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

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An all valence electron theory, based on SCF perturbation theory, for the excited state energies of crystals with energy bands of low to intermediate dispersion is presented. It is shown that molecular theory leads to results equivalent to those of the valence bond treatments of Davydov and Choi, Silbey, Jortner, and Rice. The advantages of the proposed MO approach are twofold. First, the explicit inclusion of all valence electrons permits an unambiguous calculation of any structural changes that may accompany electronic excitation. Second, and more important, it provides a convenient method for calculating the excited states of crystals composed of relatively strongly interacting molecules, such as those within lattices of hydrogen bonded or charge transfer crystals.

Key words: Hydrogen bonding – Exciton – SCF perturbation theory

Introduction

An SCFMO (self consistent field molecular orbital) theory for molecular crystals has recently been reported [1–7]. So far, the theory has been largely applied to the theoretical investigation of hydrogen bonding within crystal lattices. It is based on conventional single determinant molecular orbital theory, but differs from the usual approach [9, 10] to solid state theory in that it is independent of the wave-vector concept. The introduction of wave-vectors is avoided by solving the SCF matrix equation for the crystal by means of high order SCF perturbation theory [11], using the orbitals of hypothetically non-interacting lattice molecules as the zero order solutions. In other words, the method starts with an oriented gas and then allows for intermolecular electron delocalization by means of SCF perturbation theory. The result is a method for calculating the crystal density matrix and energy per unit cell, and all quantities calculable therefrom. The crystal orbitals and band structure are not calculated directly because of the way the theory circumvents the introduction of wave-vectors. However, these quantities may be calculated [4] on completion of the main calculation by a suitable unitary transformation of the perturbation series for the Fock and orbital matrices. This transformation serves to introduce wave-vectors into the theory [4].

Although the above approach is not based on the use of Bloch symmetrized crystal orbitals, the space group symmetry nonetheless plays an important role in the theory. It is introduced in a particularly simple and direct manner to decouple various perturbation sub matrix equations which occur, thereby appreciably reducing the computational effort required.

The above single determinant theory can be confidently applied to the study of those molecular crystals where the lattices are bound by predominantly hydrogen bonded or charge transfer interactions. However, many crystals are thought to be bound by predominantly dispersive forces [12, 13]. As these result from the Coulombic correlation of electron motion [14], they are not included in any single determinant treatment of intermolecular forces. This dispersive component of the binding energy can be included in the molecular orbital treatment through the introduction of the interaction between the crystal ground and excited state electron configurations. Since the crystal orbitals discussed here are solutions, albeit approximate, to the crystal Hartree-Fock equations, only double electron excitations will contribute to the ground state energy [15].

The overall objective of the present investigation is to extend the above theory of crystals by the inclusion of the dispersive contribution to the lattice binding energy. As with the original non-dispersive theory, the aim is to do this independently of any assumptions concerning the pairwise additivity of intermolecular forces. This can be achieved by considering the configurational interaction problem for the crystal as a whole. The theory presented here is for single electron excitations only, and represents the first step towards the dispersive theory. Although incomplete from the point of view of the above objective, the theory may nonetheless be of interest to theorists working on crystal spectra, especially of charge transfer systems.

Both the theoretical and experimental aspects of the spectra of dispersive crystals have extensive literatures that have been reviewed in several books [16]. Of the two basic theoretical approaches, the present most closely resembles that of Choi, Silbey, Jortner and Rice [17]. It does, however, differ in two important respects. First, and most fundamental, the present approach starts with delocalized crystal orbitals that are solutions to the crystal SCF equations. Thus, many of the interactions that lead to the creation of charge transfer as opposed to Frenkel excitons are included at an early stage of the theory. This should prove advantageous when the theory is applied to crystals composed of relatively strongly interacting molecules. Second, the present treatment makes no distinction between σ and π electrons; both are included equivalently. This permits an unambiguous calculation of possible structural changes, both crystal and molecular, that may accompany electronic excitation.

The content of the present paper is entirely theoretical. The resultant theory has been used to calculate the excited state properties of two rather different types of crystals, naphthalene and formamide. The results from these calculations will be reported in a subsequent paper.

Theoretical Section

We discuss here the relationship between the band structure and the electronic excited states of a molecular crystal. A convenient starting point for this is the virtual orbital approximation to excited states. That is, it will be assumed that 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. As the discussion progresses, we shall find that this simple approach has to be modified in order to achieve a realistic representation of the electronic excited states of molecular crystals.

The crystal orbitals, $O_i(k, \lambda)$, are characterized by three indices, i, k, and λ. The first index, i, identifies the free molecule molecular orbital from which the crystal orbital is derived. Such an identification is possible only for crystals composed of relatively weakly interacting lattice molecules. The second index, the wave-vector k, labels the irreducible representations of the crystal's translational subgroup under which the orbital is classified. Finally, the third index, λ, may be taken as the corresponding label for the unit cell group.

The zero order crystal orbital is given by [4]

$$O_i^{(0)}(k, \lambda) = Z^{-\frac{1}{2}} N^{-\frac{1}{2}} \sum_u \omega_{\lambda u} \sum_T \exp[2\pi i k \cdot (T+u)]\, C_i^{(0)}(T, u) \tag{1}$$

where N and Z are, respectively, the number of unit cells in the Born von Karman repeat unit and the number of molecules in the unit cell. T and u, which are both vectors, serve to label molecules by pointing to the unit cells and the sites within these cells, they occupy. In the summations, u goes from 1 to Z and T from 1 to N. $\omega_{\lambda u}$ is the orbital coefficient for the u^{th} single site function [4] in the λ^{th} crystal orbital. If the discussion is limited to those crystals where 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 λ^{th} representation of this group. This is an approximation if the wave-vector associated with the single site functions is a member of a star of wave-vectors [18]. In this case, the ω's are strictly k dependent and cannot be determined by symmetry arguments alone. The neglect of this dependence is a common approximation often referred to as the restricted Frenkel limit [19]. There is some reason to believe that for the present application this approximation is unimportant [4]. $C_i^{(0)}(T, u)$ is the i^{th} molecular orbital localized on the T, u^{th} molecule to the zeroth order. It is an infinite column vector with zeros everywhere except for the positions allocated to the atomic orbitals of the Tu^{th} molecule in the crystal basis set. It will be assumed that this basis set is ordered so all atomic orbitals associated with a given molecule are collected together as a group. With this arrangement, $C_i^{(0)}(T, u)$ will be zero everywhere except the Tu^{th} block which will house the atomic orbital coefficients for the i^{th} molecular from the hypothetically isolated Tu^{th} lattice molecule.

The notation for the crystal orbitals has been slightly modified from the previous paper [4] to emphasize the relationship between T and 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 role in the theory and, consequently, a considerable clarification of the forthcoming equations can be achieved by adapting the orbital notation to reflect it. As a first step, points in real and reciprocal space are labelled by ζ and η, respectively. The crystal orbital, Eq. (1), is thus given by

$$O_i^{(0)}(k_\eta, \lambda_\eta) = Z^{-\frac{1}{2}} N^{-\frac{1}{2}} \sum_{u_\zeta} \omega_{\lambda_\eta u_\zeta} \sum_{T_\zeta} \exp(2\pi i k_\eta \cdot R_\zeta)\, C_i^{(0)}(T_\zeta, u_\zeta) \tag{2}$$

where, for convenience the u has been combined with T to give R. R may be used interchangably with T, u to label a molecule when we are not concerned with the structure of the unit cell. We may now introduce the following convention

$$i^{\eta} \equiv 0_i(k_{\eta}, \lambda_{\eta}), \tag{3}$$

$$i_{\zeta} = C_i(T_{\zeta}, u_{\zeta}). \tag{4}$$

The approximate ground state electronic wave function for the crystal is given by the usual antisymmetrized product. This can be conveniently written by making use of the above convention, Eq. (5).

$$\Psi_0 = \mathscr{A}\{\dots i^{\eta}\overline{i^{\eta}}\dots\} \tag{5}$$

where $\mathscr{A}$ is the antisymmetrization operator and a bar indicates orbital occupation by an electron of β spin. Similarly, crystal singlet and triplet wave functions, corresponding to the excitation of an electron from the $i^{1\,\text{th}}$ level in the filled band to the $l^{2\,\text{th}}$ level in the vacant, are given by

$${}^{3,1}\Psi_{i^1 l^2} = 2^{-\frac{1}{2}}(\mathscr{A}\{\dots i^1\overline{l^2}\dots\} \pm \mathscr{A}\{\dots \overline{i^1}l^2\dots\}). \tag{6}$$

The excitation energies are given directly by the well known expression derived by Roothaan [8] for the corresponding molecular process.

$${}^{1,3}E_{i^1\to l^2} = \varepsilon(l^2) - \varepsilon(i^1) - J(i^1, l^2) + 2\tau K(i^1, l^2) \tag{7}$$

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

$$\varepsilon(l^2) \equiv \varepsilon_{l,\lambda_2}(k_2). \tag{8}$$

J and K are Coulomb and exchange integrals, respectively.

$$J(i^1, l^2) = \langle i^1 l^2 | i^1 l^2 \rangle = \int\int i^1(1)^* l^2(2)^* \frac{1}{r_{12}} i^1(1)\, l^2(2)\, dz_1\, dz_2 \tag{9}$$

and

$$K(i^1, l^2) = \langle i^1 l^2 | l^2 i^1 \rangle. \tag{10}$$

The τ in Eq. (7) equals zero for a triplet state and one for a singlet.

Equation (7) is the crystal analogue of the virtual orbital expression for the excitation energy of a finite molecule. In contrast to the molecular case [20], the virtual orbital approximation is fundamentally in error for molecular crystals and does not even provide an acceptable first approximation. From the physical point of view, the problem with the virtual orbital approximation is that it describes 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.

From the point of view of molecular orbital theory, the adoption of Eq. (7) would lead to two serious problems. First, it has the incorrect limiting behaviour as the intermolecular potential tends to zero [4]. At this limit, the oriented gas, the excitation energies should be infinitely degenerate and all correspond to that for an isolated molecule. It can easily be shown, using the important result of

Ladik *et al.* [21], that Eq. (7) does not possess this essential property. Second, under the $\Delta k = 0$ selection rule, Eq. (7) yields an infinity of almost degenerate states for a crystal with low dispersion bands. Under these circumstances an appreciable level of configurational mixing would have to be included in order to achieve realistic results.

The above discussion leads to the conclusion that single configurational representations of crystal excited states are unacceptable. Moreover, the theoretical investigation of these states would require 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 travelling through the crystal as a Frenkel exciton. This suggests that the configuration interaction problem could be appreciably simplified by transforming the delocalized electron-hole basis functions into a localized representation.

We now consider the organization of such a localized state basis set for the crystal infinite configurational interaction problem. These functions can be generated, following Slater and Shockley [22], by a double Fourier transformation of the excited state functions given in Eq. (6). Thus, if ${}^{1,3}L_{il}(1;2)$ is a function in which the hole is localized on the $T_1 u_1{}^{\text{th}}$ molecule and the excited electron on the $T_2 u_2{}^{\text{th}}$ then

$$\begin{aligned} &{}^{1,3}L_i(R_1, R_2) \\ &\quad = N^{-1} Z^{-1} \sum_{\lambda_1} \sum_{\lambda_2} \omega_{\lambda_1 u_1} \omega_{\lambda_2 u_2} \sum_{k_1} \sum_{k_2} \exp[2\pi i (k_1 \cdot R_1 - k_2 \cdot R_2) \times {}^{1,3}\Psi_{i^1 l^2} \end{aligned} \tag{11}$$

where R_1 labels molecule (T_1, u_1).

These functions are the new basis functions for the proposed configuration interaction calculation and replace the ${}^{1,3}\Psi_{i^1 l^2}$ set. The number of functions in these two sets are equal, as may be seen as follows. For a given i and l, there are $(N \times Z)^2$ different ${}^{1,3}\Psi_{i^1 l^2}$ functions, where Z is the number of molecules in the unit cell. Noting that ${}^{1,3}L_{il}(1, 2) \neq {}^{1,3}L_{il}(2, 1)$, it can be seen that this is just the number of distinct L functions. Thus, nothing has been omitted by this change in basis set.

The L-type basis functions, being localized, transform reducibly under the crystal space group. The next step is, therefore, to simplify the eventual configuration interaction secular equation by taking linear combinations of these functions to generate new functions, M, that transform irreducibly under the space group. Of all the different possible symmetries, only the $k = 0$ representations are of interest. This is because the selection rule for electronic transitions is $\Delta k \simeq 0$ and the crystal ground state wave functions transforms as the $k = 0$ representation. The $k = 0$ M functions are given by

$${}^{1,3}M_{il}^{\lambda}(\beta, \varrho) = Z^{-\frac{1}{2}} N^{-\frac{1}{2}} \sum_{u} \omega_{\lambda u} \sum_{T} {}^{1,3}L_{il}(T, u; T + \beta, u + \varrho) \,. \tag{12}$$

The lattice vectors β and ϱ 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 unit cell representations, for each value of β and ϱ; that is for every conceivable 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 β unit cells and ϱ sites. The Frenkel exciton corresponds to the special case where both β and ϱ are zero.

Symmetrization of the localized L functions by means of the space group symmetry confers delocalized character on the final M basis functions. It would appear, therefore, that the basis function transformations have gone full circle. The original state functions, ${}^{1,3}\Psi_{i^1l^2}$, which represent highly delocalized excitations, were transformed to localized L functions which in turn were transformed into the M functions, which also represent delocalized excitations. There is, however, an important difference in the character of the delocalizations represented by the Ψ and M functions. In the former case, the excited electron and hole are represented as being in independent motion in the crystal lattice; that is, their motion is uncorrelated. In the case of the M functions, the electron and hole, even though they may be on different molecules, travel through the crystal together as a single entity; their motions are completely correlated. The Ψ and M basis functions represent the two extremes in crystal and excited state properties.

The M state basis functions of a given symmetry, λ, form the chosen basis set for the configuration interaction calculation; the final crystal excited state wave function will have contributions from all M's of a given symmetry and multiplicity. The corresponding secular equation will therefore be of infinite dimension. Hopefully, because of the choice of basis set, nearly all off diagonal matrix elements will be negligible in comparison with the diagonal elements. In any event, as a first approximation, the crystal excited state energies will be approximated by the appropriate diagonal elements of the configuration interaction matrix.

It may appear that the above approach neglects any possible admixture of, for example, charge transfer character into states that are largely Frenkel exciton in character. This is not the case. The crystal orbitals, O, used to construct the L functions are solutions to the crystal SCF equation and are thus not perfectly localizable. As a result, the L functions are only perfectly localized to the zeroth order and in general have a more or less delocalized component. This confers some charge transfer character even on the Frenkel-type M functions.

Implementation of the configuration interaction procedure requires the evaluation of the following type of matrix element:

$${}^{1,3}H_{il,mn}(1,2;3,4) = \langle {}^{1,3}L_{il}(R_1;R_2) | H - E_{\text{ground}} | {}^{1,3}L_{mn}(R_3;R_4) \rangle \tag{13}$$

where H is the crystal electronic Hamiltonian and E_{ground} the crystal ground state energy. Expanding the localized, L, functions using Eq. (11), we find this element equals

$$\begin{aligned} Z^{-2}N^{-2} & \sum_{\lambda_1}\sum_{\lambda_2}\sum_{\lambda_3}\sum_{\lambda_4} \omega_{\lambda_1 u_1}\omega_{\lambda_2 u_2}\omega_{\lambda_3 u_3}\omega_{\lambda_4 u_4} \\ & \cdot \sum_{k_1}\sum_{k_2}\sum_{k_3}\sum_{k_4} \exp[-2\pi i(k_1 \cdot R_1 - k_2 \cdot R_2 - k_3 \cdot R_3 + k_4 \cdot R_4)] \\ & \cdot \langle {}^{1,3}\Psi_{i^1l^2} | H - E_{\text{ground}} | {}^{1,3}\Psi_{m^3n^4} \rangle \,. \end{aligned} \tag{14}$$

The integral can readily be evaluated using the standard formulae of configuration interaction theory, such as those for example given in Ref. [15]. Remembering that the crystal orbitals are eigenfunctions of the Fock matrix for the crystal, we find Eq. (14) equals

$$\begin{aligned} Z^{-2}N^{-2} & \sum_{\lambda}^{(4)} \omega_{\lambda_1 u_1}\omega_{\lambda_2 u_2}\omega_{\lambda_3 u_3}\omega_{\lambda_4 u_4} \\ & \cdot \sum_{k}^{(4)} \exp[-2\pi i(k_1 \cdot R_1 - k_2 \cdot R_2 - k_3 \cdot R_3 + k_4 \cdot R_4) \\ & \{\delta_{ln}\varepsilon(l^2) - \delta_{im}\varepsilon(i^1)\}\, \delta^{1,3}\delta^{2,4} + \{2\tau\langle m^3 l^2 | n^4 i^1\rangle - \langle m^3 l^2 | i^1 n^4\rangle\} \end{aligned} \tag{15}$$

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. $\Sigma_{\lambda}^{(4)}$ represents the fourfold summation of λ's explicitely written out in Eq. (14).

The next step is to expand Eq. (15) using the special properties of the crystal perturbation algebra introduced in previous papers [2, 4, 5, 8]. We start with the orbital energy terms:

$$\begin{aligned} Z^{-2}N^{-2} & \sum_{\lambda_1}\sum_{\lambda_2} \omega_{\lambda_1 u_1}\omega_{\lambda_2 u_2}\omega_{\lambda_1 u_3}\omega_{\lambda_2 u_4} \\ & \cdot \sum_{k_1}\sum_{k_2} \exp[-2\pi i(k_1 \cdot (R_1 - R_3) - k_2 \cdot (R_2 - R_4))]\,(\delta_{ln}\varepsilon(l^2) - \delta_{im}\varepsilon(i^1))\,. \end{aligned} \tag{16}$$

To the zero order, $\varepsilon(l^2)$ is independent [4] of k_2 and λ_2 and equals $\varepsilon^{(0)}(l_2)$, the l^{th} 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 k and λ completed. The final zero order result is

$$\{\delta_{ln}\varepsilon^{(0)}(l_2) - \delta_{im}\varepsilon^{(0)}(i_1)\}\, \delta_{1,3}\delta_{2,4} \tag{17}$$

where $\delta_{1,3} = 1$ if $R_1 = R_3$, that is $T_1 = T_2$ and $u_1 = u_3$, and is zero otherwise. In the notation of the previous paper

$$\varepsilon^{(0)}(l_2) \equiv \varepsilon_l^{(0)}\,.$$

The first order orbital energy $\varepsilon^{(1)}(l^2)$ depends [4] on both λ_2 and k_2. The expression [4] for $\varepsilon^{(1)}$ is given in Eq. (18)

$$\varepsilon^{(1)}(l^2) = (NZ)^{-1} \sum_{u_5}\sum_{u_6} \omega_{\lambda_2 u_5}\omega_{\lambda_2 u_6} \sum_{T_5}\sum_{T_6} \exp[2\pi i k_2 \cdot (R_6 - R_5)]\; {}^{5,6}F_{ll}^{(1)} \tag{18}$$

where once more the notation of the previous paper has been condensed

$${}^{5,6}F_{ll}^{(1)} = {}^{T_5 u_5, T_6 u_6}F_{ll}^{(1)}\,. \tag{19}$$

${}^{5,6}F^{(1)}$ is the submatrix from the full crystal first-order Fock matrix which has elements between all atomic orbitals on molecule $T_5 u_5$ and all atomic orbitals on molecule $T_6 u_6$.

$${}^{5,6}F_{ll}^{(1)} = \tilde{l}_5\; {}^{5,6}F^{(1)}\, l_6\,. \tag{20}$$

Substitution of Eq. (18) for the appropriate orbital energy in Eq. (16) yields, on completing the summation over λ's and k's:

$${}^{2,4}F_{ll}^{(1)}\, \delta_{1.3} - {}^{1,3}F_{ii}^{(1)}\, \delta_{2.4}\,. \tag{21}$$

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

$$(\delta_{ln}\varepsilon^{(0)}(l_2) - \delta_{mi}\varepsilon^{(0)}(i_1))\,\delta_{1,3}\delta_{2,4} + {}^{2,4}F^{(1)}_{ll}\,\delta_{1,3} - {}^{1,3}F^{(1)}_{ii}\,\delta_{2,4}\,. \tag{22}$$

We now proceed to expand the electron repulsion integrals. The contribution from the zero order crystal orbitals is derived as follows. First, we expand the $\langle m^3 l^2 | n^4 i^2 \rangle$ integral in terms of zero order molecular orbitals:

$$\begin{aligned}\langle m^3 l^2 | n^4 i^1 \rangle = N^{-2} Z^{-2} \sum_u^{(4)} \omega_{\lambda_3 u_5} \omega_{\lambda_2 u_6} \omega_{\lambda_4 u_7} \omega_{\lambda_1 u_8} \\ \cdot \sum_T^{(4)} \exp[2\pi i(-k_3 \cdot R_5 - k_2 \cdot R_6 + k_4 \cdot R_7 + k_1 \cdot R_8) \\ \cdot \langle m_5 l_6 | n_7 i_8 \rangle\,.\end{aligned} \tag{23}$$

Next, this is substituted into the appropriate position in Eq. (15), and the summations over λ and k completed. The final result is

$$\langle m_3 l_2 | n_4 i_1 \rangle\,. \tag{24}$$

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

$$2\tau \langle m_3 l_2 | n_4 i_1 \rangle - \langle m_3 l_2 | i_1 n_4 \rangle\,. \tag{25}$$

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

$$\begin{aligned}\langle m^3 l^2 | n^4 O^{(1)}_i (k_1 \lambda_1) \rangle + \langle m^3 l^2 | O^{(1)}_n (k_4, \lambda_4)\, i^1 \rangle + \langle m^3 O^{(1)}_l (k_2 \lambda_2) | n^4 i^1 \rangle \\ + \langle O^{(1)}_m (k_3, \lambda_3)\, l^2 | n^4 i^1 \rangle\,.\end{aligned} \tag{26}$$

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

$$O^{(1)}(k,\lambda) = O^{(0)}(k,\lambda)\,\mathscr{A}(k,\lambda) \tag{27}$$

where $\mathscr{A}$ is the matrix of mixing coefficients. 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 k and λ. This result is self-evident for wave vectors that are invariant with respect to unit cell group operators. In the case of a more general 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.

The matrix elements of $\mathscr{A}$ are given by

$$\mathscr{A}_{pi} = \tilde{O}^{(0)}_p (k_1, \lambda_1)\, F^{(1)}\, O^{(0)}_i (k_1 \lambda_1) / (\varepsilon^{(0)}_i - \varepsilon^{(0)}_p)\,, \tag{28}$$

$$\mathscr{A}_{ii} = 0 \tag{29}$$

where $F^{(1)}$ is the first-order change in the crystal Fock matrix. Both $F^{(1)}$ and $\mathscr{A}$ are of infinite dimension but may be partitioned into finite dimensioned submatrices by making use of the special ordering of the basis set [5]. On expanding $F^{(1)}$ into submatrices we find

$$\mathscr{A}_{pi}(k,\lambda)=(ZN)^{-1}\sum_{u_5}\sum_{u_6}\omega_{\lambda u_5}\omega_{\lambda u_6}\sum_{R_5}\sum_{R_6}\exp[2\pi i k\cdot(R_6-R_5)]\ {}^{5,6}\mathscr{A}_{pi} \tag{30}$$

where, in the notation introduced in Eq. (19)

$${}^{5,6}\mathscr{A}_{pi}={}^{5,6}F^{(1)}_{pi}/(\varepsilon_i^{(0)}-\varepsilon_p^{(0)})\,,\qquad p\neq i\,. \tag{31}$$

On substituting for $O_i^{(1)}(k_1\lambda_1)$ in $\langle m^3 l^3|n^4 O_i^{(1)}(k_1\lambda_1)\rangle$ using Eqs. (27) and (31), then substituting into Eq. (15) and completing the fourfold summations over the λ's and k's we find the contribution to be

$$\sum_{u_5}\sum_{T_5}\sum_{p}{}'\ {}^{5,1}\mathscr{A}_{pi}\langle m_3 l_2|n_4 p_5\rangle\,. \tag{32}$$

The prime on the summation over all of the orbitals of molecule five excludes the case $p=i$. Equation (32) represents the first order change in the electron repulsion integral under discussion as a lattice sum, over R_5, with molecule 1 as the origin.

Thus, the total first order contribution from $2\tau\langle m^3 l^2|n^4 i^1\rangle-\langle m^3 l^2|i^1 n^4\rangle$ is

$$\begin{aligned}\sum_{u_5}\sum_{T_5}\sum_{p}{}'\,[&{}^{5,1}\mathscr{A}_{pi}\{2\tau\langle m_3 l_2|n_4 p_5\rangle-\langle m_3 l_2|p_5 n_4\rangle\}\\ &+{}^{5,4}\mathscr{A}_{pn}\{2\tau\langle m_3 l_2|p_5 i_1\rangle-\langle m_3 l_2|i_1 p_5\rangle\}\\ &+{}^{5,2}\mathscr{A}_{pl}\{2\tau\langle m_3 p_5|n_4 i_1\rangle-\langle m_3 p_5|i_1 n_4\rangle\}\\ &+{}^{5,3}\mathscr{A}_{pm}\{2\tau\langle p_5 l_2|n_4 i_1\rangle-\langle p_5 l_2|i_1 n_4\rangle\}]\,.\end{aligned} \tag{33}$$

It is our intention to work with the theory in a simplified form based on a neglect of differential overlap approximation. The systematic integral approximation of this method leads to an appreciable simplification of the theory without loss of the essential SCF features of inter electron repulsion; the simplified equations still reflect the underlying structure of the more detailed theory. Recent work [23, 24] strongly suggests this step to be unwarranted in the case of calculations on triplet excitons. The same may also be true for singlet excitons from states with very small Davydov splittings. However, for the singlet states of strongly interacting molecules, such as charge transfer and hydrogen bonded crystals, the neglect of these integrals should be relatively unimportant.

Under the intended approximation all charge distributions involving two molecules are neglected. Thus, applying the approximation to Eq. (32) we find that the only term from the summation over the lattice to survive is that for which $R_5=R_2$. Furthermore, R_3 must equal R_4. Thus, the only terms from (32) remaining are

$$\sum_{p}{}'\ {}^{2,1}\mathscr{A}_{pi}\langle m_3 l_2|n_3 p_2\rangle\,\delta_{3,4}\,. \tag{34}$$

The final approximate expression, to the first-order, is given by

$$\begin{aligned}H_{il,mn}(1,2;3,4) = {} & (\delta_{ln}\varepsilon^{(0)}(l_2) - \delta_{im}\varepsilon(i_1))\,\delta_{1,3}\delta_{2,4} + \delta_{l,n}\delta_{1,3}\;{}^{2,4}F^{(1)}_{ll} - \delta_{im}\delta_{2,4}\;{}^{1,3}F^{(1)}_{ii} \\ & + \{2\tau\langle m_3 l_1 | n_3 i_1\rangle\,\delta_{3,4}\delta_{1,2} - \langle m_1 l_2 | i_1 n_2\rangle\,\delta_{1,3}\delta_{2,4}\} \\ & + \sum_p{}' 2\tau\{{}^{2,1}\mathscr{A}_{pi}\langle m_3 l_2 | n_3 p_2\rangle\,\delta_{3,4} + {}^{3,4}\mathscr{A}_{pn}\langle m_3 l_1 | p_3 i_1\rangle\,\delta_{1,2} \\ & + {}^{1,2}\mathscr{A}_{pl}\langle m_3 p_1 | n_3 i_1\rangle\,\delta_{3,4} + {}^{4,3}\mathscr{A}_{pm}\langle p_4 l_2 | n_4 i_2\rangle\,\delta_{1,2}\} \\ & - \{{}^{2,4}\mathscr{A}_{pn}\langle m_3 l_2 | i_1 p_2\rangle\,\delta_{1,3} + {}^{3,1}\mathscr{A}_{pi}\langle m_3 l_2 | p_3 n_2\rangle\,\delta_{2,4} \\ & + {}^{4,2}\mathscr{A}_{pl}\langle m_3 p_4 | i_3 n_4\rangle\,\delta_{1,3} + {}^{1,3}\mathscr{A}_{pm}\langle p_1 l_2 | i_1 n_2\rangle\,\delta_{2,4}\}\,.\end{aligned} \tag{35}$$

Frenkel Excitons: The Davydov Splitting

The Frenkel exciton corresponds to the situation where 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; it will be remembered that these functions have some charge transfer character as a result of their construction 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, $\varDelta^{1,3}E^{\lambda}_{il}(0,0)$ corresponding to $M^{\lambda}_{il}(0,0)$ is given by

$$\varDelta^{1,3}E^{\lambda}_{il}(0,0) = \frac{1}{NZ}\sum_{u_1}\sum_{u_2}\omega_{\lambda u_1}\omega_{\lambda u_2}\sum_{T_1}\sum_{T_2}{}^{1,3}H_{il,il}(1,1;2,2)\,. \tag{36}$$

Substituting for ${}^{1,3}H$ we find to the zeroth order

$$\begin{aligned} & = \varepsilon^{(0)}(l_1) - \varepsilon^{(0)}(i_1) + \{2\tau\langle i_1 l_1 | l_1 i_1\rangle - \langle i_1 l_1 | i_1 l_1\rangle\} \\ & \quad + \frac{2\tau}{Z}\sum_{u_1}\sum_{u_2}\omega_{\lambda u_1}\omega_{\lambda u_2}\sum_{T_2}{}'\langle i_1 l_2 | l_1 i_2\rangle \end{aligned} \tag{37}$$

where the prime over the lattice sum is to omit the origin cell when $u_1 = u_2$. It is appropriate to point out here that the $\varepsilon^{(0)}$'s are the free molecule orbital energies and the first two electron repulsion integrals are the molecular K_{il} and J_{il}, respectively.

Now, the first four terms when taken together give the excitation energy, singlet and triplet, for an isolated molecule under the virtual orbital approximation [8]. Thus, Eq. (27) for the crystal excitation energy has the desired limiting behaviour as the intermolecular potential tends to zero. That is, as all $\langle i_1 l_2 | l_1 i_2\rangle$ tend to zero, $\varDelta^{1,3}E^{\lambda}_{il}$ tends to the corresponding excitation energy for an isolated molecule. The last term in Eq. (37), the lattice sum, corresponds to the dipole lattice sum of the Davydov theory [16]. Its origin, as shown by the factor 2τ, is in the exchange integral K of the Roothaan expression [8] for the excitation energy. Since $\tau = 0$ for triplet states, the present treatment also yields a zero Davydov splitting for triplet excitons, at least to the zeroth order.

If the terms associated with the free molecule excitation energy, $\Delta^{1,3}E_{il}$, are collected together, the zero order crystal excitation energy may be conveniently expressed as

$$\Delta^{1,3}E_{il} + Z^{-1}2\tau \sum_{u_1} \sum_{u_2} \omega_{\lambda u_1}\omega_{\lambda u_2} \sum_{T_2}{}' \langle i_1 l_2 | l_1 i_2 \rangle . \tag{38}$$

The first order correction to the excitation energy is likewise easily evaluated on substituting for ${}^{1,3}H_{il,il}(1,1;2,2)$ in Eq. (36). This contribution is given by

$$\begin{aligned} &\Delta^{1,3}E_{il}^{(1)} + Z^{-1}2\tau \sum_{p}{}' \sum_{u_1} \sum_{u_2} \omega_{\lambda u_1}\omega_{\lambda u_2} \sum_{T_2} ({}^{2,2}\mathscr{A}_{pl}\langle i_2 l_1 | p_2 i_1 \rangle + {}^{1,1}\mathscr{A}_{pl}\langle i_2 p_1 | l_2 i_1 \rangle) \\ &\quad + 2\tau Z^{-1} \sum_{p}{}' \sum_{u_1} \sum_{u_2} \omega_{\lambda u_1}\omega_{\lambda u_2} \sum_{T_2}{}' ({}^{1,1}\mathscr{A}_{pi}\langle i_2 l_1 | l_2 p_1 \rangle + {}^{2,2}\mathscr{A}_{pi}\langle p_2 l_1 | l_2 i_1 \rangle) \end{aligned} \tag{39}$$

where $\Delta^{1,3}E_{il}^{(1)}$ is the crystal induced first-order change in the molecular excitation energy, given by:

$$\begin{aligned} \Delta^{1,3}E_{il}^{(1)} = {}^{1,1}F_{ll}^{(1)} - {}^{1,1}F_{ii}^{(1)} + 2 \sum_{p}{}' \{ &{}^{1,1}\mathscr{A}_{pl}(2\tau\langle i_1 l_1 | p_1 i_1 \rangle - \langle i_1 l_1 | i_1 p_1 \rangle) \\ &+ {}^{1,1}\mathscr{A}_{pi}(2\tau\langle i_1 l_1 | l_1 p_1 \rangle - \langle i_1 l_1 | p_1 l_1 \rangle)\} . \end{aligned} \tag{40}$$

All the $\mathscr{A}$ matrix elements in Eq. (40) are classifield as intramolecular [5] in character since they are between molecular orbitals belonging to a single molecule, here arbitrarily chosen as the first. Thus, the charge transfer or delocalization character of the crystal orbitals do not contribute to the crystal excited state energy to the first order. It should be noted, in this context, that to the first order the triplet Davydov splitting is zero. It can be shown that the second order triplet splitting is non-zero.

Charge Transfer Excitons

The diagonal elements for the charge transfer states from the configuration interaction matrix are given by

$$\begin{aligned} &\langle {}^{1,3}M_{il}^{\lambda}(\beta, \varrho) | H - E_{\text{ground}} | {}^{1,3}M_{il}^{\lambda}(\beta, \varrho) \rangle \\ &\quad = Z^{-1}N^{-1} \sum_{u_1} \sum_{u_3} \omega_{\lambda u_1}\omega_{\lambda u_2} \sum_{T_1} \sum_{T_3} {}^{1,3}H_{il,il}(1,2;3,4) \end{aligned} \tag{41}$$

where molecules 2 and 4 are β unit cells and ϱ sites away from molecules 1 and 3, respectively. Selecting the zero order terms, we find

$$\Delta^{1,3}E_{il}^{\lambda}(\beta, \varrho) = \varepsilon^{(0)}(l_1) - \varepsilon^{(0)}(i_1) - \langle i_1 l_2 | i_1 l_2 \rangle . \tag{42}$$

The necessary J and K integrals to complete the free molecule excitation energy expression are missing. On adding and substracting these we find

$$\Delta^{1,3}E_{il}^{\lambda}(\beta, \varrho) = \Delta^{1,3}E_{il}^{(0)} - \langle i_1 l_2 | i_1 l_2 \rangle + \langle i_1 l_1 | i_1 l_1 \rangle - 2\tau\langle i_1 l_1 | l_1 i_1 \rangle \tag{43}$$

where, as before $\Delta^{1,3}E_{il}^{(0)}$ is the free molecule excitation energy. It can be seen that at the zeroth level of approximation, the charge transfer states have been displaced, relative to the Frenkel state, by

$$-\langle i_1 l_2 | i_1 l_2 \rangle + \langle i_1 l_1 | i_1 l_1 \rangle - 2\tau \langle i_1 l_1 | l_1 i_1 \rangle \tag{44}$$

where all the integrals are positive. The lattice sums from Eq. (37) have been neglected for the purpose of this comparison. Since the intramolecular Coulomb integral will typically be appreciably larger than the intermolecular integral, the charge transfer states will be higher in energy than the corresponding Frenkel state. In the case of the singlet excitons, this could be offset by a favourable value for the exchange integral in Eq. (43). Of course, there will be a whole series of charge transfer states which correspond to different values of electron-hole separation. As this separation increases, the intermolecular Coulomb 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 will give rise to a stack of levels, with each succesive level closer to the next. The series limit for these levels, corresponding to infinite electron-hole separation, will be, to the zeroth order, the difference in the corresponding free molecule orbital energies.

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

$$\begin{aligned} {}^{1,1}F^{(1)}_{ll} - {}^{1,1}F^{(1)}_{ii} - \sum_p \{ & {}^{2,2}\mathscr{A}_{pl} \langle i_1 l_2 | i_1 p_2 \rangle + {}^{1,1}\mathscr{A}_{pi} \langle i_1 l_2 | p_1 l_2 \rangle \\ & + {}^{2,2}\mathscr{A}_{pl} \langle i_1 p_2 | i_1 l_2 \rangle + {}^{1,1}\mathscr{A}_{pi} \langle p_1 l_2 | i_1 l_2 \rangle \} \,. \end{aligned} \tag{45}$$

Clearly, the $\mathscr{A}$ matrix elements would have to be especially large here in order to override the positive term in Eq. (43). This may perhaps be the case in the rather strongly interacting charge transfer crystals, such as the trinitrobenzene indole system.

Discussion

In the previous sections a discussion of the excited states of molecular crystals has been presented from the point of view of molecular orbital theory. It was shown that this approach leads to a result equivalent to that of the valence bond treatment of Davydov.

The problem concerning the calculation of excited states for infinite systems, which was discussed by Ladik *et al.*, has been resolved. Clearly, it is necessary to include the configuration interaction approach developed here in order to obtain realistic representations of the excited state for crystals, or polymers, with low dispersion bands.

A method for calculating the excited state energies of crystals composed of relatively strongly interacting molecules was presented. This method has several attractive features. Although the intervening algebra is fairly labourious, the final expression for the excited state energies for both Frenkel and charge transfer excitons are reasonably straightforward. Moreover, the necessary $\mathscr{A}$ parameters are readily available, at least under the CNDO/2 (complete neglect of differential overlap) approximation [25] by means of the computer program PREDEN/

CRYDEN [7]. This program is capable of supplying all data necessary for the calculation of the spectra up to the third order. This level may indeed be necessary when the theory is applied, as it is intended, to relatively strongly interacting hydrogen bonded or charge transfer crystals.

Since the theory includes all valence electrons, it leads unambiguously to a calculation of molecular geometries and charge distributions. Furthermore, it is well known that the CNDO/2 theory works exceptionally well for calculations of molecular geometries, even for excited molecules; the charge distributions closely parallel those from more detailed calculations. Thus, the application of empirical molecular orbital methods to the calculations of the properties of molecular crystals promises to provide useful information at the semi-quantitative level.

Finally, an important property of the perturbation approach is that it is still viable when applied to molecular aggregates with no space group symmetry. Thus, the theory has been recently extended [26] to include calculations for molecules within regions of the crystal where the symmetry has been destroyed by the presence of a lattice defect or the proximity of a surface. It would be a relatively straightforward matter to extend the theory presented here for excited states in the same way. A theory of this type may prove useful for the calculation of the orientations of host molecules within lattices, or for model calculations on the solvation effects on molecular spectra.

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