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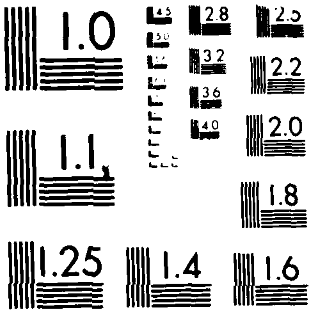

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The effect of exciton formation in solid Hydro-Carbons is studied and structural instabilities which accompany such are examined. An abinitio theory of such effects is presented.

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THEORY OF THE ELECTRONIC STRUCTURE AND OPTICAL PROPERTIES OF ORGANIC SOLIDS: COLLECTIVE EFFECTS*

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Abstract: In this series of lectures we briefly consider two complimentary approaches to the study of organic solids: The method of simulation by finite clusters of molecules, and the methods of energy band theory. In both cases, the initial starting point is the Hartree-Fock method, which, as expected, turns out to be inadequate for any reasonable level of quantitative accuracy. Solids, being essentially infinite sized systems, restrict our choice of correlation methods to those which are *size consistent*. We are furthermore interested in properties such as optical excitation and need to be able to obtain the finite difference between extensive total energies. This further restricts our choices. Methods based upon ordinary Rayleigh-Schrodinger Perturbation-Theory are chosen and extensive results for solid CH_4 are used as an illustration.

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I. Introduction.

Theoretical studies on the electronic structure of three dimensional solids have largely excluded the organic or molecular solids. The vast majority of existing calculations have been performed for the solid rare gases.[1] More complicated molecular solids, such as those with two or more atoms per molecu-

J. Ladik et al. (eds.), Quantum Chemistry of Polymers - Solid State Aspects, 83–99.

lar unit, or more than one molecular unit per unit cell, have been largely ignored. The principal exception to this tendency has been for solid H_2. It should be further noted, that the interest in solid H_2 stems largely from interest in its possible transformation to a monatomic metal, exhibiting high temperature BCS type superconductivity.[2] In addition, a recent resurgance of interest in the solid rare gases has been generated by speculations that "low" pressure (~0.3 M bar) metal phases of solid Xe might exist.[3] In addition, some theoretical studies on solid N_2[4] and H_2O[5] exist. In addition, quite a few studies on properties of polymer systems exist.[6] There are probably many reasons for the neglect of this interesting and technologically interesting class of solids. Several of the reasons are likely related to the complicated and at times ill-defined crystal structure of such systems and the associated difficulties in constructing adequate theoretical models. A second and perhaps more serious problem relates to the question of which approach one might use to determine the electrical structure. As an example, the spectrum of solid CH_4 has been determined over an energy range of 8 to about 35 eV. The fundamental spectral region of from threshold (>8.5 eV) to about 14 eV shows marked similarity in both solid and gas phase. It is generally conceded that the gas phase spectra in this energy region is dominated by transitions from the bonding to antibonding bound state orbitals or to Rydberg series like transitions.[7] It seems reasonable to expect that the crystalline spectrum is likely to be similarly dominated by transitions to bound rather than free final states. That is we do not expect the contributions from energy band theory to play a major role in the low lying excitations of solid CH_4. On the other hand the spectral region above 14 or so eV may well be dominated by band to band transitions and this may account for the apparent differences between the high lying spectrum of gas phase CH_4 and solid CH_4. Similar considerations apply to many other molecular solids.

The previous theoretical study on solid methane lends credibility to this argument, as the calculation of Piela, Pietronero, and Resta finds a band gap in excess of 27.2 eV for solid methane.[8] It is not likely that this result is quantitatively accurate as these authors used a very abbreviated basis set in their calculation and found the conduction results to be highly sensitive to the virtual basis set. A further source of error in this early study is the use of the Hartree-Fock approximation uncorrected for any correlation corrections. Similar studies by Mickish and Kunz on the somewhat similar solid rare gases have found that the Hartree-Fock method consistently overestimates the band gap of these systems by about 4 or 5 eV.[1] In addition all band methods are inaccurate, in that, all neglect

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We believe new approaches are needed if one is to truly interpret the electronic structure of such systems as solid Methane. Recent theoretical results of Kunz and Flynn have demonstrated that it is possible to include the effect of electron-hole interaction and exciton formation without violating Bloch's theorem in calculations of the optical properties of such divergent solids as LiF and Mg or Ca. This is accomplished by means of a degenerate perturbative calculation using the $\vec{k}$-conserved one body valence to conduction band excitations as a basis.[9] This model retains the periodic symmetry of the lattice avoiding complications introduced by the use of finite cluster models to describe the local excitations. These finite cluster models, nonetheless, are useful and accurate approximates as we shall see. The formulationm of the problem in this way by Kunz and Flynn causes one to wish to begin with Hartree-Fock descriptions of the solid since a well defined Many-Body wavefunction is needed. The Hartree-Fock model neglects all correlations and the limited basis set used to describe excitonic effects does not describe properly the relaxation or polarization properties of the system. In these lectures, the correlation effects are incorporated by means of a simple Many Body Perturbation Theory Model (MBPT). The necessary theoretical methods are described in Section II. The numerical calculations are described in Section III, and conclusions are given in the final section.

II. Theoretical Development

The initial step in this development is the choice of the Hartree-Fock method. This choice is largely determined by the need to perform extensive correlation calculations in addition to the initial Hartree-Fock study. To facilitate development, we employ variants on the familiar Linear-Combination-of-Atomic-Orbitals method (LCAO). In the case of cluster calculations, these AO's are first rotated into molecular orbitals (MO's) spanning the entire cluster, and in the case of the band calculations, the AO's are rotated into MO's spanning the crystallographic unit cell. This rotation into MO's is advantageous because for unit cells of ever increasing size or complexity, an adequate description in terms of AO's yields rather large secular determinants. The LCMO scheme reduces substantially the size of the secular determinant. This method was first introduced by Piela *et al.*[8] for studies on solid methane. In such a simple case the basis set for the occupied orbitals is reduced from 9 to 5 orbitals. Furthermore, the MO's may contain polarization functions in them and therefore yield far greater accuracy than a much larger set of AO's.

The essential features of this approach is this. Let each unit cell be divided into molecules (real ones or not), and we devise a basis set to represent the MO's of these molecules. The primitive basis set used are spherical-harmonic Gaussian Type Orbitals (GTO's) centered about different origins, and have the form

$$\chi_i(\vec{r}-\vec{R}_i) = \exp\,[-Z_i(\vec{r}-\vec{R}_i)^2]\; Y_\ell^m\,(\theta,\phi). \qquad (1)$$

The $\vec{R}_i$ are the origins about which these functions are centered and need not be an actual nuclear site, the Y_ℓ^m are the usual spherical harmonics. The orbital exponent Z_i is chosen by energy minimization. The MO's in turn are just linear combinations of these GTO's,

$$\phi_j\,(\vec{r}-\vec{R}_\alpha) = \sum_i a_i^j\, \chi_i(\vec{r}-\vec{R}_i), \qquad (2)$$

The $\vec{R}_\alpha$'s are the locations of the molecules in the system. From the MO's, one forms Bloch orbitals which span the entire system:

$$\psi_j(\vec{k},\vec{r}) = N^{-1/2} \sum_\alpha e^{i\vec{k}\cdot\vec{R}_\alpha}\, \phi_j(\vec{r}-\vec{R}_\alpha). \qquad (3)$$

The MO's (Eq. (2)) or the Bloch functions (Eq. (3)) form the basis by which we solve the HF problem or its extensions.

The first point is that the Hartree-Fock equation need be solved *self-consistently*. For a finite molecular cluster, this is achieved by conventional iterative means. However, the infinite periodic system imposes special difficulties. These are simply that the occupied canonical Bloch orbitals are infinite in number and therefore enumerating the contribution of each orbital to the Fock operator imposes a strain on ones computer budget. Two options are available. The first is to use a *finite mesh in* $\vec{k}$*- space and use some form of quadrature to* construct the Fock operator. The second is to rotate into a basis set of local orbitals.[10,11,12] In the early stages, both methods were tried with negligible differences in numerical result between them. However, at the current stage of our code development, the local orbitals method enjoys a substantial speed advantage.

The intent of the present study is to obtain spectroscopic information and hence we need examine the meaning of the energy bands. The occupied bands are the negative of the ionization energy for that band for the state of wave vector $\vec{k}$. The virtual bands are similar representations for the electron affinities. In this event one is assuming the use of the Hartree-Fock eigenvalue and also of Koopmans' theorem as is

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In order to improve upon the Hartree-Fock results one must include correlation corrections. In doing this, initially the author will maintain the same physical definition for the energy bands as in the Koopmans' case. That is, the bands now become quasi-particle bands in which the energy of an occupied level is the negative of the energy needed to create it, and the energy of the virtual states are the negative of the energy recovered in creating it. This is in keeping with the earlier usage of the electronic polaron model and its extensions as discussed by Pantelides *et al.*[13,14,15]

It is now necessary to discuss correlation corrections. The first problem is that of size consistency (The total energy is an extensive quantity).[16,17] In fact the total energy of an infinite solid is infinite and only the energy/molecule is finite. Unfortunately, the energy change upon ionization is also finite and the energy change/molecule vanishes. That is the energy difference is still finite. Similar considerations apply to excitations of the n-electron system. A simple classical way to view this is to realize that the size of the wave created by hurling a brick into a pond is largely independent of the size of the pond. Therefore we must establish a size consistent framework for the system total energies in such a way that formally we can obtain differences in extensive quantities, cancelling the infinities before we compute finite differences. Alternately, we may reduce the size of the systems so that total energy determinations are possible.

Let us work in a local representation here. This is appropriate since many molecular solids are filled shell systems. For notational simplicitiy, designate the Wannier function $W_{iN}(\vec{r})$ as the i^{th} Wannier function about site $\vec{R}_N$. Form a complete set of Wannier orbitals describing the ground state of the neutral, N-electron solid in the Hartree-Fock limit. We will use them to generate the ion states as well. For a system of N-electrons the Hamiltonian is

$$H = \sum_{i=1}^{n} -\frac{\hbar^2}{2m}\nabla_i^2 - \sum_{i=1}^{N}\sum_{I=1}^{M}\frac{Z_I e^2}{|\vec{r}-\vec{R}_I|} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \frac{e^2}{|\vec{r}_{ij}|} \qquad (4)$$

The electronic has mass m, and is charge e, Z_I is the atomic number of the nucleus at site I. The i^{th} electron has coordinate $\vec{r}_i$ and the I^{th} nucleus has coordinate $\vec{R}_I$. In terms of Wannier Functions, in the single determinant limit, the energy of the system is

$$E_N = \sum_{i_j}^{(N)} < w_{iI}| - \frac{\hbar^2}{2m} \nabla^2 - \sum_{J=1}^{M} \frac{Z_J e^2}{|\vec{r}-\vec{R}_j|} |w_{iI}> \tag{5}$$

$$+ \frac{1}{2} \sum_{\substack{iI\\ jJ}}^{(N)} [<w_{iI} w_{jJ}|\frac{e^2}{r_{12}}|w_{iI} w_{jJ}> - < w_{iI} w_{jJ}|\frac{e^2}{r_{12}}|w_{jJ} w_{iI}>]$$

The symbol (N) on the summation implies sums over all states in the occupied N electron space. To keep the physics of the energy bands discussed earlier we need to look at the N-1 and N+1 *electron system* next.

Let the ground state of the N-electron Hartree-Fock system be designated as $|N>$ and let α^+_{pI}, α_{pI} create or destroy a Wannier function at site I with other quantum numbers p. We adopt the conventive that quantum numbers i, j, k etc., refer to occupied orbitals, a, b, c to virtual orbitals and o, p, q to either/both. A Slater determined of the N-1 body system is

$$|N-1;\ jB > \equiv \alpha_{jB}|N > \tag{6}$$

This will by symmetry adapted later. The energy expectation value of this state is simply

$$E^{jB}_{N-1} = E_N - < w_{jB}|F(N)|w_{jB}> \tag{7}$$

Here F(N) is simply the N-electron ground state Hartree-Fock operator. Similarly one may obtain the off diagonal matrix elements between two states $|N-1,\ iA>$ and $|N-1,\ jB>$. These are:

$$D^{iAjB}_{N-1} = <w_{jB}|F(N)|w_{iA}>. \tag{8}$$

One may project on the state $|N-1,\ jb>$ to form a proper translational invariant Bloch function, $\psi_j^{N-1}(\vec{k})$:

$$\psi_j^{(N-1)}(\vec{k}) = \sum_B \frac{1}{\sqrt{N}} e^{i\vec{k}\cdot\vec{R}_B} |N-1;\ jB> \tag{9}$$

In terms of eqs (5)-(9) one may construct a band structure in terms of Wannier-functions and Slater determinante for the occupied orbitals. These are yet uncorrelated. One may treat the N+1 body states similarly. Furthermore, recognizing that E_N in eq (11) is infinite and also irrelevant, since energy changes are needed, we proceed to define E_n as 0, and thus simplify our computation.

A framework is needed in order to simply correlate this problem since the simple single Slater determinants $|n-1,\ jB>$ are highly degenerate, and within a band, the $\psi_j(\vec{k})$ are nearly degenerate. Consider the problem in a general framework initially. H is a Hamiltonian,

$|w_{iI}\rangle$ (5)

$w_{jJ}|\frac{e^2}{r_{12}}|w_{jJ}w_{iI}\rangle$]

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$$H = H_o + V. \tag{10}$$

We assume that the eigenstates of H_o are known as

$$H_o\phi_i = w_i\phi_i. \tag{11}$$

The projector onto a given eigenstate of H_o say ϕ_i is P_i and is given as

$$P_i = |\phi_i\rangle\langle\phi_i|.$$

Furthermore a projector onto the first n states say is $\overline{P}$ and

$$\overline{P} = \sum_{i=1}^{n} |\phi_i\rangle\langle\phi_i| = \sum_{i=1}^{n} P_i. \tag{12}$$

Assume we order our eigenfunction of H_o so that the states of interest lie in the range 0 to n. Furthermore no other states are degenerate with these states. Now let us solve the desired equation:

$$H\psi = E\psi = (H_o+V)\psi. \tag{13}$$

Let us chose a w_j for $1 < j < n$, then:

$$(1-\overline{P})(H_o-w_j)\psi = (1-\overline{P})(E-w_j-V)\psi \tag{14}$$

One may commute $(1-\overline{P})$ with H_o-w_j and proceed to see

$$\psi = \overline{P}\psi + (H_o-w_j)^{-1}\ (1-\overline{P})\ (E-w_j-V)\psi. \tag{15}$$

Furthermore;

$$P_i\psi = \pi_i\phi_i,\ \pi_i = \langle\phi_i|\psi\rangle,$$

so that

$$\overline{P}\psi = \sum_{k=1}^{n} \pi_k\phi_k = \phi. \tag{16}$$

Therefore

$$[1 - (H_o-w_j)^{-1}\ (1-\overline{P})(E-w_j-V)]\psi = \phi. \tag{17}$$

If one defines

$$T = \{1 - (H_o-w_j)^{-1}\ (1-\overline{P})(E-w_j-V)\}^{-1}, \tag{18}$$

then

$$\psi = t\phi. \tag{19}$$

Furthermore one can show that

$$(E-w_i)\,\pi_i = \sum_{k=1}^{n} \pi_k \,\overline{V}_{ik}, \tag{20}$$

where

$$\overline{V}_{ik} = \langle \phi_i | VT | \phi_k \rangle. \tag{21}$$

Eqs. (20) and (21) define a perfectly good algebraic eigenvalue equation for the system energies. To proceed further, one expands the inverse appearing in T. That is,

$$\begin{aligned} VT &= N + V \frac{1}{H_o - w_j} (1-\overline{P})(E-w_j-V) + \dots \,. \\ &= \overline{V}, \end{aligned} \tag{22}$$

or

$$\overline{V}_{ik} = V_{ik} + \sum_{a=N+1}^{\infty} \frac{a}{w_j - w_a} V_{ia} V_{ak}. \tag{23}$$

The structure of the eigenvalue problem defined by Eqs (20), (21) and (23) is now clear. The matrix elements to lowest approximation are similar to those of second order R.S.P.T. and this is clearly a size consistent approach. If all the eigenvectors in the first n are degenerate, one recovers normal degenerate perturbation theory. Consider our problem, where we use Wannier functions, this framework makes our approach clear. First correlate the single Slater determinant of Wannier functions, then proceed with Bloch symmetry projection to remove the degeneracy. The N-body wavefunction has proper Bloch symmetry for closed band systems. By using a proper choice of A in the Adams-Gilbert local orbital formulation called A^W one may obtain Wannier orbitals.[11] The actual choice of A^W is not important, only that such exist. Then

$$[F + PA^{W}P]\, w_{iI} = \epsilon_{iI} w_{iI} \tag{24}$$

The first order Fock-Dirac density matrix is ρ. From this one constructs a zero order Hamiltonian. For a system of M-electrons, H_o is defined as

$$H_o = \sum_{i=1}^{M} [F(\vec{r}_i) + \rho_i A_i^{W} \rho_i] \tag{25}$$

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and then the perturbation, V becomes

$$V \equiv H - H_o \tag{26}$$

$$E(N) = E_N + \sum_{iI>jJ}^{(N)} \sum_{aA>bB} \frac{|V_{iIjJ}^{aAbB}|^2}{\epsilon_{iI}+\epsilon_{jJ}-\epsilon_{aA}-\epsilon_{aB}}. \tag{27}$$

Here the summation (N) indicates all Wannier orbitals in the N-electron state. The matrix element is simply

$$V_{iIjJ}^{aAbB} = \langle w_{iI} w_{jJ} | \frac{e^2}{r_{12}} | w_{aA} w_{bB} \rangle - \langle w_{iI} w_{jJ} | \frac{e^2}{r_{12}} | w_{bB} w_{aA} \rangle \tag{28}$$

The N-body orbitals will be used to describe both the N-1 and N+1 body states. Brillouin's theorem is not valid for such states. Consider first the N-1 body problem. Let Wannier orbital w_{iB} be deleted from the N-body ground state. Then to second order one finds that

$$\begin{aligned} E(N-1,iB) = E_n - D_{N-1}^{iBiB} &+ \sum_{jI}^{(N+1)} \sum_{aA} \frac{|F(N-1;iB)_{jI}^{aA}|^2}{\epsilon_{jI}-\epsilon_{aA}} \\ &+ \sum_{kK>jJ}^{(N-1)} \sum_{aA>bC} \frac{|V_{kK,jJ}^{aAbB}|^2}{\epsilon_{kK}+\epsilon_{jJ}-\epsilon_{aA}-\epsilon_{bC}}. \end{aligned} \tag{29}$$

In Eq (19) the V is still as defined in Eq (18) and F(N-1;iB) is obtained by deleting terms referring to orbital w_{iB} from F(N). Therefore

$$F(N-1;iB)_{jI}^{aA} = \langle w_{jI} | F(N-1,iB) | w_{aA} \rangle. \tag{30}$$

One proceeds in like fashion for the N+1 electron case, adding W_{CB} to the N electron state.

$$\begin{aligned} E(N+1;cB) = E_N + D_{N+1}^{cBcB} &+ \sum_{jJ}^{(N+1)} \sum_{aA} \frac{|F(N+1,cB)_{jJ}^{aA}|^2}{\epsilon_{jJ}-\epsilon_{aA}} \\ &+ \sum_{jJ>kK}^{(N+1)} \sum_{aA>dD} \frac{|V_{jJkK}^{aAdD}|^2}{\epsilon_{jJ}+\epsilon_{kK}-\epsilon_{aA}-\epsilon_{\alpha D}} \end{aligned} \tag{31}$$

In Eq (21) V remains as in Eq (18) and F(N+1;cB) is obtained by adding terms referring to orbital w_{cB} to the N-electron Fock operator.

One may obtain the physically interesting energy differences from these expressions. The ionization potentials are defined by E(N) - E(N-1;iB). This difference called here Δ_{iB} is given as

$$\Delta_{iB} = D^{iBiB}_{N-1} + -\sum_{jJ}^{(N-1)} \sum_{aA} \frac{|F(N-1,iB)^{aA}_{jJ}|^2}{\epsilon_{jJ} - \epsilon_{aA}} + \sum_{jJ \neq iB}^{(N)} \sum_{aA>cC} \frac{|V^{aAcC}_{iBjJ}|^2}{\epsilon_{iB}+\epsilon_{jJ}-\epsilon_{aA}-\epsilon_{cC}} - \sum_{\substack{jJ>kK\\ \neq iB}} \sum_{aA} \frac{|V^{iBaA}_{jJkK}|^2}{\epsilon_{jJ}+\epsilon_{kK}-\epsilon_{iB}-\epsilon_{aA}} \qquad (32)$$

Likewise the electron affinity terms are obtained by letting $\Delta_{CB} = E(N+1;CB)-E(N)$. Then

$$\Delta_{cB} = D^{cBcB}_{N+1} + \sum_{jJ}^{(N+1)} \sum_{aA} \frac{|F(N+1,\ CB)^{aA}_{jJ}|^2}{\epsilon_{jJ} - \epsilon_{aA}} + \sum_{iI}^{(N+1)} \sum_{aA>dD\neq cB} \frac{|V^{aAdD}_{iIcB}|^2}{\epsilon_{iI} + \epsilon_{cB} - \epsilon_{aA} - \epsilon_{dD}} - \sum_{iI>jJ}^{(N+1)} \sum_{aA\neq cB} \frac{|V^{cBaA}_{iIjJ}|^2}{\epsilon_{iI} + \epsilon_{jJ} - \epsilon_{cB} - \epsilon_{aA}} \qquad (33)$$

It is these formulas we will use in this study.

One final piece is needed to complete this theory. This is to include the actual effect of electron-hole interaction upon excitation. An accurate method of doing this for both tightly bound or loosely bound excitations has been recently given by Kunz and Flynn.[9]

The essential point is to use the Hartree-Fock bands as a basis set after incorporation of correlation corrections into the band energies. The Fock ground state $|N\rangle$ is then used to describe schematically the process. Let $\alpha_v(\vec{k})$ annihilate a valence electron of wavevector $\vec{k}$ and let $\alpha_c^+(\vec{k})$ create a conduction electron of wavevector $\vec{k}$. Consider the state then:

$$|N,\vec{k}\rangle = \alpha_c^+(\vec{k})\ \alpha_v(\vec{k})\ |N\rangle \qquad (34)$$

It is only states like this which can be reached from the ground state via optical processes. Furthermore all such ground states $|N,\vec{k}\rangle$ correspond to the same total crystal wavevector; that of the ground state. The most general excited state that one may access is then $|N, E\rangle$, where

$$|N,e\rangle = \sum_{\vec{k}} a_{\vec{k}}\ |N,\vec{k}\rangle \qquad (35)$$

In this sum, the ground state $|N\rangle$ is excluded because it differs in parity from the excited state. By finding the $a_{\vec{k}}$ and $\langle N, E|H|N, E\rangle$, one may determine the spectrum of the solid including electron-hole interaction. This is achieved by means of a CI calculation among the states $|N, \vec{k}\rangle$. The formation of such ex-

$$\frac{|V^{iBaA}_{jJkK}|^2}{\epsilon_{jJ}+\epsilon_{kK}-\epsilon_{iB}-\epsilon_{aA}} \quad (32)$$

obtained by letting

$$\sum^{(N+1)}_{iI} \sum_{aA>dD\neq cB}$$

$$\frac{|V^{cBaA}_{iIjJ}|^2}{+\epsilon_{jJ}-\epsilon_{cB}-\epsilon_{aA}} \quad (33)$$

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citon states is not an extensive property and size consistency is not a problem as demonstrated by Kunz and Flynn.[9] Exact implementation of such an infinite CI is of course impossible and we use a finite number of states, some 270 configurations. A second approximation is made as well. This is to truncate the coulomb interaction at the boundary of a unit cell. This is not unreasonable for tightly bound excited systems as in the case of CH_4 particularly since the large lattice constant (11.14 au) encloses a substantial volume in a unit cell. The dominant consequence of this is to allow the formation of only a single bound exciton, not an entire Rydberg series below the bands. However when the coefficients a_k are used to evaluate the optical response one finds substantial adjustment over the Hartree-Fock results. These changes are due to the redistribution of oscillator strength to the bottom of the conduction band due to the inclusion of electron-hole interaction.

The alternate approach employed is to use a finite molecular cluster simulation. This is also done using the method of local orbitals. In this case one partitions the system into the cluster and the environment. The environment imposes itself on the cluster by means of a bounding potential. The methods of doing this are well represented in the literature, and a general approach is given by Kunz and Klein[18] which need not be repeated here. Correlation is imposed using the technique of this section and in particular eqs. (20), (21) and (23) as needed. For non-degenerate states of course, these reduce to ordinary second order RSPT. Most cases considered here are not degenerate in the cluster limit, but for those cases for which degeneracy is a problem, we have found the full approach to be very powerful.[19]

III. Results for Solid CH_4

A Gaussian basis set was first developed for the CH_4 molecule in free space and then reoptimized for the crystal to allow accurate description of the energy bands, occupied and virtual. It was found easy to obtain accurate valence bands, but that the conduction bands were quite sensitive to the choice of outer orbital. The variational principal applies to the solution of the one particle states in a LCMO formalism, and the selection of the basis is quite easy. In practice, the conduction bands are found to be stable against small changes in basis set. The valence structure here agrees well with that obtained after corrections to formalism by Piela *et al.*[8,20,21] The conduction bands are in very poor agreement however. This is due to the far too restrictive basis set employed in the Piela *et al.*[8] calculation of the virtual bands. In performing this calculation, some idealizations are needed. A lattice constant of 11.14 au, in agreement with Piela *et al.* is used and the C sub lattice is fixed as a fcc one as per experiment. The four H's form in tetrahedra about the C in a unit cell. In the real world, the tetrahedra do not allign from one cell to another but have orientational disorder. We, as did Piela *et al.* fix the H's in an ordered fcc lattice as well. The current calculation uses the same geometry as does Piela *et al.* The C-H distance is obtained computationally from Beck[22] and for a lattice constant of 11.14 au, the equilibrium constant, is essentially the same C-H distance as in the free molecule.

Although the Hartree-Fock band results overestimate any reasonable band gap, they do reduce the Piela gap by about 13.6 eV however,[8] and one need add correlation along the lines suggested in Section II. In performing the correlation correction computations, the author deviates from the ideals expressed in the preceding section to the extent that instead of solving for a set of rather complicated, orthogonal Wannier functions as implied by the derivations, one approximates these by a set of local orbitals. In obtaining these the unit on which localization occurs is the CH_4 molecule is used, and also the appropriate multicenter localization.[23] These orbitals are quite local, the valence-valence overlaps being 0.03 or less here. First order overlap corrections are made in the inter molecular terms for further precision. Due to the procedure adopted, *all* orders of overlap in the *large* intra molecular overlaps are included exactly. The inclusion of these corrections is essential if one wishes to achieve quantitative accuracy. In evaluating the perturbation sums, d orbitals on the C atom and p orbitals on the H atoms were added to the band structure basis set. The effect of the several contributions to Eqs (32) and (33) are given in Table 1. There we call the second term on the right hand sides of Eqs (32) and (33) the relaxation and the sum of the second and third terms, which come from two electron virtual excitations, clearly represent correlation terms.

The energy bands for CH_4 including correlation are shown in Figure 1. The density of electron states is also seen in these figures. As is clear from these figures, the band gap is indirect and from Γ_{15v} to $X_{5'c}$. The direct gap is at the X point and is $X_{5'v}$ to $X_{5'c}$. The correlated indirect gap is found to be 13.0 eV, and the correlated direct gap is found to be 13.3 eV.

Finally, one computes the position of the exciton levels in CH_4. This is accomplished using the method given in Section II which has been more fully described in Ref. 9. In this calculation the coulomb interactive is treated as a one molecule interaction. The effective electron-hole interaction is here computed to be 5.4 eV. This is the value of the V_0 discussed in

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Table 1

Contributions to the ionization potential and electron affinity of solid CH_4 are shown as a function of lattice parameter. Results are given for the correlation correction and the relaxation correction. Results are in eV.

a	11.14 au	10.50 au	10.00 au
valence correlation	0.1 eV	0.2 eV	0.4 eV
valence relaxation	1.2 eV	1.2 eV	1.2 eV
conduction correlation	-.7 eV	-.8 eV	-.9 eV
conduction relaxation	~0.0 eV	~0.0 eV	~0.0 eV
net gap change	-2.0 eV	-2.2 eV	-2.5 eV

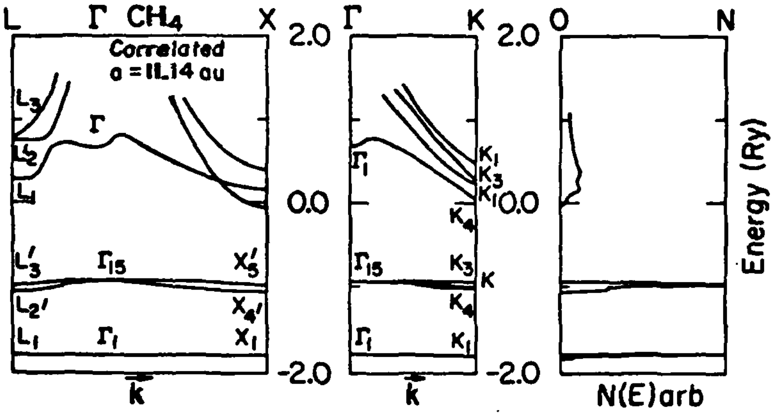

Figure 1 The correlated band structure of solid CH_4 and density of states in shown for lattice parameter = 11.14 au.

Ref. 9. Using this value, the exciton is found to be at 10.9 eV. The optical spectrum of Koch and Skihowski[24] does find a spectral peak at 11.0 eV and this may well be our exciton. A more quantitative analysis of the optical response is not possible at this time because the highest valence and lower conduction bands are of like symmetry and the techniques developed in Ref. 9 and currently available do not permit a calculation of the optical response for the case in which the band to band transitions are dipole forbidden only the positions. Therefore, the author reluctantly contents himself with using only the $\vec{k}$ conserved joint density of states in comparison with the measured reflectance spectrum shown in Figure 2.[24] As is clear from this figure, even if one were to include the exciton at 11.0 eV, a fair degree of discrepancy remains. This is largely at low energy. This discrepancy is expected. A similar result is seen in the free CH_4 molecule and is due to the mobility of the H nuclei and their large zero point motion. The excited CH_4 molecule can lower its energy by about 1.6 eV by relaxing from ideal T_D geometry to D_{2h} geometry. Due to large zero point motion it may be possible to excite from the ground state T_D geometry directly into the relaxed, distorted D_{2h} geometry directly. This certainly appears to be the case in the free molecule and a discussion of this is being prepared by Beck and Kunz.[25] If one assumes the same type of Jahn-Teller distortion is present in the solid, a distorted exciton line would then appear at about 9.3 eV. This is shown as a dotted line in Figure 1. Since the first experimental peak in solid CH_4 lies at 9.6 eV, this inclusion greatly enhances the comparison of theory and experiment. In addition the low energy continuous spectrum between about 12 and 14 eV would be enhanced in strength by the redistribution of oscillator strength due to exciton formation as was seen in LiF.[9]

Large scale cluster calculation for bulk CH_4 (13 molecules or 65 atoms) and for the CH_4 surface (9 molecules or 45 atoms), including all electrons and correlation via the perturbative route, have been recently performed by Beck.[26] These calculations are for the excitons alone and tend to confirm the energy band results qualitatively and quantitatively. The specific details of the perturbation treatment for large systems is well described in the literature.[27]

IV. Conclusions

The essential conclusions are few and simple. These are one can construct a satisfactory, self-consistent Hartree-Fock band structure for molecular solids, including the conduction bands, if one carefully optimizes the basis set. If one wishes

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to obtain quantitative comparisons with experiment, the inclusion of correlation corrections is essential. Furthermore, in describing the ion states in terms of the neutral system orbitals corrections termed relaxation corrections are needed. It is seen here, using a Wannier basis, how such arise and may be included. It is also seen that inclusion of electron-hole interaction is needed if one is to quantitatively study the optical spectrum. In addition, due to the light mas of H one need also be prepared to include Jahn-Teller distortion if one is to be fully quantitative.

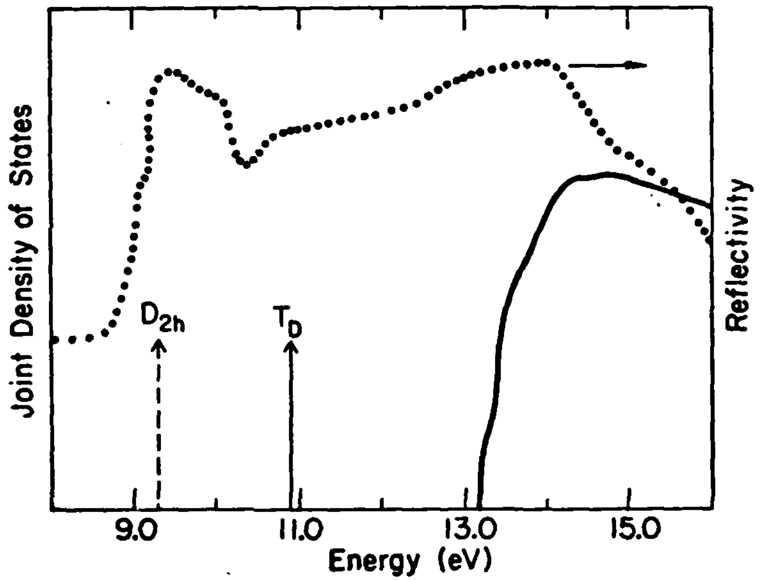

Figure 2 The optical joint density of state is shown for solid CH_4 along with the T_D geometry exciton position and probable D_{2N} geometry exciton. The optical reflectivity of Ref. 24 is also shown

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