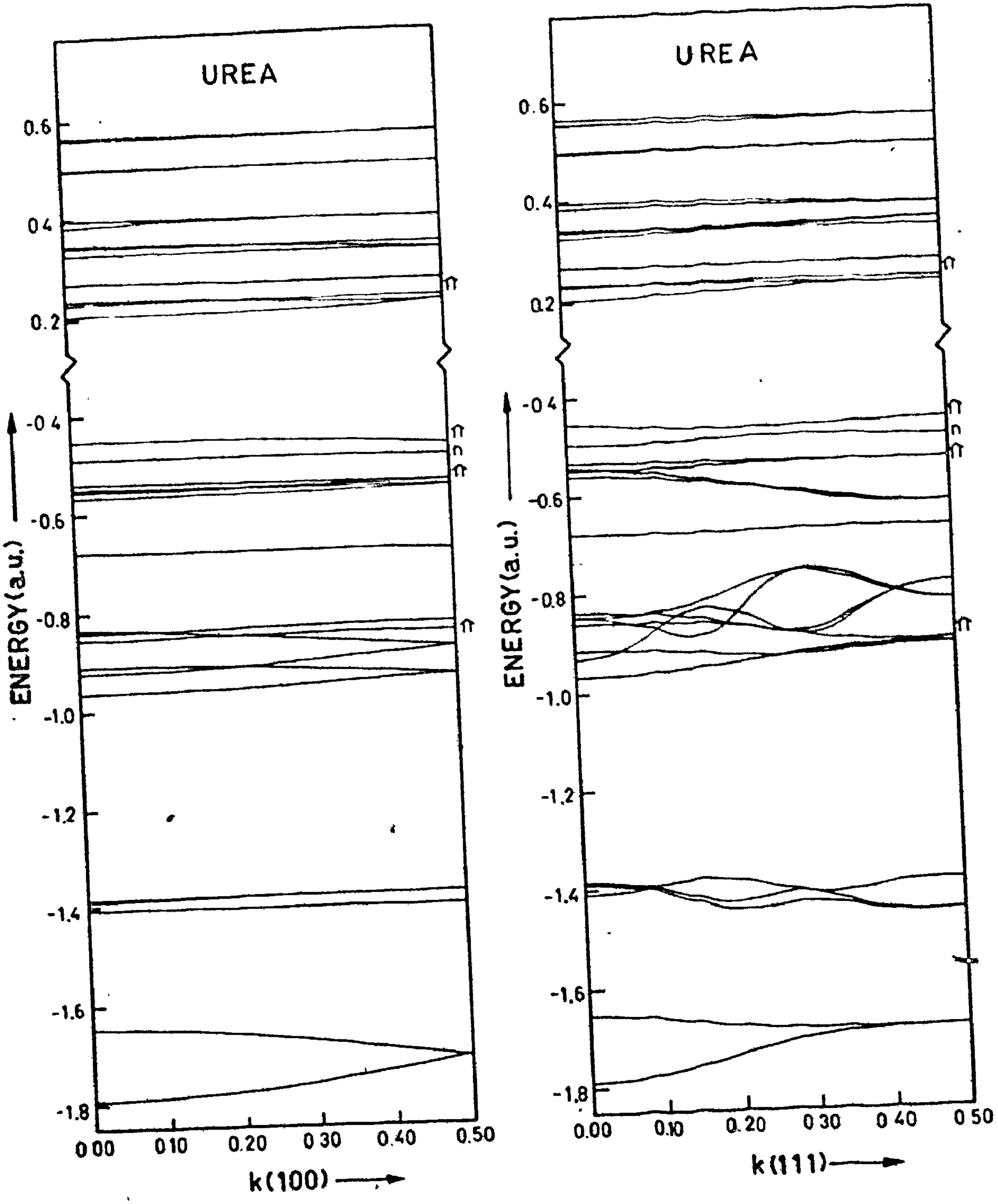
Sections of the band structure for formamide along the 100 and 111 directions. The ordering of the bands from highest to lowest in energy at k = 0 is A_u, B_u, A_g, B_g, A_u, A_g, B_g, B_u, A_g, B_g, B_u, A_u, B_u, A_u, B_g, A_g, A_g, A_u, B_u, B_g, A_u, B_g, A_g, B_u, B_g, A_g, B_g, B_u, A_u, A_g, B_u, A_u, A_g, A_u, B_g, B_u, B_u, A_u, B_u, B_g, A_u, B_g, A_g, A_g, B_u, B_g, A_g, A_u, B_u, A_u, A_g, B_g, A_g, A_u, B_g, B_u, B_u, A_u, B_g, A_g.

Figure 3.3



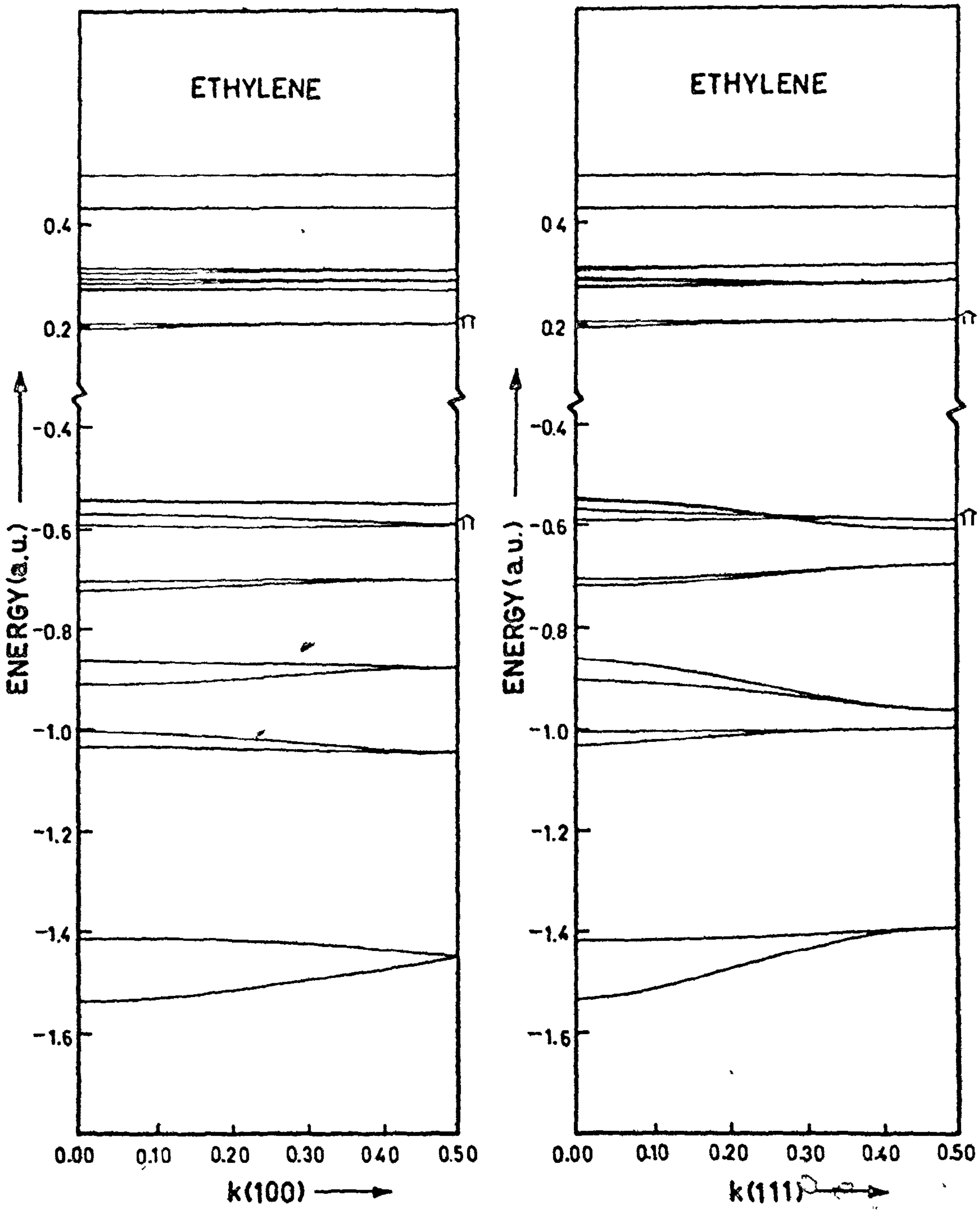
Sections of the band structure for formic acid along the 100 and 111 directions. The ordering of the bands from highest to lowest in energy at $k = 0$ is B_1, A_2, A_1, B_2, B_2, B_1, A_1, A_2, B_2, A_1, B_1, A_2, A_2, A_1, B_1, B_2, A_2, B_1, A_1, B_2, B_2, A_1, B_1, A_2, A_1, B_2, A_2, B_1, B_1, A_2, B_2, A_1, A_1, B_2, A_2, B_1, B_2, A_1, A_2, B_1, A_2, B_1, A_1, B_2, A_1, B_2, A_2, B_1, B_2, A_1, B_1, A_2, B_1, A_2, B_2, A_1.

Figure 3.4



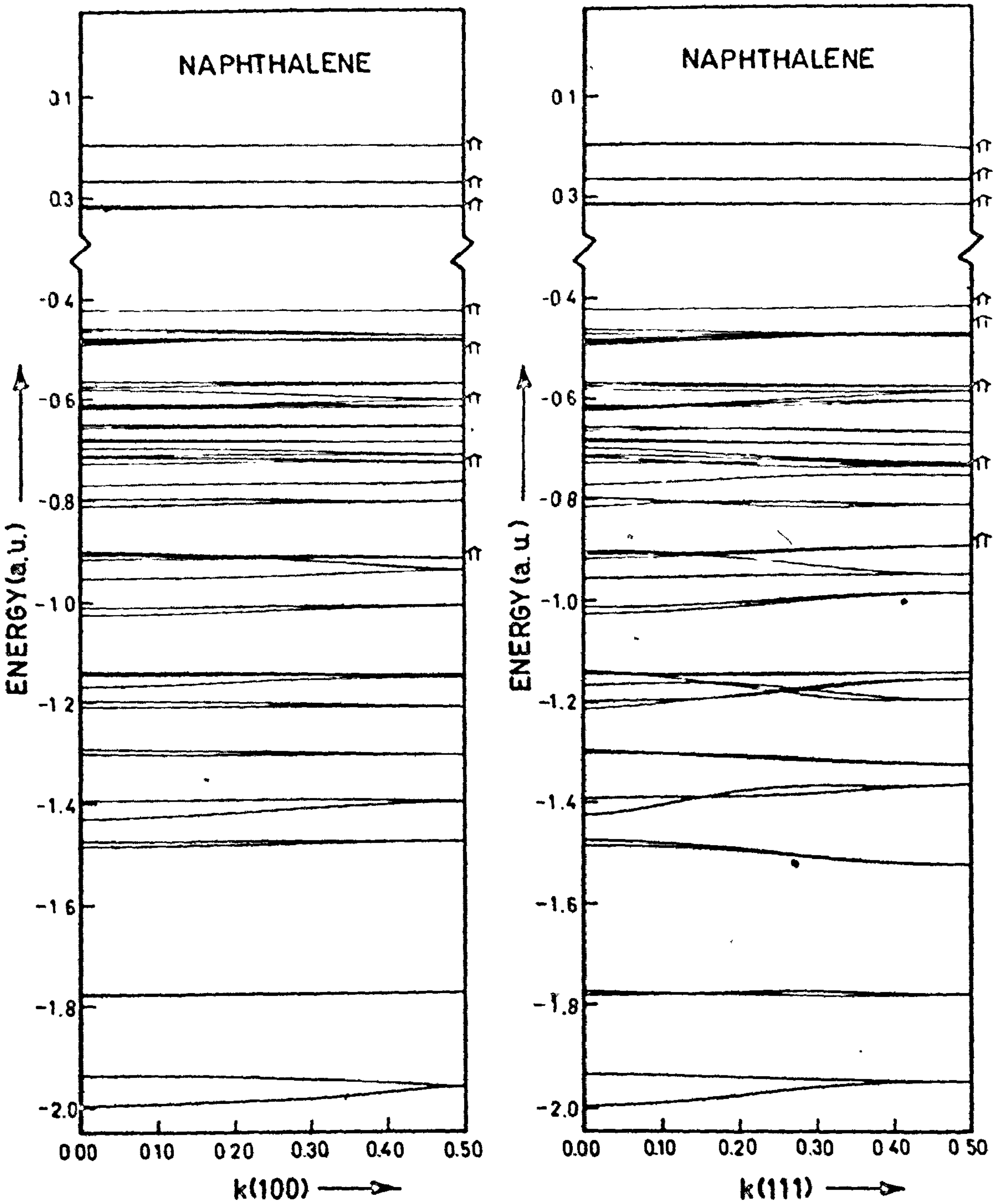
Sections of the band structure for urea along the 100 and 111 directions. The ordering of the bands from highest to lowest in energy at k = 0 is B_2, A_1, E, B_2, A_1, E, B_2, A_1, E, B_2, E, A_1, E, E, A_2, A_1, B_2, B_1, E, E, A_1, E, A_1, B_2, B_2, A_1, B_2, E, B_2, A_1.

Figure 3.5



Sections of the band structure for ethylene along the 100 and 111 directions. The ordering of the bands from highest to lowest in energy at k = 0 is B_{1u}, B_{2u}, B_{2g}, B_{1g}, B_{3g}, A_g, A_u, B_{3u}, B_{1u}, B_{2u}, A_g, B_{3g}, B_{2g}, B_{1g}, B_{1u}, B_{2u}, B_{3g}, A_g, B_{3u}, A_u, B_{1u}, B_{2u}, B_{3g}, A_g.

Figure 3.6



Sections of the band structure for naphthalene along the 100 and 111 directions. The ordering of the bands from highest to lowest in energy at k = 0 is B_u, A_u, B_g, A_g, A_g, B_g, A_u, B_u, B_g, A_g, A_g, B_g, A_u, B_u, A_u, B_u, B_g, B_u, A_g, A_u, A_u, B_u, A_g, B_g, B_u, A_u, B_g, A_g, B_g, A_g, A_g, B_g, A_u, A_g, B_g, B_u, A_u, B_u, B_u, A_u, B_u, A_u, B_g, A_g, A_g, B_g, B_g, A_g, A_u, B_u, A_u, B_u, B_g, A_g.

bands, calculated by perturbation theory at the point at which they cross, are in general too small to be plotted on the scale used.

Broadly, the dispersion shown in the bands for formamide, formic acid and urea is greater than that for ethylene and naphthalene. This is likely due to the relatively stronger interactions in the hydrogen bonded crystals. All the crystals studied show a general increase in dispersion of the bands from the highest vacant to the lowest occupied band. The relative increase and the especially strong dispersion in the lowest occupied bands reflects the fact that the hydrogen bonding interactions involve the hydrogen atomic orbitals which contribute in increasing amounts to the molecular orbitals of the isolated molecule from highest to lowest in energy. For all the crystals studied, the bands derived from the pi molecular orbitals, in general, show less dispersion than those from sigma molecular orbitals. Also, the bands derived from the nonbonding orbitals on the carbonyl groups are relatively undispersed. This small dispersion reflects the fact that the hydrogen bonding interactions do not involve the electrons in pi or nonbonding molecular orbitals to any great extent.

§ 3.5 The Density of States for Formamide, Formic Acid and Urea [122]

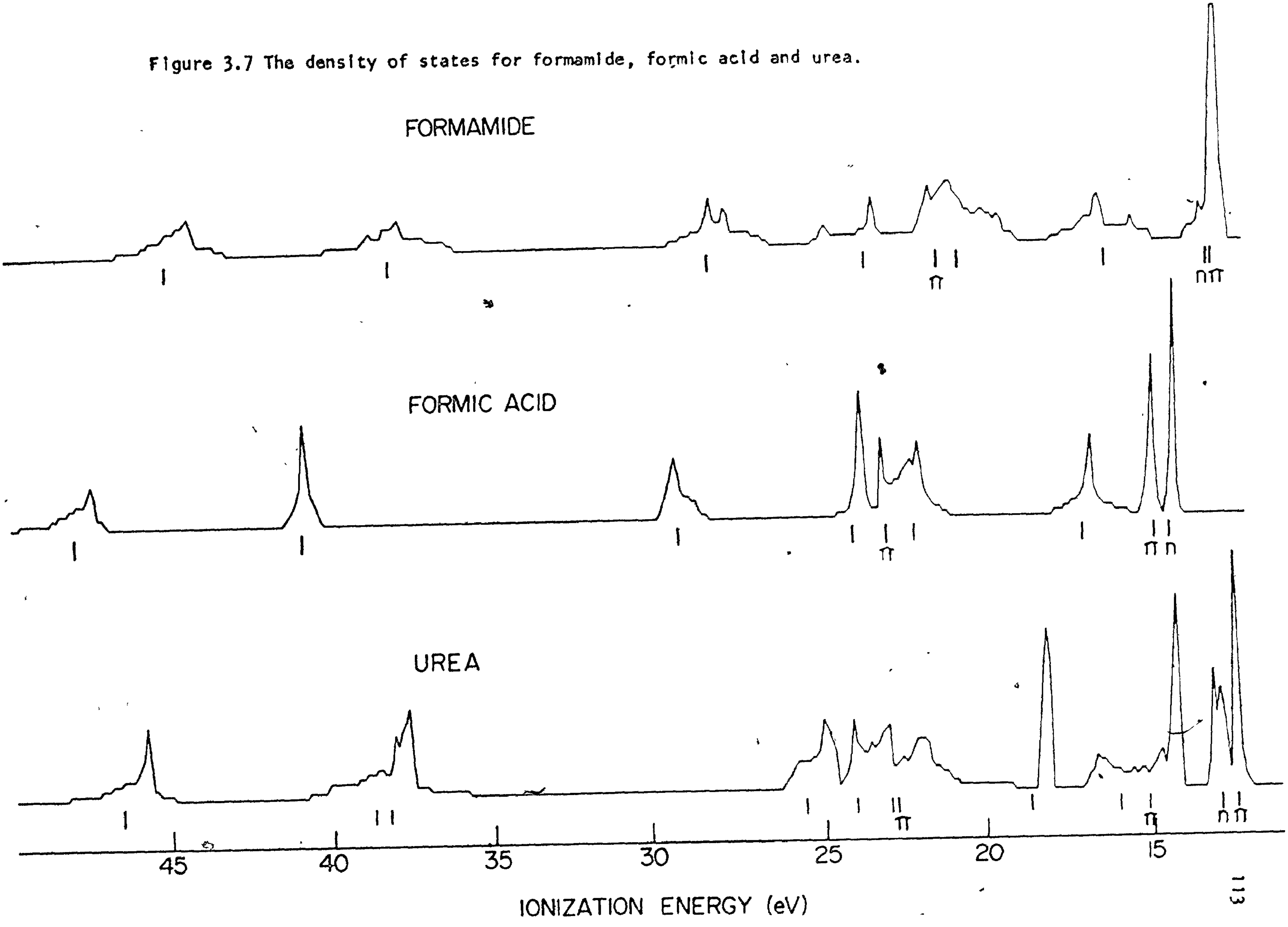
The electronic density of states for formamide, formic acid and urea were obtained in much the same manner as those of André et al [116] for a system which is periodic in only one direction, polyethylene. The energy of all the occupied valence levels was calculated for 9261 wave vectors by means of a Lagrangian interpolation procedure based on 125 directly calculated points. Then the density of states was obtained by counting the number of states within intervals of .004 a.u. in energy.

As a check on the accuracy of the interpolation procedure, the areas under the plots for the three crystals were measured. These areas should be in the ratio of (the number of molecular levels) X (the number of molecules in the unit cell). This area relationship was found to be accurate to within 5%.

The density of states for the three crystals are given in figure 3.7. Note, for the purpose of this diagram, the plots have been scaled to make the highest peak in each of equal height. The positions of the levels in the free molecule are given below each plot. The breadth of a given peak in the diagram reflects the degree of dispersion in the corresponding energy band in the space of the wave vector, reciprocal space. The dispersion of some bands is sufficient to cause overlapping of the peaks, so that not all can be assigned to a unique molecular level. While others have little dispersion and give rise to sharp peaks. These bands are associated with the molecular orbitals that are affected little by the hydrogen bonding interaction. The most prominent of these are the bands derived from the carbonyl lone pair and highest occupied pi orbitals which show little dispersion and hence give rise to sharp peaks. However, there are some examples of dispersed pi orbital and sharp sigma orbital peaks. Overall, the formamide density of states appears more dispersed than those of the other two crystals. Since the binding energy of formamide lies between that of formic acid and urea, this is likely a consequence of crystal packing rather than a stronger hydrogen bonding environment.

The symmetry of the urea crystal is unusually high and could affect the dispersion by limiting the amount of mixing allowed between

Figure 3.7 The density of states for formamide, formic acid and urea.



the zero order molecular orbitals under the crystal field. Formic acid has a somewhat lower symmetry but the crystal may be viewed as being composed of pairs of strongly interacting molecules, related by a plane of reflection, situated throughout the lattice. Intermolecular interactions within the dimers are expected to be stronger than between dimers. This situation could lead to a significant factor group splitting for zero wave vector but relatively small dispersion of the resultant components. The presence of a repetitive centre of inversion in the formamide crystal leads to the presence of dimers also. However, unlike formic acid, the interactions between the dimers in formamide are relatively strong forming an extended hydrogen bonded network which strongly disperses the energy bands.

An important result from this study is simply that the hydrogen bonding interaction within molecular lattices apparently strongly disperses some of the molecular energy levels while leaving others relatively unaffected. It also provides a means of calculating when bands should be broad which should help in the assignment of ESCA [116] spectra, which give the experimental density of states. Thus, it provides an opportunity for the use of theoretical studies in conjunction with an experimental technique, ESCA [116] to investigate the hydrogen bonding potential.

CHAPTER 4

The Self Consistent Field Perturbation Theory for the Frenkel and Charge Transfer States of Hydrogen Bonded Crystals

§ 4.1 Introduction

The formulation of a theory for the excited states of molecular crystals within the SCF perturbation approach partially fulfils the objective set out in the introductory chapter. That is, with the inclusion of a theory of the excited states into the approach, the SCF perturbation method could be used to calculate many of the electronic properties of molecular crystals.

In this chapter, a theory of the electronic excited states for molecular crystals is developed within the molecular orbital formalism of the SCF perturbation theory. Although the approach is quite different, the resultant excitation energies are shown to be comparable to those from the basically valence bond approach of Davydov [25].

§ 4.2 Band Structures and Crystal Excited States

Theoretical band structures are obviously of considerable interest from a spectroscopic point of view. A possible approach to the calculation of the crystal excitation energies is the virtual orbital approximation [45] in which an electron is excited from a filled band to a vacant band. Unfortunately, however, the band energies cannot be used directly, since the single configuration molecular orbital approximation is particularly unsatisfactory when applied to the excited states of molecular crystals. This can be illustrated by an analysis of the excited states of, for example, a linear chain of closed shell atoms, such as helium.

Consider first the approximate excitation energy for the 1s→2s transition of an isolated He atom. Using the well known expression of Roothaan [45] for the virtual orbital approximation, this energy is given by

$$\Delta E_{1s\rightarrow 2s} = \varepsilon_{1s} - \varepsilon_{2s} - J_{1s,2s} + 2\tau K_{1s,2s} , \qquad (4.1)$$

where the ε's are the orbital energies and J and K are the Coulomb and exchange integrals respectively. The τ in equation (4.1) is equal to one for singlet states and zero for triplets. For comparison, consider the excitation energy of an infinite chain of He atoms with very large, almost infinite, repeat atomic separation. The interatomic interactions in such a chain will be negligible so that its excitation energies should be degenerate and all equal to the corresponding energy for an isolated atom, equation (4.1). Following the procedure outlined in chapter 3, the translational symmetry is used to generate highly delocalized symmetry adapted orbitals for the chain. Under the virtual orbital approximation and the Δk=0 selection rule, the excitation energies of the chain are,

$$\Delta E_{1s\rightarrow 2s}(\bar{k}) = \varepsilon_{2s}(\bar{k}) - \varepsilon_{1s}(\bar{k}) - J_{1s,2s}(\bar{k}) + 2\tau K_{1s,2s}(\bar{k}). \qquad (4.2)$$

Clearly, for the chain under discussion, there is zero dispersion of the bands so that $\varepsilon_{2s}(\bar{k}) = \varepsilon_{2s}$ and $\varepsilon_{1s}(\bar{k}) = \varepsilon_{1s}$; the orbital energy difference in (4.2) will therefore be the same as in (4.1). However, it has been shown that as the number of atoms in such a chain tend to infinity, both $J(\bar{k})$ and $K(\bar{k})$ tend to zero [123]. Thus, the excitation energy for a chain of noninteracting atoms tends to

$$\Delta E_{1s\rightarrow 2s} = \varepsilon_{2s} - \varepsilon_{1s}, \tag{4.3}$$

as a limiting value as the number of atoms in the chain approaches infinity. This result contradicts the predicted value from equation (4.1).

This contradiction arises because the single configuration virtual orbital approximation is seriously in error for systems in which the interactions between the units are small such as the helium atom chain or molecular crystals. From a physical point of view, this approximation describes the crystal excited states in terms of an independently delocalized electron and hole, whereas there is strong experimental evidence which suggests that, for the lower π-states of aromatic molecules at least, the electron and hole are tightly bound and delocalize together as a Frenkel exciton [36b].

From the point of view of molecular orbital theory, the adoption of equation (4.2) would lead to serious problems. First, as shown, it has the incorrect limiting behaviour as the intermolecular potential tends to zero, and second, under the $\Delta\bar{k}=0$ selection rule, equation (4.2) yields, for a crystal with low dispersion bands, an infinite number of almost degenerate states of different wavevectors. Under these circumstances an appreciable level of mixing between these states, configuration interaction, would have to be included in order to achieve realistic results. Hence, the theoretical investigation of the excited states of molecular crystals in terms of molecular orbital theory requires the resolution of a configuration interaction problem over an infinite basis of almost degenerate virtual orbital states. The solution of this problem is not as difficult as it would appear at first sight, since the lower states are known to closely correspond to a bound electron and hole delocalizing together through the crystal as a Frenkel exciton [36b]. This suggests that the configuration interaction problem could be simplified by transforming the delocalized electron-hole functions into a localized representation. In the next section, such a transformation is used to develop the basis functions for the crystal configuration interaction problem.

§ 4.3 The Wave Functions in the Localized Representation [124].

The relationship between the band structure and the electronic states of a molecular crystal is developed here. As pointed out in the previous section, a convenient starting point for this is the virtual orbital approximation to the excited states. That is, it will be assumed that the crystal excited states can be represented by the excitation of an electron from a level in the filled band to one in a vacant band. However, this simple approach has to be modified by a suitable transformation in order to achieve a realistic representation of the electronic excited states of molecular crystals.

The zero order crystal orbital as given by (3.9), is

$$0_l^{(0)}(\bar{k},\lambda) = Z^{-\frac{1}{2}}N^{-\frac{1}{2}} \sum_{u}^{\text{unit cell}} \omega_{\lambda,u} \sum_{\bar{T}}^{\text{crystal}} e^{2\pi i\bar{k}\cdot(\bar{T}+\bar{u})} C_l^{(0)}(\bar{T},\bar{u}) \qquad (4.4)$$

The notation for the crystal orbitals has been changed slightly from the notation used in the previous chapter to emphasise the relationship between $\bar{T}$ and $\bar{k}$ and u and λ. This reciprocity carries over to the orbital label i, in the sense that it labels two sets of orbitals, which to the zeroth order, are related as the three dimensional Fourier transforms of one another. This duality plays an important part in the theory and, consequently, a considerable clarification of the forthcoming equations can be achieved by adapting the orbital notation to reflect it. Firstly, variables in real and reciprocal space are labelled by ζ and η respectively. The zero order crystal orbital, equation (4.4), is thus given by

$$O_i^{(0)}(\bar{k}_\eta,\lambda_\eta) = Z^{-\frac{1}{2}}N^{-\frac{1}{2}} \sum_{u_\zeta} \omega_{\lambda_\eta,u_\zeta} \sum_{\bar{T}_\zeta} e^{2\pi i\bar{k}_\eta\cdot\bar{R}_\eta} \; C_i^{(0)}(\bar{T}_\zeta,\bar{u}_\zeta), \tag{4.5}$$

where, for convenience, the $\bar{u}$ has been combined with $\bar{T}$ to give $\bar{R}$. $\bar{R}$ may be used interchangeably with $\bar{T}+\bar{u}$ to label a molecule when the structure of the unit cell is unimportant. The following convention may now be introduced

$$i^\eta \equiv O_i^{(0)}(\bar{k}_\eta,\lambda_\eta) \tag{4.6}$$

$$i_\zeta \equiv C_i^{(0)}(\bar{T}_\zeta,\bar{u}_\zeta) \tag{4.7}$$

The approximate ground state electronic wave function for the crystal is given by the usual determinantal function. This can be conveniently written by making use of the above convention for a crystal of 2n electrons,

$$\Psi_0 = (2n!)^{-\frac{1}{2}} \left| \cdots i^n \bar{i}^n \cdots \right| . \qquad (4.8)$$

Similarly, approximate crystal singlet and triplet wave functions, corresponding to the excitation of an electron from the (i^1)th level in the filled band to the (ℓ^2)th level in the vacant, are given by [45]

$$^{3,1}\Psi_{i^1\ell^2} = 2^{-\frac{1}{2}}(2n!)^{-\frac{1}{2}}\left(\left| \cdots i^1 \bar{\ell}^2 \cdots \right| \pm \left| \cdots \bar{i}^1 \ell^2 \cdots \right| \right) . \qquad (4.9)$$

The excitation energies are given directly by the well known expression derived by Roothaan [45] for the corresponding molecular process.

$$^{1,3}E_{i^1 \rightarrow \ell^2} = \varepsilon(\ell^2) - \varepsilon(i^1) - J(i^1,\ell^2) + 2\tau K(i^1,\ell^2), \qquad (4.10)$$

where $\varepsilon(\ell^2)$ is the level from the energy band associated with the crystal orbital ℓ^2. In the notation of the previous chapter,

$$\varepsilon(\ell^2) \equiv E_{\ell,\lambda_2}(\bar{k}), \qquad (4.11)$$

J and K are the Coulomb and exchange integrals respectively.

$$J(i^1,\ell^2) = \langle i^1\ell^2 | i^1\ell^2 \rangle \qquad (4.12)$$

and

$$K(i^1,\ell^2) = \langle i^1\ell^2 | \ell^2 i^1 \rangle . \qquad (4.13)$$

Equation (4.10) is the crystal analogue of the virtual orbital expression for the excitation energy of a finite molecule. This single determinantal approximation is fundamentally in error for molecular crystals and a multiconfigurational analysis of the type discussed in the previous section must be carried out. In order to simplify the configurational problem, the delocalized electron-hole wave functions are first transformed to a localized representation. These localized functions are generated, following Slater and Shockly [125], by a double Fourier transformation of the excited state functions given in equation (4.9). Thus,

$$^{1,3}L_{1\ell}(\bar{R}_1,\bar{R}_2) = N^{-1}Z^{-1}\sum_{\lambda_1}\sum_{\lambda_2}\omega_{\lambda_1,u_1}\omega_{\lambda_2,u_2}\sum_{k_1}\sum_{k_2}e^{2\pi i(\bar{k}_1\cdot\bar{R}_1-\bar{k}_2\cdot\bar{R}_2)}\ {}^{1,3}\Psi_{1 1_\ell 2}, \tag{4.14}$$

where $^{1,3}L(\bar{R}_1,\vec{R}_2)$ is a function in which the hole is localized on the T_1u_1th molecule and the excited electron on the T_2u_2th.

The L-type basis functions, being localized, transform reducibly under the crystal space group. In order to simplify the eventual configuration interaction equations, linear combinations of these functions are taken to generate new functions, M, that transform irreducibly under the operations of the space group. Of all the different possibilities, the $\bar{k}$=0 representations are of the most interest. This is so because the ground state transforms as the $\bar{k}$=0 representation and the selection rule for electronic transitions is $\Delta\bar{k}$=0. Hence, the wave vector for the excited state is approximately zero. The $\bar{k}$=0 M functions are given by

$$^{1,3}M^{\lambda}_{1\ell}(\bar{\beta},\bar{\rho}) = Z^{-\frac{1}{2}}N^{-\frac{1}{2}}\sum_{u}\omega_{\lambda,u}\sum_{T}{}^{1,3}L_{1\ell}(\bar{T},\bar{u};\bar{T}+\bar{\beta},\bar{u}+\bar{\rho}). \tag{4.15}$$

The vectors $\bar{\beta}$ and $\bar{\rho}$ give the separation between the molecule on which the hole is centered and that on which the excited electron is centered. There is a set of M functions, corresponding to all of the representations of the unit cell group given by λ, for each value of $\bar{\beta}$ and $\bar{\rho}$; that is, for every electron hole separation. The M functions describe the crystal excited states in terms of a generalized exciton for which, although they are bound together, the electron and hole are on different molecules separated by $|\bar{\beta}|$ unit cells and $|\bar{\rho}|$ sites. The Frenkel [36b] exciton corresponds to the special case where both $\bar{\beta}$ and $\bar{\rho}$ are zero.

Symmetrization of the localized L functions by means of the space group symmetry gives delocalized character to the final M basis functions. There is, however, an important difference in the type of delocalizations represented by the Ψ and M functions. In the former, the excited electron and hole are represented as being in independent motion in the crystal lattice; their motion is uncorrelated. In the case of the M functions, the electron and hole, even though they may be on different molecules, are represented as being bound together as a single entity; their motions are completely correlated. The Ψ and M basis functions represent the two extremes in crystal excited state approximate wavefunctions.

The M type basis functions of a given symmetry, λ, form the basis set for the configuration interaction calculation; the final crystal excited state wavefunction will have contributions from all the M's of a given symmetry with every possible separation $\bar{\beta}+\bar{\rho}$. The configuration interaction equations can be written in a matrix form referred to as the secular equation. The diagonal elements of this matrix are given by $\bar{\beta}+\bar{\rho}=\bar{\beta}'+\bar{\rho}'$ and the off diagonal elements correspond to $\bar{\beta}+\bar{\rho}\neq\bar{\beta}'+\bar{\rho}'$. Thus, the secular equation is of infinite dimension. However, because of the choice of basis set, nearly all of the off diagonal matrix elements should be negligible in comparison with the diagonal ones. Hence, as a first approximation, the crystal excitation energies will be approximated by the appropriate diagonal elements of the configuration interaction matrix.

It should be noted that the configuration interaction calculation has been transformed from an infinite basis of functions of wave vectors to one of electron hole separations. The advantage of the latter is that even though it still is of infinite dimension very few functions are expected to contribute to any particular excitation.

It may appear that the above approach neglects any possible mixture of charge transfer character into states that are Frenkel exciton in character. This is not the case. The crystal orbitals, $O(\bar{k},\lambda)$, used to construct the L functions are solutions to the crystal SCF perturbation equation and are thus only perfectly localizable to the zeroth order. This confers some charge transfer character even to the Frenkel-type M functions.

§ 4.4 The Evaluation of the Matrix Elements

The implementation of the configuration interaction procedure requires the evaluation of the following type of matrix element;

$$^{1,3}H_{i\ell,mn}(1,2;3,4) = \langle ^{1,3}L_{i\ell}(\bar{R}_1;\bar{R}_2)|H-E_{ground}|^{1,3}L_{mn}(\bar{R}_3;\bar{R}_4)\rangle \qquad (4.16)$$

where H is the crystal electronic Hamiltonian and E_{ground} the crystal ground state energy. Expanding the localized, L, functions using equation (3.14), this matrix element equals

$$Z^{-2}N^{-2}\sum_{\lambda_1}\sum_{\lambda_2}\sum_{\lambda_3}\sum_{\lambda_4}\omega_{\lambda_1,u_1}\omega_{\lambda_2,u_2}\omega_{\lambda_3,u_3}\omega_{\lambda_3,u_3}\sum_{k_1}\sum_{k_2}\sum_{k_3}\sum_{k_4}e^{-2\pi i(\bar{k}_1\cdot\bar{R}_1-\bar{k}_2\cdot\bar{R}_2-\bar{k}_3\cdot\bar{R}_3+\bar{k}_4\cdot\bar{R}_4)}$$

$$\cdot\langle{}^{1,3}\Psi_{l^1\ell^2}|H-E_{\text{ground}}|{}^{1,3}\Psi_{m^3n^4}\rangle. \qquad (4.17)$$

The integral can readily be evaluated using equation (4.10). Expression (4.17) then becomes,

$$Z^{-2}N^{-2}\sum_{\lambda}^{(4)}\omega_{\lambda_1,u_1}\omega_{\lambda_2,u_2}\omega_{\lambda_3,u_3}\omega_{\lambda_4,u_4}\sum_{k}^{(4)}e^{-2\pi i(\bar{k}_1\cdot\bar{R}_1-\bar{k}_2\cdot\bar{R}_2-\bar{k}_3\cdot\bar{R}_3+\bar{k}_4\cdot\bar{R}_4)}$$

$$\cdot\left(\{\delta_{\ell n}\epsilon(\ell^2)-\delta_{lm}\epsilon(l^1)\}\delta^{1,3}\delta^{2,4}+\{2\tau\langle m^3\ell^2|n^4i^1\rangle-\langle m^3\ell^2|i^1n^4\rangle\}\right), \qquad (4.18)$$

where $\delta^{1,3}=1$ if $k_1=k_3$ and $\lambda_1=\lambda_3$ and is zero otherwise. The superscript convention has been introduced for the Kronecker delta to make it consistent with later usage. $\sum\limits_{\lambda}^{(4)}$ and $\sum\limits_{k}^{(4)}$ represent the four fold summations over λ's and k's explicitly written out in expression (4.17).

The next step is the expansion of (4.18) using the special properties of the crystal perturbation algebra introduced previously. Starting with the orbital energy terms:

$$Z^{-2}N^{-2}\sum_{\lambda_1}\sum_{\lambda_2}\omega_{\lambda_1,u_1}\omega_{\lambda_2,u_2}\omega_{\lambda_3,u_3}\omega_{\lambda_4,u_4}\sum_{k_1}\sum_{k_2}e^{-2\pi i(\bar{k}_1\cdot(\bar{R}_1-\bar{R}_3)-\bar{k}_2\cdot(\bar{R}_2-\bar{R}_4))}$$

$$\cdot\{\delta_{\ell n}\epsilon(\ell^2)-\delta_{lm}\epsilon(l^1)\}. \qquad (4.19)$$

As shown in chapter 3, to zero order, $\varepsilon(\ell^2)$ is independent of $\bar{k}_2$ and λ_2 and equals $\varepsilon^{(0)}(\ell^2)$, the $\ell^{\underline{th}}$ molecular orbital energy of an arbitrary lattice molecule (here set to T_2, u_2). Thus, to this order, the orbital energies may be taken outside of the summations, and the summations over $\bar{k}$ and λ evaluated. The final zero order result is

$$\{\delta_{\ell n}\varepsilon^{(0)}(\ell^2) - \delta_{im}\varepsilon^{(0)}(i_1))\delta_{1,3}\delta_{2,4} \quad , \tag{4.20}$$

where $\delta_{1,3} = 1$ if $\bar{R}_1 = \bar{R}_3$, that is $\bar{T}_1 = \bar{T}_3$ and $\bar{u}_1 = \bar{u}_3$, and is zero otherwise.

The first order correction to the orbital energy, $\varepsilon^{(1)}(\ell^2)$, depends on both λ_2 and $\bar{k}_2$. The expression for $\varepsilon^{(1)}$ is given in equation (3.18); in terms of the new notation it is;

$$\varepsilon^{(1)}(\ell^2) = (NZ)^{-1} \sum_{u_5}\sum_{u_6} \omega_{\lambda_2,u_5}\omega_{\lambda_2,u_6} \sum_{T_5}\sum_{T_6} e^{2\pi i\bar{k}_2\cdot(\bar{R}_6-\bar{R}_5)}\ {}^{5,6}F^{(1)}_{\ell\ell} \quad , \tag{4.21}$$

where

$${}^{5,6}F^{(1)}_{\ell\ell} = {}^{T_5u_5,T_6u_6}F^{(1)}_{\ell\ell} \quad . \tag{4.22}$$

Substitution of (4.21) for the appropriate orbital energy in expression (4.19) yields, on evaluation of the summations of λ's and $\bar{k}$'s:

$${}^{2,4}F^{(1)}_{\ell\ell}\delta_{1,3} - {}^{1,3}F^{(1)}_{ii}\delta_{2,4} \quad . \tag{4.23}$$

Thus, to the first order, the orbital energy difference is given by

$$(\delta_{\ell n}\varepsilon^{(0)}(\ell_2) - \delta_{mi}\varepsilon^{(0)}(i_1))\delta_{1,3}\delta_{2,4} + {}^{2,4}F^{(1)}_{\ell\ell}\delta_{1,3} - {}^{1,3}F^{(1)}_{ii}\delta_{2,4} \quad . \tag{4.24}$$

Next, the electron repulsion terms are expanded. First, the integral $<m^3\ell^2|n^4 i^1>$ is expanded in terms of the zero order molecular orbitals:

$$<m^3\ell^2|n^4 i^1> = N^{-2}Z^{-2} \sum_{u}^{(4)} \omega_{\lambda_3,u_5}\omega_{\lambda_2,u_6}\omega_{\lambda_4,u_7}\omega_{\lambda_2,u_8} \cdot \sum_{T}^{(4)} e^{2\pi i(-\bar{k}_3\cdot\bar{R}_5-\bar{k}_2\cdot\bar{R}_6+\bar{k}_4\cdot\bar{R}_7+\bar{k}_1\cdot\bar{R}_8)} <m_5\ell_6|n_7 i_8>. \qquad (4.25)$$

Next, this is substituted into the appropriate position in expression (4.18) and the summations over λ, $\bar{k}$, $\bar{T}$ and $\bar{u}$ evaluated. The final result is

$$<m_3\ell_2|n_4 i_1>. \qquad (4.26)$$

The effect of the multiple summations is simply to convert the superscripts on the crystal orbitals to subscripts on molecular orbitals. Thus, the total zero order electron repulsion contribution is

$$2\tau<m_3\ell_2|n_4 i_1> - <m_3\ell_2|i_1 n_4>. \qquad (4.27)$$

The procedure for the evaluation of the first and higher order contributions to the electron repulsion integrals is very similar to the evaluation of the zero order. The integral $<m^3\ell^2|n^4 i^1>$, for example is expanded to first order as

$$<m^3\ell^2|n^4 O_i^{(1)}(\bar{k}_1,\lambda_1)> + <m^3\ell^2|O_n^{(1)}(\bar{k}_4,\lambda_4)i^1> + <m^3 O_\ell^{(1)}(\bar{k}_2,\lambda_2)|n^4 i^1> + <O_m^{(1)}(\bar{k}_3,\lambda_3)\ell^2|n^4 i^1>. \qquad (4.28)$$

As in the conventional perturbation theory, outlined in chapter

1, the first order change in the crystal orbitals, $O^{(1)}$, is expanded in terms of the zero order orbitals, $O^{(0)}$,

$$O^{(1)}(\bar{k},\lambda) = O^{(0)}(\bar{k},\lambda)\underline{A}(\bar{k},\lambda) \tag{4.29}$$

where $\underline{A}$ is a matrix of mixing coefficients. The matrix elements of $\underline{A}$ are given by a relationship similar to (1.75),

$$A_{pi}(\bar{k},\lambda) = \tilde{O}_p^{(0)}(\bar{k},\lambda)\underline{F}^{(1)}O_i^{(0)}(\bar{k},\lambda)/(\varepsilon_i^{(0)} - \varepsilon_p^{(0)}) \tag{4.30}$$

$$A_{ii}(\bar{k},\lambda) = 0. \tag{4.31}$$

On expanding $\underline{F}^{(1)}$ into submatrices,

$$A_{pi}(\bar{k},\lambda) = (NZ)^{-1}\sum_{u_5}\sum_{u_6}\omega_{\lambda,u_5}\omega_{\lambda,u_6}\sum_{R_5}\sum_{R_6}e^{2\pi i\bar{k}\cdot(\bar{R}_5-\bar{R}_6)}\,{}^{5,6}A_{pi}\ , \tag{4.32}$$

where,

$${}^{5,6}A_{pi} = {}^{5,6}F_{pi}^{(1)}/(\varepsilon_i^{(0)} - \varepsilon_p^{(0)}). \tag{4.33}$$

The intermolecular potential within the crystal which provides the perturbation, can only mix zero order crystal orbitals of the same symmetry, that is, the same $\bar{k}$ and λ. This result is self evident for wave vectors that are invariant with respect to the unit cell operators. In the case of a more general $\bar{k}$ belonging to a star, mixing between orbitals associated with the star is presumably allowed. However, as this mixing will be of a unitary nature and corresponds to a rotation of a degenerate basis, it will be neglected.

On substitution for $O_i^{(1)}(\bar{k}_1,\lambda_1)$ in $<m^3\ell^2|n^4O_i^{(1)}(\bar{k}_1,\lambda_1)>$ using equations (4.29) and (4.33), then substituting into equation (4.18) and evaluating the summations over $\bar{k}$'s and λ's, the contribution is found to be

$$\sum_{u_5}\sum_{T_5}\sum_{p}{}' \; {}^{5,1}A_{pi}<m_3\ell_2|n_4p_5>. \qquad (4.34)$$

The prime on the summation over all the orbitals on molecule five excludes the case p=i. Expression (4.34) represents the first order change in the electron repulsion integral under discussion as a lattice sum, over $\bar{R}_5$, with molecule 1 as the origin. Thus, the total first order contribution from the electron repulsion integrals is

$$\sum_{T_5}\sum_{u_5}\sum_{p}{}' \Big({}^{5,1}A_{pi}\{2\tau<m_3\ell_2|n_4p_5> - <m_3\ell_2|p_5n_4>\}$$

$$+ {}^{5,4}A_{pn}\{2\tau<m_3\ell_2|p_5i_1> - <m_3\ell_2|i_1p_5>\} + {}^{5,2}A_{p\ell}\{2\tau<m_3p_5|n_4i_1> - <m_3p_5|i_1n_4>\}$$

$$+ {}^{5,3}A_{pm}\{2\tau<p_5\ell_2|n_4i_1> - <p_5\ell_2|i_1n_4>\}\Big). \qquad (4.35)$$

In order to be consistent with the SCF perturbation theory used to evaluate the crystal orbitals and Fock matrices, the CNDO approximation [47-51] should be used. The systematic integral approximation of this method, given in chapter 1, leads to an appreciable simplification of the theory without the loss of essential SCF features of inter-electron repulsion; the simplified equations still reflect the underlying structure of the more detailed theory. Recent work [126,127] strongly suggests that this step is unwarranted in the case of calculations on triplet excitons.

The same may also be true for singlet excitons from states of very small Davydov splittings. However, for the singlet states of strongly interacting molecules, such as for charge transfer and hydrogen bonded crystals, the neglect of differential overlap should be relatively unimportant.

Under the intended approximation all charge distributions involving two molecules are neglected. Thus, after the application of the approximation to expression (4.34) the only term to remain from the summation over the lattice is the one for which $\bar{R}_5=\bar{R}_2$. Furthermore, $\bar{R}_3$ must equal $\bar{R}_4$. Hence, the only terms from (4.34) are

$$\sum_p{}' \; {}^{2,1}A_{pi}\langle m_3\ell_2|n_3p_2\rangle\delta_{3,4}. \tag{4.36}$$

The final approximate expression for the matrix element (4.16), to the first order, is given by

$$\begin{aligned}
H_{i\ell,mn}(1,2;3,4) &= (\delta_{\ell n}\varepsilon^{(0)}(\ell_2) - \delta_{im}\varepsilon(i_1))\delta_{1,3}\delta_{2,4} + {}^{2,4}F^{(1)}_{\ell\ell}\delta_{\ell,n}\delta_{1,3} \\
&- {}^{1,3}F^{(1)}_{ii}\delta_{i,m}\delta_{2,4} + \{2\tau\langle m_3\ell_1|n_3i_1\rangle\delta_{3,4}\delta_{1,2} - \langle m_1\ell_2|i_1n_2\rangle\delta_{1,3}\delta_{2,4}\} \\
&+ \sum_p{}'\big(2\tau\{{}^{2,1}A_{pi}\langle m_3\ell_2|n_3p_2\rangle\delta_{3,4} + {}^{3,4}A_{pn}\langle m_3\ell_1|p_3i_1\rangle\delta_{1,2} + {}^{1,2}A_{p\ell}\langle m_3p_1|n_3i_1\rangle\delta_{3,4} \\
&+ {}^{4,3}A_{pm}\langle p_4\ell_2|n_4i_2\rangle\delta_{1,2}\} - \{{}^{2,4}A_{pn}\langle m_3\ell_2|i_1p_2\rangle\delta_{1,3} + {}^{3,1}A_{pi}\langle m_3\ell_2|p_3n_2\rangle\delta_{2,4} \\
&+ {}^{4,2}A_{p\ell}\langle m_3p_4|i_3n_4\rangle\delta_{1,3} + {}^{1,3}A_{pm}\langle p_1\ell_2|i_1n_2\rangle\delta_{2,4}\}\big).
\end{aligned} \tag{4.37}$$

§ 4.5 Frenkel Excitons and the Davydov Splitting [124]

The Frenkel exciton [36b] corresponds to the situation in which the electron and hole are strongly bound together on the same molecule. In the present treatment, the wave functions which most closely correspond to this type of state are the M(0,0) functions. However, these functions have some charge transfer character as a result of their construnction from crystal orbitals that are eigenfunctions of the crystal Hartree-Fock equation.

The diagonal element of the configuration interaction matrix and the first approximation to the crystal excited state energy, $\Delta^{1,3}E^{\lambda}_{i\ell}(0,0)$ corresponding to $M^{\lambda}_{i\ell}(0,0)$ is given by

$$\Delta^{1,3}E^{\lambda(0)}_{i\ell}(0,0) = (NZ)^{-1} \sum_{u_1} \sum_{u_2} \omega_{\lambda,u_1} \omega_{\lambda,u_2} \sum_{\bar{T}_1} \sum_{\bar{T}_2} {}^{1,3}H_{i\ell,i\ell}(1,1;2,2). \tag{4.38}$$

Substitution for $^{1,3}H$ to the zeroth order yields

$$\Delta^{1,3}E^{\lambda(0)}_{i\ell}(0,0) = \varepsilon^{(0)}(\ell_1) - \varepsilon^{(0)}(i_1) + \{2\tau\langle i_1\ell_1|\ell_1 i_1\rangle - \langle i_1\ell_1|i_1\ell_1\rangle\}$$

$$+ 2\tau Z^{-1} \sum_{u_1} \sum_{u_2} \omega_{\lambda,u_1} \omega_{\lambda,u_2} {\sum_{\bar{T}_2}}' \langle i_1\ell_2|\ell_1 i_2\rangle, \tag{4.39}$$

where the prime over the lattice sum is to omit the origin cell when $\bar{u}_1 = \bar{u}_2$.

The $\varepsilon^{(0)}$'s are the free molecule orbital energies and the first two electron repulsion integrals are the molecular exchange and Coulomb integrals respectively. Hence, the first four terms when taken together give the excitation energy, singlet and triplet, for an isolated molecule under the virtual orbital approximation [45]. If the terms associated with the free molecule excitation energy are collected together and written as $\Delta^{1,3}E^{(0)}_{i\ell}$, the zero order crystal excitation energy may be expressed as

$$\Delta^{1,3}E^{(0)}_{i\ell}(0,0) = \Delta^{1,3}E^{(0)}_{i\ell} + Z^{-1}\,2\tau \sum_{u_1}\sum_{u_2} \omega_{\lambda,u_1}\omega_{\lambda,u_2} \sum_{T_2}{}' \langle i_1\ell_2|\ell_1 i_2\rangle. \tag{4.40}$$

The first order correction to the excitation energy is likewise evaluated. Substitution of the first order correction to ${}^{1,3}H_{i\ell,i\ell}(1,1;2,2)$ in equation (4.38) yields

$$\begin{aligned}\Delta^{1,3}E^{\lambda(1)}_{i\ell}(0,0) = {} & \Delta^{1,3}E^{(1)}_{i\ell} \\ & + Z^{-1}2\tau\sum_{p}{}'\sum_{u_1}\sum_{u_2}\omega_{\lambda,u_1}\omega_{\lambda,u_2}\sum_{T_2}{}'({}^{2,2}A_{p\ell}\langle i_2\ell_1|p_2i_1\rangle + {}^{1,1}A_{p\ell}\langle i_2p_1|\ell_2i_1\rangle) \\ & + Z^{-1}2\tau\sum_{p}{}'\sum_{u_1}\sum_{u_2}\omega_{\lambda,u_1}\omega_{\lambda,u_2}\sum_{T_2}{}'({}^{1,1}A_{pi}\langle i_2\ell_1|\ell_2p_1\rangle + {}^{2,2}A_{pi}\langle p_2\ell_1|\ell_2i_1\rangle),\end{aligned} \tag{4.41}$$

where $\Delta^{1,3}E^{(1)}_{i\ell}$ is the crystal induced first order change in the molecular excitation energy, given by:

$$\begin{aligned}\Delta^{1,3}E^{(1)}_{i\ell} = {} & {}^{1,1}F^{(1)}_{\ell\ell} - {}^{1,1}F^{(1)}_{ii} + 2\sum_{p}{}'\{{}^{1,1}A_{p\ell}(2\tau\langle i_1\ell_1|p_1i_1\rangle - \langle i_1\ell_1|i_1p_1\rangle) \\ & + {}^{1,1}A_{pi}(2\tau\langle i_1\ell_1|\ell_1p_1\rangle - \langle i_1\ell_1|p_1\ell_1\rangle)\}.\end{aligned} \tag{4.42}$$

All the $\underline{A}$ matrix elements in equation (4.42) are intramolecular in character since they are between molecular orbitals belonging to a single molecule, arbitrarily chosen as the first. Thus, the charge transfer or delocalized character of the crystal orbitals does not contribute to the crystal excited state to the first order. However, there is some crystal induced mixing of molecular orbitals on individual molecules.

The excitation energy to the first order is given by the sum of (4.40) and (4.41). This form has the correct limiting behaviour as the intermolecular potential tends to zero. That is, as all the intermolecular integrals, first order Fock matrices and mixing coefficients tend to zero, the crystal excitation energy tends to that of an isolated molecule.

The excitation energy may be broken down into three terms which are analogous to the three of the Davydov theory [25] given in equation (1.4). The excitation energy of the isolated molecule is the first term in both (1.4) and (4.40), the shift in excitation energy of a molecule due to the interaction with the lattice, which contributes to the term D in equation (1.4), is $\Delta^{1,3}E^{(1)}_{i\ell}$ in (4.41) and all the remaining parts of equations (4.40) and (4.41) contribute to a term comparable to the last in (1.4), $\sum_{i}\sum_{\ell}\sum_{j}{}'\,\omega_{\lambda,i}\,\omega_{\lambda,\ell}\,M_{ij,\ell m}$, with the intermolecular exchange integral $M_{ij,\ell m}$ given by

$$M_{u_2T_2,u_1T_1} = 2\tau\Big(\langle i_1\ell_2|\ell_1 i_2\rangle + \sum_{p}{}'\{{}^{2,2}A_{p\ell}\langle i_2\ell_1|p_2 i_1\rangle + {}^{1,1}A_{p\ell}\langle i_2 p_1|\ell_2 i_1\rangle$$

$$+ {}^{1,1}A_{pi}\langle i_2\ell_1|\ell_2 p_1\rangle + {}^{2,2}A_{pi}\langle p_2\ell_1|\ell_2 i_1\rangle\}\Big). \qquad (4.43)$$

The lattice sums of these exchange integrals for $u_1=u_2$ contribute to the displacement of the centre of the manifold of Frenkel states from the corresponding molecular excitation energy and the sums for $u_1 \neq u_2$

contribute to the Davydov splittings within the manifold.

Since the Davydov theory neglects any crystal field effects on the molecular orbitals, only the zero order term of (4.43) corresponds to the usual dipole dipole approximation used to evaluate the lattice summations and the corrections to the orbital energy levels, ${}^{1,1}F^{(1)}_{\ell\ell}$ and ${}^{1,1}F^{(1)}_{ii}$, do not occur in the term D. However, under the present approach, the neglect of differential overlap removes the lattice sums of integrals in $\Delta^{1,3}E^{(1)}_{i\ell}$ which contribute to D in the Davydov approach [25]. Also, it should be noted that, since $\tau=0$ for triplet states, the Davydov splitting of triplet excitons in the present treatment is zero to the first order. However, it can be shown that the second order triplet exciton splitting is nonzero.

§ 4.6 Charge Transfer Excitons [124]

The diagonal elements of the configuration interaction matrix that correspond to the charge transfer states are given by

$$\Delta^{1,3}E^{\lambda}_{i\ell}(\bar{\beta},\bar{\rho}) = \langle {}^{1,3}M^{\lambda}_{i\ell}(\bar{\beta},\bar{\rho})|H-E_{\text{ground}}|{}^{1,3}M^{\lambda}_{i\ell}(\bar{\beta},\bar{\rho})\rangle$$

$$= (NZ)^{-1}\sum_{u_1}\sum_{u_2}\omega_{\lambda,u_1}\omega_{\lambda,u_2}\sum_{T_1}\sum_{T_2}{}^{1,3}H_{i\ell,i\ell}(1,2;3,4) \qquad (4.44)$$

where molecules 2 and 4 are $|\bar{\beta}|$ unit cells and $|\bar{\rho}|$ sites away from molecules 1 and 3 respectively. To the zero order,

$$\Delta^{1,3}E^{\lambda(0)}_{i\ell}(\bar{\beta},\bar{\rho}) = \varepsilon^{(0)}(\ell_1) - \varepsilon^{(0)}(i_1) - \langle i_1\ell_2|i_1\ell_2\rangle \qquad (4.45)$$

The necessary Coulomb and exchange integrals to complete the free molecule excitation energy expression are missing from (4.44). Addition and subtraction of these integrals yields

$$\Delta^{1,3}E^{\lambda(0)}_{i\ell}(\bar{\beta},\bar{\rho}) = \Delta^{1,3}E^{(0)}_{i\ell} - \langle i_1\ell_2|i_1\ell_2\rangle + \langle i_1\ell_1|i_1\ell_1\rangle - 2\tau\langle i_1\ell_1|\ell_1 i_1\rangle, \tag{4.46}$$

where, as before, $\Delta^{1,3}E^{(0)}_{i\ell}$ is the free molecule excitation energy. From equation (4.46) it can be seen that the charge transfer excited states are just displaced from the free molecule excitation energy and not split into several components.

To the zeroth level approximation, the charge transfer states are displaced, relative to the centre of the Davydov manifold, by

$$- \langle i_1\ell_2|i_1\ell_2\rangle + \langle i_1\ell_1|i_1\ell_1\rangle - 2\tau\langle i_1\ell_1|\ell_1 i_1\rangle - 2\tau Z^{-1}\sum_{u_2}\{\omega_{\lambda,u_2}\}^2 {\sum_{T_2}}' \langle i_1\ell_2|\ell_1 i_2\rangle \tag{4.47}$$

where all the integrals are positive. The lattice sums from equation (4.40) for $u_1 \neq u_2$ do not contribute to the position of the centre of the Davydov manifold and hence do not appear in (4.47). Since the intramolecular Coulomb integral, $\langle i_1\ell_1|i_1\ell_1\rangle$, will typically be appreciably larger than the sum of the other integrals in (4.47), the charge transfer state will be higher in energy than the corresponding Frenkel state. In the case of singlet excitons this could be offset by a favourable value of the intramolecular exchange integral $\langle i_1\ell_1|\ell_1 i_1\rangle$.

There will be a whole series of charge transfer states which correspond to different values of the electron hole separation. As this separation increases, the intermolecular Coulomb integral in equation (4.45) will decrease in value until it reaches zero for infinite separation. Moreover, the rate of decrease of this integral will decrease with increasing separation. Thus, the charge transfer states give rise to a stack of levels, with each successive level closer to the next. The series limit for these levels, corresponding to infinite electron hole separation, is, to zero order, the difference in the corresponding free molecule orbital energy levels.

For relatively strongly interacting molecules, the positive displacement of the charge transfer exciton energy could be conceivably offset by negative higher order corrections. The first order correction is given by:

$$\Delta^{1,3}E_{i\ell}^{\lambda(1)}(\bar{\beta},\bar{\rho}) = {}^{1,1}F_{\ell\ell}^{(1)} - {}^{1,1}F_{ii}^{(1)} - \sum_{p}{}' \{ {}^{2,2}A_{p\ell}\langle i_1\ell_2|i_1p_2\rangle + {}^{1,1}A_{pi}\langle i_1\ell_2|p_1\ell_2\rangle$$

$$+ {}^{2,2}A_{p\ell}\langle i_1p_2|i_1\ell_2\rangle + {}^{1,1}A_{pi}\langle p_1\ell_2|i_1\ell_2\rangle\}. \qquad (4.48)$$

Clearly, the A matrix elements would have to be especially large in order to override the positive term in equation (4.46)

§ 4.7 The Polarization ratio $P_{i\ell}(\frac{b}{a})$

The polarization ratio $P_{i\ell}(\frac{b}{a})$ is the ratio of the oscillator strength for light polarized parallel to the $\bar{b}$ crystallographic axis to that polarized parallel to the $\bar{a}$ axis for a particular transition. The theoretical value can be obtained from (4.49)

$$P_{i\ell}(\tfrac{b}{a}) = \{T_{i\ell}^{b}\cdot\bar{b}/T_{i\ell}^{ac}\cdot\bar{a}\}^2$$

where $\bar{b}$ and $\bar{a}$ are unit vectors in the b and a crystallographic directions and $T_{i\ell}^{b}$ and $T_{i\ell}^{ac}$ are the components of the transition moment in the b direction and the ac plane respectively.

The transition moment in the above is given by

$$T^{\lambda}_{I\ell}(\bar{\beta},\bar{\rho}) = \int \Psi_0 \bar{p} M^{\lambda}_{I\ell}(\bar{\beta},\bar{\rho})\, d\tau, \tag{4.50}$$

where Ψ_0 is the ground state wavefunction in the delocalized representation, $M^{\lambda}_{I\ell}(\bar{\beta},\bar{\rho})$ is the excited state wavefunction in which the electron and hole are separated by $|\beta|$ unit cells and $|\rho|$ sites and $\bar{p}$ is the dipole moment operator.

Slater and Schockley [125] have shown the equivalence of the ground state wave functions in the localized and delocalized representations. Hence, the ground state wavefunction in the localized representation, L_0, can be used to evaluate the transition moment integral rather than Ψ_0. The substitution of L_0 for Ψ_0 and equation (4.15) for $M^{\lambda}_{I\ell}(\bar{\beta},\bar{\rho})$ in equation (4.50) yields

$$T^{\lambda}_{I\ell}(\bar{\beta},\bar{\rho}) = (NZ)^{-\frac{1}{2}} \sum_{u_1} \omega_{\lambda,u_1} \sum_{\bar{T}_2} \int L_0 \bar{p} L_{I\ell}(\bar{T}_1,\bar{u}_1;\bar{T}_2,\bar{u}_2)\, d\tau. \tag{4.51}$$

In the above $\bar{T}_2=\bar{T}_1+\bar{\beta}$ and $\bar{u}_2=\bar{u}_1+\bar{\rho}$. Evaluation of the summation over $\bar{T}_1$ and integration yields to the zeroth order,

$$T^{\lambda(0)}_{I\ell}(\bar{\beta},\bar{\rho}) = (2N)^{\frac{1}{2}} Z^{-\frac{1}{2}} \sum_{u_1} \omega_{\lambda,u_1} \int i_1 \bar{p} \ell_2\, d\tau, \tag{4.52}$$

The first order correction is obtained by substituting the first order corrections for i_1 and ℓ_2, given by (1.78), into (4.52)

$$T^{\lambda(1)}_{I\ell}(\bar{\beta},\bar{\rho}) = (2N)^{\frac{1}{2}} Z^{-\frac{1}{2}} \sum_{u_1} \omega_{\lambda,u_1} \sum_{q} \sum_{\bar{R}_3} \{ {}^{3,1}A_{qi} \int q_3 \bar{p} \ell_2\, d\tau + {}^{3,2}A_{q\ell} \int i_1 \bar{p} q_3\, d\tau \}. \tag{4.53}$$

Under the neglect of differential overlap approximation, integrals of the type

$$\int i_1\bar{p}\ell_2 d\tau = \delta_{12} \int i_1\bar{p}\ell_1 d\tau. \tag{4.54}$$

Obviously, the neglect of differential overlap, at this point, is unacceptable for the study of charge transfer excitons as it gives, to the zero order, zero intensity. If the theory is used to investigate these states the neglect of overlap should not be used at this point. As a result of (4.54), the intermolecular contribution to the intensity of the Frenkel exciton is at least second order. This is consistent with the result for the intermolecular contribution to the splitting of the Frenkel exciton which is also a second order effect. The bulk of the intensity of the Frenkel exciton arises through the intramolecular exciton and thus the neglect of overlap does not present a serious problem in the calculation of the polarization ratio. Hence, to first order, the transition moment integral for the Frenkel states is given by:

$$T^{\lambda}_{i\ell} = (2N)^{\frac{1}{2}}Z^{-\frac{1}{2}} \sum_{u_1} \omega_{\lambda,u_1}\{\int i_1\bar{p}\ell_1 d\tau + \sum_{q} ({}^{1,1}A_{qi}\int q_1\bar{p}\ell_1 d\tau + {}^{1,1}A_{q\ell}\int i_1\bar{p}q_1 d\tau)\}. \tag{4.55}$$

Using (4.55), the polarization ratio, $P_{i\ell}(\frac{b}{a})$, is easily obtained from (4.49)

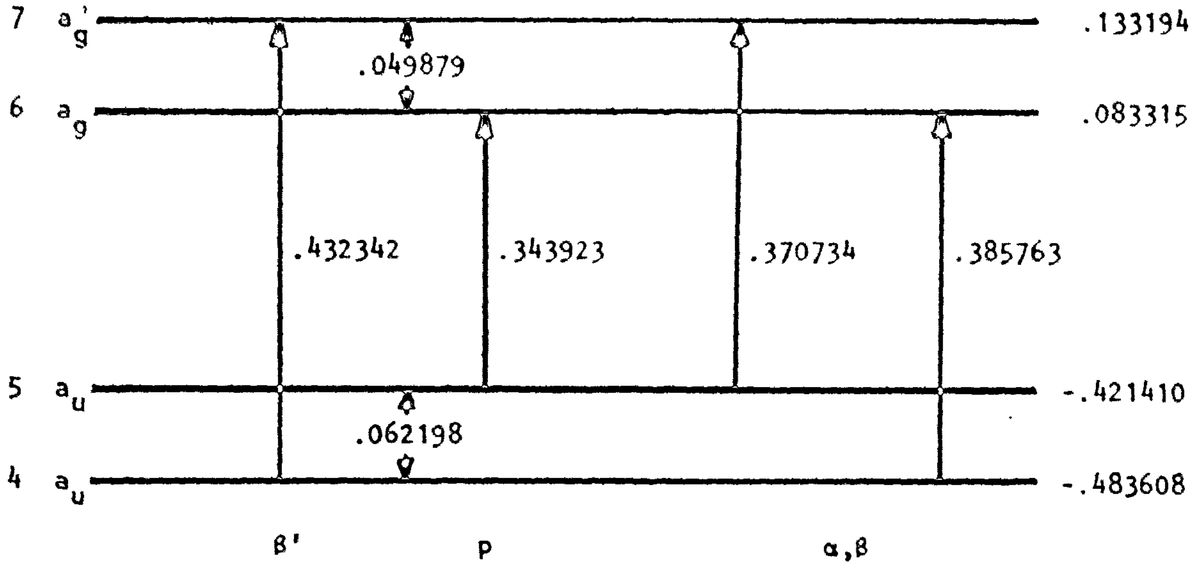
For weak allowed transitions the free molecule transition moment, the zero order integral in (4.55), is small. Thus, the first order corrections could make an appreciable contribution to the polarization ratio through mixing of molecular orbitals involved in strongly allowed transitions with those of the weak transition. This effect is comparable to the intensity "stealing" due to crystal induced mixing of exciton states proposed by Craig [31]. However, the intensity redistribution proposed by Craig is the result of the mixing of crystal states of the same symmetry but not necessarily the same molecular polarization, and hence may have a large effect on the polarization ratio. On the other hand, the first order intramolecular mixing coefficients in (4.55) mix only molecular orbitals of the same symmetry on individual molecules. Thus the effect of the first order corrections in (4.55) is expected to be small with respect to intensity "stealing".

§ 4.8 Application to the Excited States of Naphthalene and Formamide.

In this section the theory is applied to the low lying singlet Frenkel states of naphthalene and formamide crystals using the zero order molecular orbitals and $\underset{\sim}{F}$ and $\underset{\sim}{A}$ matrices from the calculations reported in chapter 2.

In order to apply the theory to the naphthalene crystal, the pi molecular orbital structure and lowest singlet states of the free molecule should be examined. The isolated naphthalene molecule is an alternate hydrocarbon under the pi electron approximation [128] and the two lowest unoccupied and two highest occupied pi levels have the same spacing. The corresponding energy level diagram for the crystal molecule is given in figure 4.1. Although the pi levels calculated for the crystal molecule under the CNDO approximation are not exactly evenly spaced, the molecule was treated as an alternate hydrocarbon. For the case of exactly even spacing, the states arising from excitations from pi levels 5 to 7 and 4 to 6 are degenerate and combine into two states labelled α and β. The states arising from transitions from level

Figure 4.1 The lowest singlet states of molecular naphthalene.



5 to 6 and level 4 to 7 are generally labelled p and β' respectively. The transitions associated with these states are classified as very weak for the α state, weak for the p and β' and strong for the β state.

In order to determine the coefficients of the α, β, p and β' exciton states due to allowed mixing at the molecular level, a molecular configuration interaction calculation using the states that arise from transitions shown in figure 4.1 was performed. This is referred to as the small set configuration interaction calculation (SSCI). Since a full single excitation configuration interaction calculation will change the order of the molecualr β and β' states [128], a second configuration calculation was performed using all $\pi\rightarrow\pi^*$ transitions that lead to states of u symmetry. This is referred to as the large set configuration interaction calculation (LSCI). The additional integrals required for the molecular configuration interaction calculations are given by Pople [129]. The coefficients for the α, β, p and β' crystal states from these calculations are given in table 4.1. The only appreciable contribution from the higher energy states to the lowest singlet states is the $^1M_{3,8}(0,0)$ contribution to the β' state. It is this contribution, presumably, that lowers the energy of the β' state below the β state.

The calculated contributions to the energies of the α, β, p and β' states of naphthalene from the SSCI and LSCI calculations are given in table 4.2. In the table, the molecular excitation energy $\Delta E^{(0)}_{i\ell}$, is the contribution from the zero order excitation energy of the crystal molecule, its first order contribution $\Delta E^{(1)}_{i\ell}$, is the crystal induced first order correction from equation (4.42), the zero order shift due to

Table 4.1 Coefficients of the M type functions in the α, β, p and β' Frenkel states of naphthalene.

a) From the small set molecular configuration interaction calculation.

Function	α	β	p	β'
$^1M_{4,6}(0,0)$	.677097	-.735893	-.000327	-.000939
$^1M_{4,7}(0,0)$	-.000275	.001072	-.509031	-.860748
$^1M_{5,6}(0,0)$	-.000482	-.000710	-.860748	.509031
$^1M_{5,7}(0,0)$	-.735894	-.677096	.000453	-.000876

b) From the large set molecular configuration interaction calculation.

Function	α	β	p	β'
$^1M_{1,6}(0,0)$	-.011988	-.004890	-.000047	-.000016
$^1M_{1,7}(0,0)$	.000027	-.000024	-.024700	.022271
$^1M_{1,10}(0,0)$	.000000	-.000001	-.002907	.008656
$^1M_{2,8}(0,0)$	.048003	.058321	-.000009	-.000133
$^1M_{2,9}(0,0)$	-.000016	.000065	.005979	-.010013
$^1M_{3,8}(0,0)$	.000027	-.000183	.007623	-.454510
$^1M_{3,9}(0,0)$	.052658	.089978	.000052	.000217
$^1M_{4,6}(0,0)$	-.675949	.729377	-.000245	-.001071
$^1M_{4,7}(0,0)$	.000225	-.001310	-.500581	-.772266
$^1M_{4,10}(0,0)$	-.000029	-.000097	-.041445	.052108
$^1M_{5,6}(0,0)$	.000385	.000847	-.864285	.440041
$^1M_{5,7}(0,0)$	.733100	.675487	.000379	-.000969
$^1M_{5,10}(0,0)$	.020864	-.014277	-.000071	-.000052

Table 4.2 Contributions to the energies of the α, β, p and β' states of crystalline naphthalene in cm^{-1}.

a) Using the small set configuration interaction coefficients.

Contribution	α	β	p	β'
$\Delta E^{(0)}_{i\ell}$	63693.5	102373.3	65061.2	105324.4
$\Delta E^{(1)}_{i\ell}$	4.2	-4.2	0.2	-0.2
$I^{(0)}_{11}$	2.4	1564.9	-210.9	-925.1
$I^{(1)}_{11}$	-0.7	0.7	0.0	0.0
$I^{1(0)}_{12}$	-9.4	-9159.1	63.2	2049.8
$I^{2(0)}_{12}$	9.4	9159.1	-63.2	-2049.8
$I^{1(1)}_{12}$	2.9	-2.5	0.4	-1.1
$I^{2(1)}_{12}$	-2.9	2.5	-0.4	1.1

$\Delta E^{(0)}_{i\ell}$, $I^{(0)}_{11}$ and the $I^{\lambda(0)}_{12}$ denote the zero order molecular excitation energy, the zero order shift due to equivalent molecules and the zero order shifts due to inequivalent molecules respectively. The corresponding first order corrections to these contributions are $\Delta E^{(1)}_{i\ell}$, $I^{(1)}_{11}$ and the $I^{\lambda(1)}_{12}$. The I^{1}_{12} components are polarized perpendicular to the b axis and the components I^{2}_{12} are parallel to the b crystal axis.

Table 4.2 continued

b) Using the large set configuration interaction coefficients.

Contribution	α	β	p	β'
$\Delta E^{(0)}_{i\ell}$	63225.7	101757.4	64843.3	96936.7
$\Delta E^{(1)}_{i\ell}$	3.7	-3.7	0.2	-0.2
$I^{(0)}_{11}$	1.5	2548.9	-203.5	-266.2
$I^{(1)}_{11}$	-0.7	0.7	0.0	0.0
$I^{1(0)}_{12}$	-9.7	-8588.6	96.6	625.0
$I^{2(0)}_{12}$	9.7	8588.6	-96.6	-625.0
$I^{1(1)}_{12}$	2.9	-3.3	0.4	-0.4
$I^{2(1)}_{12}$	-2.9	3.3	-0.4	0.4

equivalent molecules $I_{11}^{(0)}$, is the contribution to the sum $2\tau Z^{-1}\sum_{u_1}\sum_{u_2}\omega_{\lambda,u_1}\omega_{\lambda,u_2}\sum_{T_2}\langle I_1\ell_2|\ell_1 I_2\rangle$, in equation (4.40), in which molecule 2 is equivalent to molecule 1 under the full translation group of the lattice. The corresponding first order contribution is $I_{11}^{(1)}$. The shifts due to inequivalent molecules are the contributions for which molecule 2 is not equivalent to molecule 1. In the tables, the shifts due to inequivalent molecules are $I_{12}^{\lambda(0)}$ and $I_{12}^{\lambda(1)}$ for the zero and first order contributions respectively. Although the CNDO method gives poor values for the excitation energies in the virtual orbital approximation [57], these energies are reported for comparison purposes.

In the isolated formamide molecule, the lowest weak $n\rightarrow\pi^*$ and strong $\pi\rightarrow\pi^*$ transitions give rise to two states between which mixing is formally not allowed. However, in the crystal, a small distortion of the molecule induces a small amount of mixing between these states. The diagonal and off diagonal coefficients of the mixing between these states are .997782 and ±.066573. The electronic contributions to the corresponding bands in the crystal are given in table 4.3. For convenience, the bands in the crystal are labelled according to the transition which makes the larger contribution.

Since for weak and very weak transitions the mixing between excitons of the type proposed by Craig [31], is expected to have a large effect on the polarization ratio, calculations of the mixing between the α, β, p and β' states of naphthalene and the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ bands of formamide were performed. The addition matrix elements for these calculations are given in appendix 2. The calculated and experimental

Table 4.3 Contributions to the energies of the n→π* and π→π* bands of crystalline formamide in cm^{-1}.

Contribution	n→π*	π→π*	Polarization
$\Delta E_{i\ell}^{(0)}$	51372.6	95597.6	
$\Delta E_{i\ell}^{(1)}$	3614.5	-7677.1	
$I_{11}^{(0)}$	8.3	3547.7	
$I_{11}^{(1)}$	1.4	-1183.2	
$I_{12}^{1(0)}$	-27.3	-18269.2	
$I_{12}^{2(0)}$	47.6	25499.8	ac
$I_{12}^{3(0)}$	-5.5	2.4	b
$I_{12}^{4(0)}$	-14.7	-7232.9	
$I_{12}^{1(1)}$	-1.7	6687.3	
$I_{12}^{2(1)}$	9.4	-8577.4	ac
$I_{12}^{3(1)}$	-26.8	192.3	b
$I_{12}^{4(1)}$	19.0	1697.7	

The contributions are as defined in table 4.2 and in the text.

Davydov splittings and polarization ratios for naphthalene are in tables 4.4 and 4.5 respectively. The experimental and oriented gas values were taken from reference 30.

Table 4.6 contains the calculated Davydov splittings and polarization ratios for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands of formamide. The splitting was taken as the difference between the $\bar{b}$ and ac polarized components in each case.

In the crystal each of the molecular states of naphthalene gives rise to a state of A_u symmetry with transition moment parallel to the $\bar{b}$ crystallographic axis and one of B_u symmetry polarized in the ac plane. In the same manner, the formamide bands are split into four of A_g, A_u, B_g and B_u symmetries with the A_u polarized parallel to the $\bar{b}$ axis, the B_u in the ac plane and the A_g and B_g states with no net transition moment.

In general, the relatively stronger intermolecular interactions in formamide are reflected in the larger first order corrections to the molecular excitation energies. The occurence of larger contributions from the sums of exchange integrals for formamide also is a consequence of the larger intermolecular interactions. Increasing the size of the configuration interaction calculation from the SSCI to the LSCI for naphthalene has only a small effect except for dropping the energy of the β' state below that of the β state and reducing the contributions from the sums of exchange integrals to the β' state.

The large first order corrections to the molecular excitation energies of formamide, towards higher energy for the $n \rightarrow \pi^*$ band and towards lower energy for the $\pi \rightarrow \pi^*$ band, parallel the effect of hydrogen bonding

Table 4.4 The calculated and experimental Davydov splittings for the lowest singlet states of naphthalene in cm^{-1}.

State	Expt.	Calc.(SSCI)	Calc.(SSCI) E.M.	Calc.(LSCI)	Calc.(LSCI) E.M.
α	-186*	-13.2	-8.3	-12.5	-7.7
β		-18323.4	-22244.5	-17185.8	-17502.8
p	320	127.5	195.3	194.0	263.8
β'		4097.3	5750.9	1250.8	2151.2

*This is made up of 150 cm^{-1} in the 0-0 band and 36 cm^{-1} in the 0-1 band. SSCI refers to the use of the coefficients from the small set configuration interaction calculation and LSCI from the large set configuration interaction calculation. E.M. refers to the exciton mixing of Craig [31].

Table 4.5 The calculated and experimental polarization ratios, $P_{l\ell}(\frac{b}{a})$, for the lowest singlet states of naphthalene.

State	Expt.	Oriented gas	Calc.(SSCI)	Calc.(SSCI) E.M.	Calc.(LSCI)	Calc.(LSCI) E.M.
α	10.	.25	.22	.01	.23	.00
β		.25	.23	.04	.23	.00
p	3.	7.7	7.25	2.99	7.25	3.01
β'			7.20	3.73	7.18	3.98

solvents on aldehydes and ketones [130]. Also, recent calculations by Del Bene [131] on the $n \rightarrow \pi^*$ bands in carbonyl compounds upon dimerization indicate a shift towards higher energy. Hence, the major effects of the crystalline hydrogen bonding environment on the carbonyl group are reproduced by the SCF perturbation method.

Since the CNDO method gives poor values for the molecular excitation energies in the virtual orbital approximation [57] and the neglect of overlap removes a large part of the contribution to the shift of the centre of the Davydov manifold from the molecular excitation energies, only the Davydov splitting and polarization ratios for the purely electronic excited states should be directly compared to experimental results.

Generally, for naphthalene, the inter-exciton mixing strongly influences the polarization ratios and has only a small effect on the splittings. The only significant effect of increasing the size of the molecular configuration interaction is in the considerable decrease in the size of the splitting in the β' state.

The polarization ratio and Davydov splitting of the α state for naphthalene show a very poor agreement with experiment. However, it has been demonstrated previously by Craig [31] that for very weak transitions the dipole-dipole approximation cannot account for the observed Davydov splittings. Thus, since under the CNDO approximation the higher multipole moments in the lattice sums of exchange integrals are not well represented, the calculated splitting is much smaller than observed. Furthermore, the intensity of the α band in naphthalene arises largely from the p molecular state through vibronic coupling. Hence, the calculated

Table 4.6 The calculated Davydov splittings and polarization ratios for the n→π* and π→π* bands in the formamide crystal.

Band	Splitting	Polarization ratio	Splitting (E.M.)	Polarization ratio(E.M.)
n→π*	-89.3	228.03	-79.2	6.90
π→π*	-16728.4	12.69	-16737.6	12.72

The Davydov splittings were taken as the intervals between the b and ac polarized components in cm^{-1}. E.M. refers to the inclusion of the inter-exciton mixing of Craig [31].

polarization ratio is not comparable to the experimental value.

For the p state, which arises from a stronger transition than the α state, the polarization ratio agrees with experiment after inter-exciton mixing has been taken into account. The calculated Davydov splitting for the p state is about 80% of the experimental value when inter-exciton mixing and the coefficients of the molecular large size configuration interaction calculation are used. The remaining portion of the splitting in the p state of naphthalene could easily be accounted for by mixing with charge transfer states [35].

For formamide, since the $\pi\rightarrow\pi^*$ transition is much more strongly allowed than the $n\rightarrow\pi^*$ transition, the resultant Davydov splitting for the $\pi\rightarrow\pi^*$ band is much larger than that for the $n\rightarrow\pi^*$ band. The rather large change in the polarization ratio of the $n\rightarrow\pi^*$ band is the result of a mixing of only about 4% of the transition moment of the $\pi\rightarrow\pi^*$ band with that of the $n\rightarrow\pi^*$ band. Hence, in the crystal, the polarization ratio of a weak transition can be changed quite drastically by the perturbing effect of a strong transition.

In summary, a theory for the electronic excited states of molecular crystals within the molecular orbital approximation has been developed and used to calculate the Davydov splittings and polarization ratios for some transitions of a hydrogen bonded crystal, formamide, and a dispersive crystal, naphthalene.

It has been shown that the results for the Frenkel exciton can be cast into the same form as those Davydov [25] obtained from the valence bond approach. With the inclusion of the inter-exciton mixing of Craig [31,32], the polarization ratio of the p state of naphthalene and up to 80% of its Davydov splitting can be reproduced. There is some reason to believe that the agreement for the splitting could be improved by the inclusion of charge transfer states [30,33-35].

If the theory is to be applied to weak transitions or to the calculation of the excitation energies and spectral shifts, the neglect of overlap, which is not an inherent approximation of the basic theory, should be abandoned in favour of less approximate methods. However, the gross effect of the hydrogen bonding interaction on the spectrum of carbonyl compounds is predicted within the neglect of overlap approximation.

CONCLUDING DISCUSSION

The SCF perturbation method for molecular crystals outlined in Chapter 1 is a useful method for the investagation of some of the electronic properties of a wide range of these systems.

The results for the intermolecular perturbative portion of the binding energy and charge distributions given in Chapter 2 are quite reasonable. The lattice energy of hydrogen bonded crystals is reproduced quite well and the contribution from perturbative bonding interactions to van der Waals crystals is found to be small but significant. The changes in the molecular charge distribution upon crystallization are small and in the case of hydrogen bonded crystals are such that the hydrogen bonding environment is enhanced. The amount of charge transferred between molecules, due to distortions of the unit cell brought about by cooperative vibrations or rotations of the molecules, is small but may have a significant effect on the lattice vibrational spectra.

The method of calculating the band structures given in Chapter 3 is quite practical and can easily be applied to systems as large as the naphthalene crystal. The results of the band structure calculations on naphthalene and ethylene and the band structure and density of states calculations for formamide, formic acid and urea indicate that some molecular levels are dispersed more than others. Specifically, the bands derived from the lowest occupied sigma levels are strongly dispersed whilst the bands derived from the highest occupied pi and non bonding levels are relatively unaffected.

The molecular orbital method for the excited states of crystals derived in Chapter 4 reproduced the observed values for the Davydov splitting and polarization ratio for the weak p state of naphthalene and the gross effect of the hydrogen bonding environment on the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ bands of the carbonyl group of formamide. The Davydov splittings of these bands in formamide are predicted to be quite large and in proportion to the strengths of the transitions.

The SCF perturbation method for molecular crystals can be used to calculate the intermolecular perturbative bonding energy, charge distribution, electronic band structure, density of states and crystal spectra for various crystal types. Thus, the objective set out in the Introduction, in part at least, has been fulfilled. That is, a theory of the electronic properties of molecular crystals which includes all crystal interactions and makes no assumptions as to the additivity of intermolecular forces could be obtained,if the dispersive van der Waals interactions are incorporated within the framework of the SCF perturbation theory and the representation of the higher multipole moments is improved.

The removal of the requirement of the Neglect of Differential Overlap from the theory could improve the agreement with experiment. This is especially probable for properties such as the ground state energy of crystals of molecules in which quadrupole and higher moments play an important role and the spectral shift and splittings arising from very weak transitions in the crystal for which the higher transition moments make an important contribution. The theory for the calculation of the charge distributions and lattice energies without this restriction has recently been given by O'Shea and Santry [64] and its implementation seems quite possible with the increasing availability of large computers.

The inclusion of dispersive forces could be accomplished using the perturbation method outlined in the Introduction with the additional matrix elements and energy differences obtained from the theory of the excited states given in Chapter 3. In this approach, the dispersive interactions would be calculated after the completion of the SCF perturbation and its effects simply added to the results of the SCF perturbation calculation. A much more satsifactory method of the inclusion of dispersive forces would be to use the method of Mukherjee [132] in which the expansion coefficients of (1.1) and the forms of the orbitals are optimized simultaneously. Hence, the dispersive and non-dispersive forces could both be treated self consistently. However, the large amount of computer storage required for this type of calculation would likely limit its application to crystals of very small molecules.

An important application of the theory in its present form could be to charge-transfer or π-molecular complexes. Recent theoretical studies using the CNDO or a modified CNDO method for dimers [133-135], a method of building up wavefunctions for the pi electrons of the crystal from those of triads of molecules [136-137] and a treatment of the ferroelectric transition due to a distortion of the lattice of TTF-TCNQ [138] have been reported. Unlike the above calculations, the SCF perturbation method can be used to treat all the valence electrons of molecules in the crystalline environment and the effects of lattice distortions unambiguously.

APPENDIX 1

Coordinates of the atoms, in terms of the unit cell axes, for the reference molecules of the crystals studied in chapter 2. An asterisk indicates the hydrogen in a hydrogen bonded crystal which makes the shortest intermolecular contact.

a) Nitrogen[68]

Atom	a_o	b_o	c_o
N_1	.554000	.446000	-.054000
N_2	.446000	.554000	-.054000

b) S-triazine[69]

Atom	a_o	b_o	c_o
H_1	.235203	.000000	.250000
H_2	.000000	.235203	.250000
H_3	-.235203	-.235203	.250000
C_1	.131803	.000000	.250000
C_2	.000000	.131803	.250000
C_3	-.131803	-.131803	.250000
N_1	-.141205	.000000	.250000
N_2	.000000	-.141205	.250000
N_3	.141205	.141205	.250000

c) Naphthalene[70]

Atom	a_o	b_o	c_o
H_1	.136800	.062700	.466500
H_2	.031800	.297800	-.340800
H_3	.188300	.318500	.273300
H_4	.149900	.404300	-.021300
H_5	-.136800	-.062700	-.466500
H_6	-.031800	-.297800	.430800
H_7	-.188300	-.318500	-.273300
H_8	-.149900	-.404300	.021300
C_1	.085700	.017400	.326700
C_2	.009900	.186900	-.255500
C_3	.114900	.160600	.220500
C_4	.076100	.247600	-.078200
C_5	.048200	.103000	.035900
C_6	-.085700	-.017400	-.326700
C_7	-.009900	-.186900	.255500
C_8	-.114900	-.160600	-.220500
C_9	-.076100	-.247600	.078200
C_{10}	-.048200	-.103000	-.035900

d) Benzene[71]

Atom	a_o	b_o	c_o
H_1	-.104600	.250500	-.012300
H_2	.104600	-.250500	.012300
H_3	-.245800	.078100	.224100
H_4	.245800	-.078100	-.224100
H_5	-.137100	-.168100	.236000
H_6	.137100	.168100	-.236000
C_1	-.060700	.139300	-.006900
C_2	.060700	-.139300	.006900
C_3	-.137700	.044700	.126000
C_4	.137700	-.044700	-.126000
C_5	-.077000	-.095800	.132500
C_6	.077000	.095800	-.132500

e) Hydrogen cyanide[72]

Atom	a_o	b_o	c_o
H	.000000	.000000	.246544
C	.000000	.000000	.000000
N	.000000	.000000	-.265899

f) Carbon dioxide[73]

Atom	a_o	b_o	c_o
C	.000000	.000000	.000000
O_1	.120300	.120300	.000000
O_2	-.120300	-.120300	.000000

g) Sulphur dioxide[74]

Atom	a_o	b_o	c_o
S	.000000	.000000	.000000
O_1	.140000	.150000	.118000
O_2	-.140000	-.150000	.118000

h) Diborane[75]

Atom	a_o	b_o	c_o
H_1	.166000	.140000	-.194000
H_2	-.166000	-.140000	.194000
H_3	.294000	-.005000	.196000
H_4	-.294000	.005000	-.196000
H_5	-.019000	.112000	.104000
H_6	.019000	-.112000	-.104000
B_1	.146000	.042000	.002000
B_2	-.146000	-.042000	-.002000

I) Tetracyanoethylene oxide[76]

Atom	a_o	b_o	c_o
C_1	.739400	.311100	.194900
C_2	.875600	.641300	.284700
C_3	.582900	.326100	.354000
C_4	.720500	.654600	.446200
C_5	.796000	.450000	.297000
C_6	.715300	.457700	.381400
N_1	.691300	.199900	.116800
N_2	.937800	.795100	.278900
N_3	.478300	.226200	.324700
N_4	.728500	.817000	.494600
O	.848600	.342900	.407300

J) Tetracyanoethylene[77]

Atom	a_o	b_o	c_o
C_1	.069000	.500000	.500000
C_2	-.069000	.500000	.500000
C_3	.147680	.500000	.624900
C_4	-.147680	.500000	.624900
C_5	.147680	.500000	.375100
C_6	-.147680	.500000	.375100
N_1	.212870	.500000	.726100
N_2	-.212870	.500000	.726100
N_3	.212870	.500000	.278400
N_4	-.212870	.500000	.278400

k) Formic acid[78]

Atom	a_0	b_0	c_0
H_1	.107300	.428400	.320200
H_2^*	.138600	.028500	-.129800
C	.157000	.306000	.161000
O_1	.089000	.140000	.000000
O_2	.267000	.337000	.147000

l) Melamine[79]

Atom	a_0	b_0	c_0
H_1	-.018600	1.050900	.163000
H_2	-.053800	.984700	.344900
H_3^*	.064600	.364700	.505000
H_4	.161000	.255800	.391300
H_5	.271200	.537600	-.085200
H_6	.240900	.769500	-.123900
N_1	.181200	.504300	.180800
N_2	.116400	.809000	.099300
N_3	.060400	.662300	.349100
N_4	.011600	.960100	.276500
N_5	.121300	.367900	.421100
N_6	.224200	.649900	-.068200
C_1	.063500	.804700	.240000
C_2	.121300	.515200	.313900
C_3	.172900	.658300	.074300

m) Formamide[80]

Atom	a_o	b_o	c_o
H_1^*	.231000	-.262000	.176000
H_2	.420000	-.124000	-.010000
H_3	.184000	-.085000	.389000
C	.310000	-.059000	.261000
N	.330000	-.159000	.128000
O	.434000	.067000	.224000

n) Urea[81]

Atom	a_o	b_o	c_o
H_1^*	.269000	.769000	.279000
H_2	-.269000	.231000	.279000
H_3	.142000	.642000	-.028000
H_4	-.142000	.385000	-.028000
N_1	.145500	.645500	.180000
N_2	-.14500	.354500	.180000
C	.000000	.500000	.327800
O	.000000	.500000	.596600

o) Cyanuric acid[82]

Atom	a_o	b_o	c_o
H_1^*	.250000	-.140900	.250000
H_2	.242250	.384500	.073660
H_3	.247750	.384500	.426300
C_1	.250000	.417910	.250000
C_2	.245250	.105880	.146230
C_3	.254750	.105880	.353770
N_1	.250000	.011410	.250000
N_2	.244600	.309010	.150460
N_3	.255400	.309010	.349540
O_1	.250000	.598180	.250000
O_2	.242620	.013750	.057120
O_3	.257380	.013750	.442880

p) SF_3BF_4[83]

Atom	a_o	b_o	c_o
B	.483460	.750000	.176580
F_1	.628180	.750000	.159840
F_2	.424900	.750000	.034570
F_3	.440870	.552380	.250110
F_4	.440870	.947620	.250110
F_5	.804710	.554530	-.053470
F_6	.804710	.954530	-.053470
F_7	.775190	.750000	-.268220
S	.718320	.750000	-.112590

q) BF_4NH_4[84]

Atom	a_o	b_o	c_o
H_1	.225000	.250000	.346000
H_2	.347000	.250000	.234000
H_3	.346000	.121000	.372000
H_4	.346000	.379000	.372000
N	.314000	.250000	.336000
B	.940000	.250000	.693100
F_1	1.075200	.250000	.611100
F_2	.828300	.250000	.563700
F_3	.924100	.051700	.803000
F_4	.924100	.-48300	.803000

APPENDIX 2

The required matrix elements for the inter-exciton mixing calculations are those between singlet Frenkel excitons for different transitions, and are written

$$\Delta {}^1E^{\lambda}_{i\ell,mn}(0,0) = (NZ)^{-1} \sum_{u_1} \sum_{u_2} \omega_{\lambda,u_1} \omega_{\lambda,u_2} \sum_{T_1} \sum_{T_2}{}' \; {}^1H_{i\ell,mn}(1,1;2,2). \qquad \text{(A2.1)}$$

Substitution for ${}^1H_{i\ell,mn}(1,1;2,2)$ to the zeroth order yields

$$\Delta {}^1E^{\lambda(0)}_{i\ell,mn}(0,0) = Z^{-1} \, 2\tau \sum_{u_1} \sum_{u_2} \omega_{\lambda,u_1} \omega_{\lambda,u_2} \sum_{T_2}{}' \langle m_2 \ell_1 | n_2 i_1 \rangle. \qquad \text{(A2.2)}$$

The first order correction is likewise evaluated. Substitution of the first order correction to ${}^1H_{i\ell,mn}(1,1;2,2)$ in equation (A.1) yields

$$\begin{aligned} \Delta {}^1E^{\lambda(1)}_{i\ell,mn}(0,0) = Z^{-1} \, 2\tau \sum_{p}{}' \sum_{u_1} \sum_{u_1} \omega_{\lambda,u_1} \omega_{\lambda,u_2} \sum_{T_2}{}' \big(& {}^{2,2}A_{pm} \langle p_2 \ell_1 | n_2 i_1 \rangle \\ & + {}^{1,1}A_{p\ell} \langle m_2 p_1 | n_2 i_1 \rangle + {}^{2,2}A_{pn} \langle m_2 \ell_1 | p_2 i_1 \rangle \\ & + {}^{1,1}A_{pi} \langle m_2 \ell_1 | n_2 p_1 \rangle \big). \end{aligned} \qquad \text{(A2.3)}$$

APPENDIX 3

The correspondence between the theory of Bacon, Crowe and Santry [60-65] for the bond order matrix and that of McWeeny [140] for the density matrix is given here.

The coefficients of the atomic orbitals in equation (1.32) for the occupied molecular orbitals are collected together in a matrix $\underset{\sim}{T}$. Thus (1.32) is now written

$$\underset{\sim}{\phi} = \underset{\sim}{T}\underset{\sim}{\chi} \tag{A3.1}$$

with the ϕ's and χ's now row matrices. The spinless density matrix, $\underset{\sim}{\rho}$, is then defined as

$$\underset{\sim}{\rho} = \underset{\sim}{T}\underset{\sim}{T}^{\dagger} \, . \tag{A3.2}$$

The columns of $\underset{\sim}{T}$ are the coefficients of (1.32) for the occupied molecular orbitals calculated by the solution of the Hartree-Fock equations

$$\underset{\sim}{F}\underset{\sim}{C} = \underset{\sim}{C}\underset{\sim}{E} \, . \tag{A3.3}$$

This may also be written

$$\underset{\sim}{F}\underset{\sim}{T} = \underset{\sim}{T}\underset{\sim}{E} \tag{A3.4}$$

and

$$\underline{F}\underline{\rho} = \underline{\rho}\underline{F} \tag{A3.5}$$

readily follows. Because the molecular orbitals are assumed to be orthonormal, $\underline{\rho}$ is idempotent

$$\underline{\rho}^2 = \underline{\rho} \,. \tag{A3.6}$$

Conversely, (A3.5) and (A3.6) are the necessary and sufficient conditions that $\underline{E}$ is stationary against any variations of the ϕ's, subject to the preservation of orthonormality.

Proceeding in the manner of ordinary perturbation theory, the density matrix is expanded

$$\underline{\rho} = \underline{\rho}^{(0)} + \underline{\rho}^{(1)} + \underline{\rho}^{(2)} + \cdots \tag{A3.7}$$

and

$$\underline{F} = \underline{F}^{(0)} + \underline{\Delta} \,. \tag{A3.8}$$

On inserting (A3.7) and (A3.8) into (A3.5) and (A3.6), one obtains on separating the orders

$$\underline{F}^{(0)}\underline{\rho}^{(0)} - \underline{\rho}^{(0)}\underline{F}^{(0)} = 0, \tag{A3.9}$$

$$\underline{F}^{(0)}\underline{\rho}^{(1)} - \underline{\rho}^{(1)}\underline{F}^{(0)} + \underline{\Delta}\underline{\rho}^{(0)} - \underline{\rho}^{(0)}\underline{\Delta} = 0, \tag{A3.10}$$

$$\underline{F}^{(0)}\varrho^{(k)} - \varrho^{(k)}\underline{F}^{(0)} + \underline{\Delta}\varrho^{(k-1)} - \varrho^{(k-1)}\underline{\Delta} = 0 \tag{A3.11}$$

and

$$\varrho^{(0)2} = \varrho^{(0)} , \tag{A3.12}$$

$$\varrho^{(0)}\varrho^{(1)} + \varrho^{(1)}\varrho^{(0)} = \varrho^{(1)} , \tag{A3.13}$$

$$\varrho^{(0)}\varrho^{(k)} + \varrho^{(1)}\varrho^{(k-1)} + \cdots + \varrho^{(k-1)}\varrho^{(1)} + \varrho^{(k)}\varrho^{(0)} = \underline{0} . \tag{A3.14}$$

A zero order solution is assumed to exist that satisfies (A3.9) and (A3.12). Thus, (A3.11) and (A3.12) define the higher order corrections.

Since $\varrho^{(0)}$ is a projection operator for the space spanned by the occupied orbitals, the complementary projection operator

$$1 - \varrho^{(0)} = \varrho_v^{(0)} = 1 - \varrho_o^{(0)} \tag{A3.15}$$

defines the subspace spanned by the vacant orbitals. Any arbitrary matrix, $\underline{M}$, can be resolved into components as follows,

$$\underline{M} = \varrho_o^{(0)}\underline{M}\varrho_o^{(0)} + \varrho_o^{(0)}\underline{M}\varrho_v^{(0)} + \varrho_v^{(0)}\underline{M}\varrho_o^{(0)} + \varrho_v^{(0)}\underline{M}\varrho_v^{(0)}$$

$$= \underline{M}_{oo} + \underline{M}_{ov} + \underline{M}_{vo} + \underline{M}_{vv}. \tag{A3.16}$$

The components are linearly independent and $A_{ij}B_{lk} = 0$ unless $j = k$. If $\varrho^{(1)}$ is resolved into its components, equation (A3.13) yields four equations, one for each component:

$$2\varrho_{oo}^{(1)} = \varrho_{oo}^{(1)} \quad , \tag{A3.17}$$

$$\varrho_{ov}^{(1)} = \varrho_{ov}^{(1)} \quad , \tag{A3.18}$$

$$\varrho_{vo}^{(1)} = \varrho_{vo}^{(1)} \quad , \tag{A3.19}$$

$$0 = \varrho_{vv}^{(1)} \quad . \tag{A3.20}$$

Thus, $\varrho_{oo}^{(1)} = \rho_{vv}^{(1)} = 0$, whilst $\varrho_{ov}^{(1)}$ and $\varrho_{vo}^{(1)}$ are undetermined, though by Hermitian symmetry

$$\varrho_{ov}^{(1)} = \varrho_{vo}^{(1)\dagger} \quad . \tag{A3.21}$$

This means that $\underline{\varrho}^{(0)} + \underline{\varrho}^{(1)}$ is idempotent providing $\underline{\varrho}^{(1)}$ is of the form

$$\varrho^{(1)} = \varrho_{ov}^{(1)} + \varrho_{vo}^{(1)} \quad . \tag{A3.22}$$

Substitution of $\underline{\varrho}^{(1)}$ into (A3.10) and resolving $\underline{\varrho}^{(1)}$ and $\underline{\Delta}$ into components yields

$$\underline{F}^{(0)}\varrho_{ov}^{(1)} - \varrho_{ov}^{(1)}\underline{F}^{(0)} - \underline{\Delta}_{ov} = 0 \quad , \tag{A3.23}$$

$$\underline{F}^{(0)}\varrho_{vo}^{(1)} - \varrho_{vo}^{(1)}\underline{F}^{(0)} + \underline{\Delta}_{vo} = 0 \quad . \tag{A3.24}$$

Since (A3.23) and (A3.24) are each others Hermitian conjugates, then one need solve only for $\underline{\rho}_{ov}^{(1)}$. If $\underline{F}^{(0)}$ is assumed nonsingular (this is in general the case) then its inverse exists and (A3.23) can be written

$$\underline{\rho}_{ov}^{(1)} = \underline{F}^{(0)}\underline{\rho}_{ov}^{(1)}\underline{F}^{(0)-1} + \underline{\Delta}_{ov}\underline{F}^{(0)-1} \qquad \text{(A3.25)}$$

or

$$\underline{x} = \underline{F}^{(0)}\underline{x}\underline{F}^{(0)-1} + \underline{\Delta}_{ov}\underline{F}^{(0)-1} = f(\underline{x}) \qquad (\underline{x} = \underline{\rho}_{ov}^{(1)}) \quad . \qquad \text{(A3.26)}$$

A formal solution may be obtained by iteration. Thus, if $\underline{x}_0 = 0$, $\underline{x}_1 = f(\underline{x}_0) = \underline{\Delta}_{ov}\underline{F}^{(0)-1}$ and in general

$$\underline{x}_{k+1} = f(\underline{x}_k) = \underline{F}^{(0)}\underline{x}_k\underline{F}^{(0)-1} + \underline{\Delta}_{ov}\underline{F}^{(0)-1} . \qquad \text{(A3.27)}$$

Then the limit of the sequence gives

$$\underline{\rho}^{(1)} = \sum_{n=0}^{\infty} \underline{F}^{(0)^n}\underline{\Delta}_{ov}\underline{F}^{(0)^{-(n+1)}} \quad . \qquad \text{(A3.28)}$$

In order to determine under what conditions the iterative solution converges, $\underline{F}^{(0)}$ is written in terms of its eigenvalues and the projection operators for its eigenvectors. Thus

$$\underline{F}^{(0)} = \sum_{i=1}^{m} \varepsilon_i \underline{\rho}_i \ , \qquad \text{(A3.29)}$$

where $\varrho_i = \underline{c}_i \underline{c}_i^\dagger$ is the projection operator for the eigenvector $\underline{c}_i$. In general,

$$f(\underline{F}^{(0)}) = \sum_{i=1}^{m} f(\varepsilon_i)\varrho_i \ . \tag{A3.30}$$

On substituting this form into (A3.28) and making use of

$$\varrho_o^{(0)} = \sum_i^{occ} \varrho_i \tag{A3.31}$$

and

$$\varrho_v^{(0)} = \sum_i^{vac} \varrho_i \ , \tag{A3.32}$$

McWeeny obtains

$$\begin{aligned} \varrho_{ov}^{(1)} &= \sum_{n=0}^{\infty} \underline{F}^{(0)^n} \underline{\Delta}_{ov} \underline{F}^{(0)^{-(n+1)}} \\ &= \sum_{n=0}^{\infty} \sum_j^{occ} \sum_k^{vac} \varepsilon_j^n \varrho_j \underline{\Delta}_{ov} \varrho_k \varepsilon_k^{-(n+1)} \\ &= \sum_{n=0}^{\infty} \sum_j^{occ} \sum_k^{vac} \left(\frac{\varepsilon_j^n}{\varepsilon_k^{n+1}} \right) \underline{c}_k^\dagger \underline{c}_j \Delta_{jk} \ ; \end{aligned} \tag{A3.33}$$

where

$$\Delta_{jk} = \underline{c}_j^\dagger \underline{\Delta} \underline{c}_k \ . \tag{A3.34}$$

This expression is a geometric series with respect to n and converges absolutely as long as $\varepsilon_j < \varepsilon_k$ (all j occupied, all k vacant). In general this condition is met by the zero order solutions and the sum over n may be evaluated to obtain

$$\underset{\sim}{\rho}_{ov}^{(1)} = \sum_{j}^{occ} \sum_{k}^{vac} \underset{\sim}{c}_k^{\dagger} \underset{\sim}{c}_j \Delta_{jk}/(\varepsilon_k - \varepsilon_j) . \tag{A3.35}$$

Thus, from (A3.22)

$$\underset{\sim}{\rho}^{(1)} = \sum_{j}^{occ} \sum_{k}^{vac} (\underset{\sim}{c}_k^{\dagger} \underset{\sim}{c}_j + \underset{\sim}{c}_j^{\dagger} \underset{\sim}{c}_k) \Delta_{jk}/(\varepsilon_k - \varepsilon_j) . \tag{A3.36}$$

The comparison of (A3.36) and (1.84) using

$$\underset{\sim}{P} = 2\underset{\sim}{\rho} \tag{A3.37}$$

yields

$$A_{jk} = \Delta_{jk}/(\varepsilon_k - \varepsilon_j) = F_{jk}^{(1)}/(\varepsilon_k - \varepsilon_j) . \tag{A3.38}$$

Thus the correspondence of the two theories to first order is exact. Since McWeeney does not allow for changes in $\underset{\sim}{F}$ above first order, the theory of Bacon, Crowe and Santry contains extra terms and the correspondence is not exact for the second and higher orders.

It should be noted that because of the properties of the projection operators, expressions with apparent singularities do not occur in McWeeny's presentation of the theory.

REFERENCES

1. Kitaigorodsky, A.I.: Molecular Crystals and Molecules. New York: Academic Press 1973
2. Pauling, L.: Proc. Nat. Acad. Sci. 14, 359 (1928)
3. Craig, D.P., Mason, R., Pauling, P., Santry, D.P.:Proc. Roy. Soc. A286, 98 (1965)
4. Margenau, H., Kestner, N.R.: The Theory of Intermolecular Forces. Oxford: Pergamon Press 1969
5. Buckingham, A.D.: Quart. Rev. 13, 183 (1959)
6. Nagi, O., Nakamura, T.: Prog. Theor. Phys. 21, 432 (1960)
7. Mason, R.: In: Perspectives in Structural Chemistry, Vol. 3. New York: John Wiley and Sons 1970
8. Craig, D.P., Dobosh, P.A., Mason, R., Santry, D.P.: Discuss. Farady Soc. 40, 110 (1965)
9. Rae, A.I.M., Mason, R.: Proc. Roy. Soc. A304, 487 (1968)
10. Mason, R., Rae, A.I.M.: Proc. Roy. Soc.A304, 501 (1968)
11. Rae, A.I.M.: Molecular Physics 16, 257 (1969)
12. Williams, D.E.: Science 147, 605 (1965)
13. Williams, D.E.: J. Chem. Phys. 45, 3770 (1966)
14. Williams, D.E.: J. Chem. Phys. 47, 4680 (1967)
15. Hasimoto, M., Isobe, T.: Bull. Chem. Soc. Japan 46, 2581 (1973)
16. Hasimoto, M., Isobe, T.: Bull. Chem. Soc. Japan 47, 40 (1974)
17. Kollman, P.A., Allen, L.C.: Chem. Rev. 72, 283 (1972)
18. Morokuma, K., Pedern, L.: J. Chem. Phys. 48, 3275 (1968)
19. Morokuma, K., Winick, J.: J. Chem. Phys. 52, 1301 (1970)

[illegible]. Morokuma, K.: J. Chem. Phys. 55, 1236 (1971)

21. Llachka, H.: Chem. Phys. Lett. 20, 448 (1973)

22. Lischka, H.: Chem. Phys. 2, 191 (1973)

23. Del. Bene, J.E.: Chem. Phys. Lett. 24, 203 (1974)

24. Frenkel, J.: Phys. Rev. 37, 1276 (1931)

25. Davydov, A.S.: J. Exptl. Theoret. Phys. (U.S.S.R.) 18, 210 (1948)
Davydov, A.S.: Soviet Physics Uspekhi 7, 145 (1964)

26. Tanaka, J.: Bull. Chem. Soc. Japan 36, 1237 (1963)

27. Craig, D.P., Walsh, J.R.: J. Chem. Soc., 1613 (1958)

28. Craig, D.P., Hobbins, P.C.: J. Chem. Soc. 539 (1955)

29. Hochstrasser, R.M.: Revs. Modern Phys. 34, 531 (1962)

30. Silbey, R., Jortner, J., Vala, M.T. Jr., Rice, S.A.: J. Chem. Phys. 42, 2948 (1965)

31. Craig, D.P.: J. Chem. Soc., 2302 (1955)

32. Craig, D.P., Walmsley, S.H.: Mol. Phys. 4, 113 (1961)

33. Silbey, R., Jortner, J., Rice, S.A.: J. Chem. Phys. 42, 1515 (1965)

34. Silbey, R., Rice, S.A., Jortner, J.: J. Chem. Phys. 43, 3336 (1965)

35. Greer, W.L., Rice, S.A., Jortner, J.: J. Chem. Phys. 48, 5667 (1968)

36a. Knox, R.S.: Theory of Excitons, Solid State Phys. Suppl. 5. New York: Academic Press 1963

b. Craig, D.P., Walmsley, S.H.: Physics and Chemistry of the Organic Solid State, Vol. 1. New York: Interscience 1963

c. Rice, S.A., Jortner, J.: Physics and Chemistry of the Organic Solid State, Vol. 3. New York: Interscience 1963

d. Craig, D.P., Walmsley, S.H.: Excitons in Molecular Crystals. New York: Benjamin 1968

36e. Davydov, A.S.: Theory of Molecular Excitons. New York: Plenum Press 1971

f. Philpott, M.R.: Some Modern Aspects of Exciton Theory. Advan. Chem. Phys. 23, 227 (1973)

37. Levine, I.R.: Quantum Chemistry Volume 1, Quantum Mechanics and Molecular Electronic Structure. Boston: Allyn and Bacon 1970

38. Born, M., Oppenheimer, J.R.: Ann. de Physk. 84, 457 (1927)

39. Clark, R.G., Stewart, E.T.: Quart. Rev. 24, 95 (1970)

40. Arfken, G.: Mathematical Methods for Physicists. New York: Academic Press 1968

41. Hartree, D.R.: Proc. Cambridge Phil. Soc. 24, 89 (1928)

42. Slater, J.C.: Quantum Theory of Molecules and Solids Vol.1, Electronic Structure of Molecules. New York: McGraw Hill 1963

44. Lennard-Jones, J.E.: Proc. Roy. Soc. A198, 14 (1949)

45. Roothaan, C.C.J.: Rev. Mod. Phys. 23, 69 (1951)

46. Koopmans, T.: Physica 1, 104 (1933)

47. Pople, J.A., Santry, D.P., Segal, G.A.: J. Chem. Phys. 43, S129 (1965)

48. Pople, J.A., Segal, G.A.: J. Chem. Phys. 43, S136 (1965)

49. Pople, J.A., Segal, G.A.: J. Chem. Phys. 44, 3289 (1966)

50. Santry, D.P., Segal,G.A.: J. Chem. Phys. 47, 2026 (1967)

51. Pople, J.A., Beveridge, D.L.: Approximate Molecular Orbital Theory. New York: McGraw Hill 1970

52. Mulliken, R.S., Rieke, C.A., Orloff, D., Orloff, H.: J. Chem. Phys. 17, 1248 (1949)

53. Roothaan, C.C.J.: J. Chem. Phys. 19, 1445 (1951)

54. Goeppert-Mayer, M., Sklar, A.L.: J. Chem. Phys. 6, 645 (1938)

55. Elden, B.: J. Chem. Phys. 33, 98 (1960)

56. Moore, C.E.: Natl. Bur. Std. (U.S.), circ. no. 467 (1949)

57. Kroto, H.W., Santry, D.P.: J. Chem. Phys. 47, 792 (1967)

58. Dreyfus, M., Maigret, B., Pullman, A.: Theoret. Chim. Acta. 17, 109 (1970)

59. Kollman, P.A., Allen, L.C.: J. Am. Chem. Soc. 92, 753 (1970)

60. Bacon, J., Santry, D.P.: J. Chem. Phys. 55, 3445 (1971)

61. Bacon, J., Santry, D.P.: J. Chem. Phys. 56, 2011 (1972)

62. Crowe, R.W., Santry, D.P.: Chem. Phys. Lett. 22, 52 (1973)

63. Crowe, R.W., Santry, D.P.: Chem. Phys. 2, 304 (1973)

64. O'Shea, S., Santry, D.P.: Submitted to Theoret. Chim. Acta.

65. Santry, D.P.: Chem. Phys. Lett. 27, 464 (1974)

66. Coulson, C.A., Eisenberg, D.: Proc. Roy. Soc. A291, 445 (1966)

67. Onsager, L., Dupuis, M.: Electrolytes. London: Pergamon Press 1962

68. Jordan, T.H., Smith, H.W., Streib, W.E., Lipscomb, W.N.: J. Chem. Phys. 41, 756 (1964)

69. Wheatly, P.J.: Acta. Cryst. 8, 224 (1955)

70. Pawley, G.S., Yeats, E.A.: Acta. Cryst. B25, 2009 (1969)

71. Bacon, G.E., Curry, N.A., Wilson S.A.: Proc. Roy. Soc. A279, 98 (1964)

72. Dulmag, W.J., Lipscomb, W.L.: Acta. Cryst. 4, 330 (1951)

73. Keesom, W.H., Kohler, J.W.L.: Physica 1, 655 (1934)

74. Post, B., Schwartz, R.S., Fankuchen, I.: Acta. Cryst. 5, 372 (1952)

75. Smith, W.H., Lipscomb, W.L.: J. Chem. Phys. 43, 1060 (1963)

76. Matthews, D.A., Swanson, J., Mueller, M.H., Stuckly, G.D.: J. Am. Chem. Soc. 93, 5945 (1971)

77. Becker, P., Coppens, P., Ross, F.K.: J. Am. Chem. Soc. 95, 7604 (1973)

78. Holtzberg, F., Post, B., Fankuchen, I.: Acta. Cryst. 6, 127 (1953)

79. Varghese, J.N.: Ph.D. Thesis, University of Western Australia (1974)

80. Ladell, J., Post, B.: Acta. Cryst. 7, 559 (1954)

81. Sklar, N., Senko, M.E., Post, B.: Acta. Cryst. 14, 716 (1961)

82. Coppens, P., Vos, A.: Acta. Cryst. B27, 146 (1971)

83. Gibler, D.D., Adams, C.J., Fisher, M., Zalkin, A., Bartlett, N.: Inorg. Chem. 11, 2325 (1972)

84. Caron, A.P., Ragle, J.L.: Acta. Cryst.B27, 1102 (1971)

85. Crowe, R.W., Santry, D.P.: Computer Program PREDEN/CRYDEN, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana

86. Pongor, G.: Chem. Phys. Lett. 24, 603 (1974)

87. Kohin, B.C.: J. Chem. Phys. 33, 883 (1960)

88. Karapet'yants, M.K.H., Karapet'yants, M.L.: Thermodynamic Constants of Inorganic and Organic Compounds. Ann Arbor: Humphrey Science Publishers 1970

89. Hirt, R.C., Steger, J.E., Simmard, G.L.: J. Polymer Sci. 43, 319 (1960)

90. Suzuki, K., Onshi, S., Koide, T., Senki, S.: Bull. Chem. Soc. Japan 29, 127 (1956)

91. Giauque, W.F., Egan, J.C.: J. Chem. Phys. 5, 45 (1937)

92. Ree, F.H., Bender, C.F.: Phys. Rev. Lett. 32, 85 (1974)

93. Coppens, P., Willoughby, T.V., Csonka, L.N.: Acta. Cryst. A27, 248 (1971)

94. O'Connell, A.M., Rae, A.I.M., Maslen, E.N.: Acta. Cryst. 21, 208 (1966)

95. Coppens, P.: Acta. Cryst. B30, 255 (1974)

96. Maslen, E.N.: private communication, (1974)

97. Coppens, P., Sabine, T.M.: Acta. Cryst. B25, 2442 (1969)

98. Kamb, B., Hamilton, N.C., LaPlaca, S.J., Prakash, A.: J. Chem. Phys. 55, 1934 (1971)

99. Dreyfus, M., Pullman, A.: Theoret. Chim. Acta. 19, 20 (1970)

100. McConnell, H., Hoffman, B.M., Metzer, R.M.: Proc. Nat. Acad. Sci. (U.S.) 53, 46 (1965)

101. Middlemiss, K.M., Santry, D.P.: J. Chem. Phys. 61, 5400 (1974)

102. Jones, D.S., Pautler, D., Coppens, P.: Acta. Cryst. A28, 635 (1972)

103. Little, R.G., Pautler, D., Coppens, P.: Acta. Cryst. B27, 1493 (1971)

104. Stuky, G.D., Matthews, D.A., Hedman, J., Klasson, M., Nordling, C.: J. Am. Chem. Soc. 94, 8009 (1972)

105. Krause, P.F., Friedrich, H.B.: J. Phys. Chem. 76, 1140 (1972)

106. Lefebvre, J.: Phys. Stat. Sol.(b) 49, 673 (1972)

107. Lefebvre, J.: Solid State Comm. 13, 1873 (1973)

108. McCellan, A.L.: Tables of Experimental Dipole Moments. San Francisco: Freeman and Company 1963

109. Bounds, D.G., Hinchliffe, A., Munn, R.W., Hewham, R.J.: Chem. Phys. Lett. 29, 600 (1974)

110. Seitz, F.: The Modern Theory of Solids. New York: McGraw Hill (1940)

111. Ladik, J., Biczo, G.: J. Chem. Phys. 42, 1658 (1965)

112. André, J.M.: J. Chem. Phys. 50, 1536 (1969)

113. Ooshika, Y.: J. Phys. Soc. Japan 12, 1246 (1957)

114. Morokuma, K.: J. Chem. Phys. 54, 962 (1971)

115. O'Shea, S.F., Santry, D.P.: J. Chem. Phys. 54, 2267 (1971)

116. Delhalle, J., André, J.M., Delhalle, S., Pireaux, J.J, Candano, R., Verbist, J.J.: Chem. Phys. Lett. 23, 206 (1973)

117. Middlemiss, K.M., Santry, D.P.: Chem. Phys. 1, 128 (1973)

118. Born, M., Huang, K.: Dynamical Theory of Crystal Lattices. London: Oxford Univ. Press 1966

119. Bouchaert, L.P., Smoluchowski, R., Wigner, E.P.: Phys. Rev. 50, 58 (1936)

120. Colson, S.D., Kopelman, R., Robinson, G.W.: J. Chem. Phys. 47, 27 (1967)

121. Kopelman, R.: J. Chem. Phys. 47, 2631 (1967)

122. Middlemiss, K.M., Santry, D.P.: Chem. Phys. Lett. 28, 140 (1974)

123. Avery, J., Packer, J., Ladik, J., Biczo, G.: J. Mol. Spec. 29, 194 (1969)

124. Middlemiss, K.M., Santry, D.P.: Theoret. Chim. Acta. 35, 203 (1974)

125. Slater, J.C., Shockley, W.: Phys. Rev. 50, 705 (1936)

126. Craig, D.P., Sommer, B.S.: Chem. Phys. Lett. 22, 239 (1973)

127. Tiberghien, A., Delacote, G., Schott, M.: J. Chem. Phys. 59, 3762 (1973)

128. Praiser, R.: J. Chem. Phys. 24, 250 (1956)

129. Pople, J.A.: Proc. Phys. Soc. A68, 81 (1955)

130. Burawoy, A.:J. Chem. Soc., 1177 (1939)

Burawoy, A.:J. Chem. Soc., 20 (1941)

131. Del Bene, J.E.: J. Chem. Phys. 62, 666 (1975)

132. Mukherjee, N.G.: Chem. Phys. Lett. 24, 441 (1974)

133. Mo, O., Yanez, M., Fernadez-Alonso, J.I.: J. Phys. Chem. 79, 137 (1975)

134. Chesnut, D.B., Wormer, P.E.S.; Theoret. Chim. Acta. 20, 250 (1971)

135. Grein, F., Weiss, K.: Theoret. Chim. Acta. 34, 315 (1974)

136. Suzki, N., I'Haya, Y.J.: Chem. Phys. 2, 407, (1973)

137. Suzki, N., I'Haya, Y.J.: Chem. Phys. 2, 419, (1973)

138. Cohen, M.H., Hertz, J.A., Horn, P.M., Shante, V.K.S.: Int. J. Chem. Symp. 8, 491 (1974)

139. Momany, F.A., Carruthers, L.M., McGuire, R.F., Scherga, H.A.: J. Phys. Chem. 78, 1595 (1974)

140. McWeeny, R.: Phys. Rev. 126, 1028 (1962)

McWeeny, R.: Chem. Phys. Lett. 1, 567 (1968)

Diercksen, G., McWeeny, R.: J. Chem. Phys. 44, 3554 (1966)