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Electronic structure and optical properties of solid methane

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The electronic structure of solid methane, including the virtual levels, is studied in a self-consistent Hartree-Fock model as a function of the lattice constant. It is found that the band gap is a sensitive function of pressure. It is also found that the resulting accuracy of the conduction bands depends heavily upon the quality of the virtual orbitals, a fact not appreciated in previous studies on solid CH_4. It is found essential to include correlations explicitly in order to facilitate a comparison to experiment. This is done by means of perturbation theory. The inclusion of Coulomb correlations causing the formation of excitons in the excited spectra is accomplished by means of degenerate perturbation theory in the continuum. Results are compared to experiment.

I. INTRODUCTION

Theoretical studies on three-dimensional solids have largely excluded the category of molecular solids. Of the existing studies on such systems almost all have been for solid rare gases or solid H_2. In the case of H_2 much interest is stimulated, not so much by any intrinsic interest in solid H_2, but rather by interest in the insulator—to—monatomic-metal transition, and the possible presence of stable metal phases exhibiting high-temperature BCS-type superconductivity.[1] Much recent theoretical interest in the properties of the solid rare gases is also related to questions of metallization pressures as well.[2]

More complicated molecular solids, those which have more than two atoms in a molecular unit or those with more than one type of molecule in a unit cell are limited primarily to one-dimensional systems such as polymers and solid methane (CH_4). There are probably many reasons for the neglect of this 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. 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 phases. 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-type transitions.[3] 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 why 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.

The available 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.[4] 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 or 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.[5] Thus the author believes that the results of Piela *et al.* are indicative of the solid methane band structure but not quantitatively accurate. If one is to base one's judgments on the solid rare gases, the local-density method, at least in the $X\alpha$ variant, is also not likely to provide quantitatively useful band-theoretical results for this system either.[6] Furthermore, all such band methods are inaccurate in that all neglect the formation of local excited states called excitons.

Thus, the author believes that a totally new approach is needed if one is to truly interpret the electronic structure of such systems as solid methane. This paper is an attempt to begin the formulation of such a method. Recent theoretical results of Kunz and Flynn have demonstrated that it is possible to include the effect of electron-hole interaction and exciton formation in calculations of the optical properties of such divergent solids as LiF and Mg or Ca. This is accomplished by means of a complete configuration-interaction (CI) calculation using the $\vec{K}$-conserved one-body valence- to conduction-band excitations as a basis.[7] This complete CI is sufficient to describe both Wannier and Frenkel excitons in a single calculation. Furthermore, this model explicitly includes the proper periodic symmetry of the lattice and thus avoids complications induced by the use of finite-cluster models to describe the local excitations. The formulation 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 wave function is needed.

This causes other problems to appear. The Hartree-Fock model neglects all correlations and the limited CI used to describe excitonic effects does not describe properly the relaxation or polarization properties of the system. In this paper, the correlation effects are incorporated by means of a simple many-body perturbation-theory model (MBPT). The necessary theoretical methods are described in Sec. II. The numerical calculations are described in Sec. III, and conclusions are given in the final section.

II. THEORETICAL METHODS

The basic initial step in these calculations was the choice of the Hartree-Fock approach. The choices here were largely determined by the need to perform extensive correlation calculations in addition to the basic band-theoretic ones, and therefore to have done the fundamental calculations in as convenient a way as possible. In the present case this dictated that the basic method should be a variant on the familiar linear combination of atomic orbitals method (LCAO). Ultimately the goal of this project is to be able to obtain energy-band structures for rather complex molecular solids so the simple use of LCAO was not considered appropriate. This is because as one has unit cells of ever increasing size and complexity an adequate description in terms of atomic orbitals (AO's) yields very large secular determinants. There is a useful alternative, this being the linear combination of molecular orbitals scheme (LCMO). This was introduced by Piela *et al.* for their work on solid methane.[4] In even such a simple case the occupied basis size reduces from nine orbitals to five. Furthermore, the molecular orbitals (MO's) may contain polarization functions in them and yield much greater accuracy than a small number of AO's.

The essential features of the LCMO method are these. The unit cell of the solid system is divided into basic units termed molecules. These units need not be true molecules, but such is often convenient. A basis set, the MO's are then devised to represent the molecule. In this calculation, the MO's are in turn expressed as a linear combination of Gaussian type orbitals (GTO's). These Gaussian orbitals are of the form

$$\chi_i(\vec{r}-\vec{R}_i)=\exp[-Z_i(\vec{r}-R_i)^2]Y_l^m(\theta,\phi)\ . \tag{1}$$

In this expression the Y_l^m are the normal spherical harmonics, combined into real Cartesian-type functions. $\vec{R}_j$ is the origin about which these functions are placed. This origin need not be an actual nuclear site, but rather may be variationally chosen, just as are the Z_j, the orbital exponents. The MO is then simply a linear combination of these orbitals in the form,

$$\phi_j(\vec{r}-\vec{R}_j)=\sum_i a_i^j x_i(\vec{r}-\vec{R}_i)\ . \tag{2}$$

From these MO's one forms Bloch symmetry orbitals to span the entire crystal. These Bloch orbitals are of the form

$$\psi_j(\vec{k},\vec{r})=\frac{1}{\sqrt{N}}\sum_i e^{i\vec{k}\cdot\vec{R}_i}\phi_j(\vec{r}-\vec{R}_i)\ . \tag{3}$$

This then is the basis set chosen to represent the energy bands in our rather general form of the LCMO method.

The basic method is Hartree-Fock and one need achieve self-consistency. This may be accomplished in one of two ways. The first is to iterate the basic crystalline Hartree-Fock equation at a finite number of points in reciprocal space using this basis set. The other is to iterate the MO basis to self-consistency via the method of local orbitals.[8–10] In this study both were attempted with negligible differences in accuracy. It was found for this case that the method of local orbitals enjoyed substantial speed advantages, and therefore allowed one to use better basis sets and to more carefully optimize them as well. This is more fully discussed in the next section.

The essential physics of a Hartree-Fock band structure is in the meaning of the energy bands. In this approximation, 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 Koopman's theorem as is usually done. It is essential to observe that the physics here refers to ionization properties, not to excitation properties of the n-electron system. The modifications needed to incorporate excitation properties will be discussed subsequently.

In order to improve upon the Hartree-Fock results one must include correlation corrections. In doing this, the author will maintain the same physical definition for the energy bands as in the Koopman's case. That is, the bands now become quasiparticle 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 created it. This is in keeping with the earlier usage of the electron polaron model and its extensions as discussed by Pantelides *et al.*[11,13]

In performing the correlation one must exercise care from the outset since the correlation energy of an infinite solid is itself infinite. Thus one need construct models which obtain only the changes in correlation energy as one changes state. This is most simply done by using many-body perturbation theory (MBPT). An early attempt at this is the electronic polaron and the author will follow this basic philosophy here.[12]

It is useful to work in a Wannier representation here. This is appropriate since CH_4 is a filled-shell system. For notational simplicity, we designate the Wannier function $W_{iN}(\vec{r})$ as the ith Wannier function about site $\vec{R}_N$. In this instance, we form a complete set of Wannier orbitals as appropriate for the ground state of the neutral, N-electron solid in the Hartree-Fock limit. We will use those to generate the ion states as well. For a system of N electrons the Hamiltonian is

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

The electronic mass is m, its charge is e, and Z_i is the atomic number of the nucleus at site I. The ith electron has coordinate $\vec{r}_i$ and the Ith nucleus has coordinate $\vec{R}_I$. Here we let

$$|\vec{r}_{ij}|=r_{ij}=|\vec{r}_i-\vec{r}_j| \ .$$

In terms of our Wannier functions, in the Hartree-Fock limit the energy of the system is

$$E_N=\sum_{i,I}^{(N)}\left\langle w_{iI}\left|-\frac{\hbar^2}{2m}\nabla^2-\sum_J\frac{Z_Je^2}{|\vec{r}-\vec{R}_J|}\right|w_{iI}\right\rangle+\frac{1}{2}\sum_{\substack{i,I,\\ j,J}}^{(N)}\left[\left\langle w_{iI},w_{jJ}\left|\frac{e^2}{r_{12}}\right|w_{iI},w_{jJ}\right\rangle-\left\langle w_{iI},w_{jJ}\left|\frac{e^2}{r_{12}}\right|w_{jJ},w_{iI}\right\rangle\right] \ . \quad (5)$$

The symbol (N) on the summation implies sums over all states in the occupied N-electron space. In maintaining the physics describing the energy bands described earlier we need to look at the $(N-1)$- and $(N+1)$-electron systems next.

Let the ground state of the N-electron Hartree-Fock system be designated as $|N\rangle$ and let $\alpha_{pI}^{\dagger},\alpha_{pI}$ create or destroy a Wannier function at site I with other quantum numbers p, respectively. Here we adopt the notation that quantum numbers i,j,k, etc., refer to occupied orbitals, a,b,c to virtual orbitals, and o,p,q to either or both. A Slater determined of the $(N-1)$-body system is

$$|N-1;j,B\rangle\equiv\alpha_{jB}|N\rangle \ . \quad (6)$$

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

$$E_{N-1}^{jB}=E_N-\langle w_{jB}|F(N)|w_{jB}\rangle \ . \quad (7)$$

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 $|N-1;i,A\rangle$ and $|N-1;j,B\rangle$. These are simply

$$D_{N-1}^{iAjB}=\langle w_{jB}|F(N)|w_{iA}\rangle \ . \quad (8)$$

Thus one may form Bloch symmetry projections on the state $|N-1,jB\rangle$ to form a proper translational-invariant Bloch function, $\psi_j^{N-1}(\vec{k})$:

$$\psi_j^{(N-1)}(\vec{k})=\sum_B\frac{1}{\sqrt{m}}e^{i\vec{k}\cdot\vec{R}_B}|N-1;j,B\rangle \ . \quad (9)$$

In terms of Eqs. (5)–(9) one may construct a band structure in terms of Wannier functions and the Slater determinate for the occupied orbitals. These are yet uncorrelated.

One may proceed in like manner for the $(N+1)$-body states. That is, let

$$|N+1;b,B\rangle\equiv\alpha_{bB}^{\dagger}|N\rangle \ , \quad (10)$$

and then the energy expectation value of this state is

$$E_{N+1}^{bB}=E_N+\langle w_{bB}|F(N)|w_{bB}\rangle \ , \quad (11)$$

and the off-diagonal elements are

$$D_{N+1}^{aAbB}=\langle w_{bB}|F(N)|w_{aA}\rangle \ . \quad (12)$$

The analogous Bloch projection to Eq. (9) yields for the virtual state

$$\psi_a^{(N+1)}(\vec{k})=\sum_A\frac{1}{\sqrt{m}}e^{i\vec{k}\cdot\vec{R}_A}|N+1;a,A\rangle \ . \quad (13)$$

There is one point of difficulty here. For the infinite solid, $E_N=\infty$. This is no real problem since one is interested in energy changes and we may arbitrarily renormalize such that $E_N=0$. If we do this let us then simply designate the diagonal matrix elements in Eqs. (2) and (11) as

$$D_{N-1}^{jBjB}=\langle w_{jB}|F(N)|w_{jB}\rangle$$

and

$$D_{N+1}^{aAaA}=\langle w_{aA}|F(N)|w_{aA}\rangle \ .$$

At this point we are ready to correlate our band problem.

In order to proceed in a reasonable finite (from the computational standpoint) way it is necessary to make some simplifying and perhaps avoidable (in the future) approximations. These include that we choose to correlate the unprojected $(N-1)$-body and $(N+1)$-body wave functions [Eqs. (6) and (10)]. The second is that we use second-order Rayleigh-Schrödinger perturbation theory (RSPT) to accomplish this. Note that the N-body wave function here has proper Bloch symmetry if we consider 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.[9] The actual choice of A^w is not important, only that such exist. Then,

$$(F+\rho A^w\rho)w_{iI}=\epsilon_{iI}w_{iI} \ . \quad (14)$$

The first-order Fock-Dirac density matrix is ρ. From this one constructs a zero-order Hamiltonian. For a system of M electrons, H_0 is defined as

$$H_0=\sum_{i=1}^{M}[F(\vec{r}_i)+\rho_iA_i^w\rho_i] \ , \quad (15)$$

and then the perturbation, V, becomes

$$V\equiv H-H_0 \ . \quad (16)$$

H is given by Eq. (4). Since our interest is in the N-electron ground state and also the $(N+1)$- and $(N-1)$-electron ions one must proceed with some care. Consider first the N-electron ground state. In this case the Wannier orbitals of the occupied state, span exactly the N-electron Bloch space as well, and Brillouin's theorem remains valid. Therefore, to second-order RSPT one has

$$E(N)=E_N+\sum_{i,I>j,J}^{(N)}\sum_{a,A>b,B}\frac{|V_{iIjJ}^{aAbB}|^2}{\epsilon_{iI}+\epsilon_{jJ}-\epsilon_{aA}-\epsilon_{bB}} \ . \quad (17)$$

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

$$V_{iIjJ}^{aAbB}=\left\langle w_{iI},w_{jJ}\left|\frac{e^2}{r_{12}}\right|w_{aA},w_{bB}\right\rangle -\left\langle w_{iI},w_{jJ}\left|\frac{e^2}{r_{12}}\right|w_{bB},w_{aA}\right\rangle . \tag{18}$$

In this computation, the N-body orbitals are used to describe the $(N-1)$- and $(N+1)$-body states so that Brillouin's theorem is no longer valid for these ion states. In the local representation used here, this is simple to account for. Let us consider first the $(N-1)$-body problem. Assume that Wannier orbital w_{iB} has been deleted from the N-body ground state. Then to second-order RSPT one finds that

$$E(N-1;i,B)=E_N-D_{N-1}^{iBiB}+\sum_{jI}^{(N-1)}\sum_{aA}\frac{|F(N-1;i,B)_{jI}^{aA}|^2}{\epsilon_{jI}-\epsilon_{aA}} +\sum_{k,K>j,J}^{(N-1)}\sum_{aA>bC}\frac{|V_{kK,jJ}^{aAbC}|^2}{\epsilon_{kK}+\epsilon_{jJ}-\epsilon_{aA}-\epsilon_{bC}} . \tag{19}$$

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

$$F(N-1;i,B)_{jI}^{aA}=\langle w_{jI}\,|\,F(N-1;i,B)\,|\,w_{aA}\rangle . \tag{20}$$

One proceeds in like fashion for the $(N+1)$-electron case. Here one adds orbital w_{cB} to the N-electron state and has

$$E(N+1;c,B)=E_N+D_{N+1}^{cBcB}+\sum_{j,J}^{(N+1)}\sum_{a,A}\frac{|F(N+1,cB)_{jJ}^{aA}|^2}{\epsilon_{jJ}-\epsilon_{aA}} +\sum_{j,J>k,K}^{(N+1)}\sum_{a,A>d,D}\frac{|V_{jJkK}^{aAdD}|^2}{\epsilon_{jJ}+\epsilon_{kK}-\epsilon_{aA}-\epsilon_{dD}} . \tag{21}$$

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

It is now possible to obtain the physical-energy differences by taking differences of these energy expressions. The ionization potentials are defined by $E(N)-E(N-1;i,B)$. This difference called here Δ_{iB} is given as

$$\Delta_{iB}=D_{N-1}^{iBiB}-\sum_{j,J}^{(N-1)}\sum_{a,A}\frac{|F(N-1;i,B)_{jJ}^{aA}|^2}{\epsilon_{jJ}-\epsilon_{aA}} +\sum_{j,J\neq i,B}^{(N)}\sum_{a,A>c,C}\frac{|V_{iBjJ}^{aAcC}|^2}{\epsilon_{iB}+\epsilon_{jJ}-\epsilon_{aA}-\epsilon_{cC}} -\sum_{j,J>k,K\neq i,B}\sum_{a,A}\frac{|V_{jJkK}^{iBaA}|^2}{\epsilon_{jJ}+\epsilon_{kK}-\epsilon_{iB}-\epsilon_{aA}} . \tag{22}$$

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

$$\Delta_{CB}=D_{N+1}^{cBcB}+\sum_{jJ}^{(N+1)}\sum_{a,A}\frac{|F(N+1,cB)_{jJ}^{aA}|^2}{\epsilon_{jJ}-\epsilon_{aA}} +\sum_{i,I}^{(N)}\sum_{a,A>d,D\neq c,B}\frac{|V_{iIcB}^{aAdD}|^2}{\epsilon_{iI}+\epsilon cB-\epsilon_{aA}-\epsilon_{dD}} -\sum_{i,I>j,J}^{(N+1)}\sum_{a,A\neq c,B}\frac{|V_{iIjJ}^{cBaA}|^2}{\epsilon_{iI}+\epsilon jJ-\epsilon_{cB}-\epsilon_{aA}} . \tag{23}$$

It is these formulas we will use in this study. The choice of RSPT was made for several reasons. The first is that it is one of several methods which avoids problems of size consistency.[14] The second is that it is computationally tractable. The final reason is it has been seen capable of substantial levels of accuracy for studies of atoms, large or small molecules, and solid systems.[15,16] In the case of the CH_4 molecule simple second-order RSPT is able to predict a correlation energy in excess of about 0.2 hartree which is 80% of experiment.[17] Further examination of this result indicates most of the error is in underestimating the correlation of the C $1s^2$ pair of electrons which are in any event not relevant to the optical transitions considered in this article.

There is one final piece 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, and it is this method used here.[7] The essential point is to use the solid 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 wave vector $\vec{k}$ and let $\alpha_c^\dagger(\vec{k})$ create a conduction electron of wave vector $\vec{k}$. Consider the state then:

$$|N,\vec{k}\rangle=\alpha_c^\dagger(\vec{k})\alpha_v(\vec{k})\,|N\rangle . \tag{24}$$

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

$$|N,E\rangle=\sum_{\vec{k}}a_{\vec{k}}\,|N,\vec{k}\rangle . \tag{25}$$

In this sum, the ground state $|N\rangle$, is excluded because one reaches this final state by optical excitation and one changes parity. If one can determine the $a_{\vec{k}}$ and evaluate $\langle N,E\,|\,H\,|\,N,E\rangle$ 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 exciton states is not an extensive property and size consistency is not a problem as demonstrated by Kunz and Flynn.[7] Exact implementation of such a CI is of course impossible and we use a finite number of states to do so, in this case 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 a.u.) encloses a substantial volume in a unit cell. Kunz and Flynn tested this for LiF and found this a very good approximation. 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 $a_{\vec{k}}$ 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. For further details on how such a computation is performed the interested reader is referred to Ref. 7.

It is instructive to compare the current method with the earlier methods employed by the author based upon separate relaxation and correlation inclusions.[13,18] In those methods the relaxation term was imposed, whereas here it occurs naturally as the second term on the right-hand side of Eqs. (22) and (23). This term arises because the $(N+1)$- and $(N-1)$-body wave functions are not self-consistent due to the use of the N-body Wannier functions and Brillouin's theorem is not obeyed. Thus these terms are nonzero by lack of self-consistency and are properly termed relaxation corrections. The remaining third and fourth terms on the right-hand side of Eqs. (22) and (23) are correlation terms. These are computed in a way which differs radically from the earlier electronic polaron methods.[11,12,13,18] Here the matrix elements are actually computed, not estimated, from polarizabilities and sum rules as before and also we retain the third term of Eq. (22) and the fourth term of Eq. (23) which were ignored in the electron polaron model.

TABLE I. The Gaussian basis set used in the band-structure calculation is given. The basis is of the form $\chi_i(\vec{r}-\vec{R}_i)=\exp[-Z_i(\vec{r}-\vec{R}_i)^2]y_l^m(\theta,\phi)$.

i	Z_i	R_i	l	m
1	1050.0	C	0	0
2	167.9	C	0	0
3	40.75	C	0	0
4	11.76	C	0	0
5	3.65	C	0	0
6	0.566	C	0	0
7	0.154	C	0	0
8	0.110	C	0	0
9,14,19	9.689	C	1	0,±1
10,15,20	2.053	C	1	0,±1
11,16,21	0.558	C	1	0,±1
12,17,22	0.154	C	1	0,±1
13,18,23	0.095	C	1	0,±1
24,26,28,23	1.95	H	0	0
25,27,29,31	0.34	H	0	0

III. RESULTS OF THE CALCULATION

A Gaussian basis set was developed for the CH_4 molecule in free space and then reoptimized in the crystal to allow accurate description of the Hartree-Fock energy bands, both occupied and virtual. In doing this it was found that it was quite easy to obtain accurate valence bands, but that the conduction bands were quite sensitive to the choice of outer orbital. Since the variational principal applies to the solution of the one particle energies in a LCMO formalism, the selection of the preferred basis is quite easy. In practice, the conduction bands are found to be stable against small changes in basis set. The Gaussian basis set employed is shown in Table I. The valence structure here agrees well with that obtained after corrections to formalism by Piela *et al.*[4,19,20] 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.*[4] calculation of the virtual bands. One may be confident of this assessment, since Piela *et al.* acknowledge that such might be the case and since the current results are variationally preferable. In performing this calculation, some idealizations are needed. A lattice constant of 11.14 a.u., in agreement with Piela *et al.*, is used and the C sublattice 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 align from one cell to another but have orientational disorder. The author, as does Piela *et al.* fixes 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[21] and for a lattice constant of 11.14 a.u., the equilibrium constant is essentially the same C-H distance as in the free molecule. To assess the sensitivity of the bands to hydrostatic pressure, the calculation is repeated for lattice constants of 10.5 and 10.0 a.u. The C-H distances predicted by Beck are used here and are only trivially smaller than the free-molecule C-H distance. The most interesting Hartree-Fock band features are along the line $\Gamma - X$ in the first Brillouin zone and are seen for all three lattice parameters in Fig. 1.

The Hartree-Fock band-structure results overestimate any reasonable band gap; they do reduce the Piela gap by about 13.6 eV, however,[4] and one need add correlation along the lines suggested in Sec. 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 complicat-

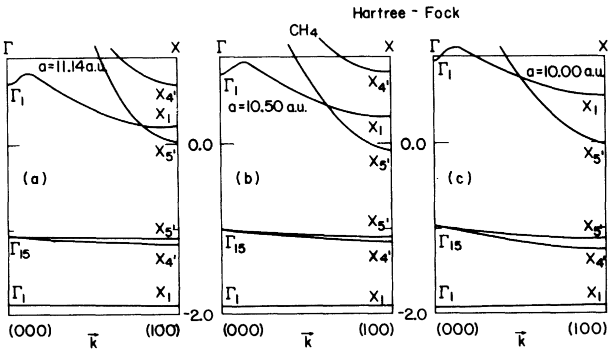

FIG. 1. Hartree-Fock band structure for solid CH_4 is shown for the direction $\Gamma - X$ in the first Brillouin zone for (a) $a=11.14$ a.u., (b) $a=10.50$ a.u., and (c) $a=10.00$ a.u.

TABLE II. 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.

	$a=11.14$ a.u.	$a=10.50$ a.u.	$a=10.00$ a.u.
Valence correlation (eV)	0.1	0.2	0.4
Valence relaxation (eV)	1.2	1.2	1.2
Conduction correlation (eV)	−0.7	−0.8	−0.9
Conduction relaxation (eV)	∼0.0	∼0.0	∼0.0
Net gap change (eV)	−2.0	−2.2	−2.5

ed, orthogonal Wannier functions as implied by the derivations, one approximates these by a set of local orbitals. The local orbitals obtained for the occupied states have a maximum overlap of 0.03 compared to unity. One may simply recover Wannier orbitals from these local orbitals by symmetric orthogonalization. In practice this is a cumbersome and difficult process. Nonetheless, for systems of small overlap the exact inverse of the overlap matrix may be obtained expanding this inverse in a power series in terms of elements of the overlap matrix. This is done in the present case and correction terms to first order are retained. The neglected quadratic term is of the order of 10^{-3}. The effect of this neglect is estimated on the basis of some large-cluster calculations to be less than 0.1 eV for the net change in correlation energy in the case of solid CH_4. The unit on which localization occurs is the CH_4 molecule, with the appropriate multicenter localization.[18] These orbitals are truly local, the valence-valence overlaps being 0.03 or less here. Of course due to the procedure adopted, *all* orders of overlap in the large intramolecular overlaps are included exactly due to the use of molecular orbitals for a basis set. 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 basis set shown in Table I, which was used for the energy bands. The effect of the several contributions to Eqs. (22) and (23) are given in Table II. In this we call the second term on the right-hand side of Eqs. (22) and (23) the relaxation and the sum of the second and third term come from two-electron virtual excitations, and clearly represent correlation terms. The second term stems from single-electron virtual excitation and is nonzero because *N*-body Wannier functions are not exact eigenstates of the $(N-1)$- or $(N+1)$-body Fock operator.

The energy bands for CH_4 including correlation are shown in Figs. 2, 3, and 4, for lattice constants 11.14, 10.50, and 10.00 a.u., respectively. 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'_{5c}. The direct gap is at the X point and is X'_{5v} to X'_{5c}. The gaps with and without correlation are given in Table III as a function of lattice parameter. It is clear that the band gap is a very sensitive function of lattice constant or pressure.

Finally, one computes the position of the exciton levels in CH_4. This is accomplished using the method given in Sec. II and more fully described in Ref. 7. In performing the calculation the Coulomb interactive is treated as a screened 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 Ref. 5. Using this value, the exciton is found to be at 10.9 eV. The optical spectrum of Koch and Skibowski[22] does find a spectral peak at 11.0 eV and this may well be our exciton. A more quantitative analysis is not possible for us at this time because the highest valence and lower conduction bands are of like symmetry and the techniques developed in Ref. 5 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. Therefore, the author reluctantly contents himself with using only the $\vec{k}$-conserved

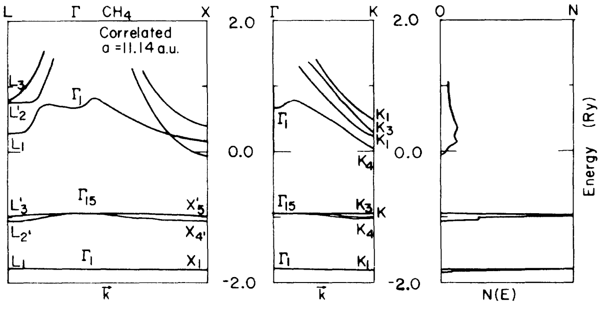

FIG. 2. Correlated band structure of solid CH_4 and density of states is shown for a lattice parameter of 11.14 a.u.

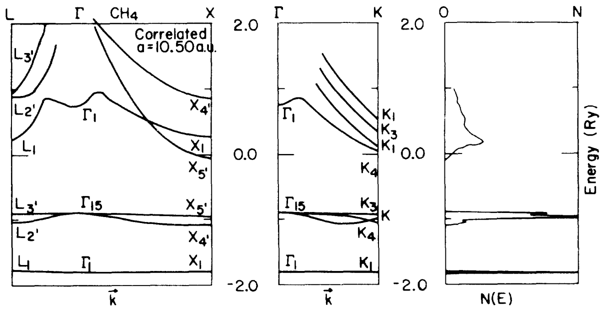

FIG. 3. Correlated band structure and density of states for solid CH_4 is given. The lattice parameter is 10.50 a.u.

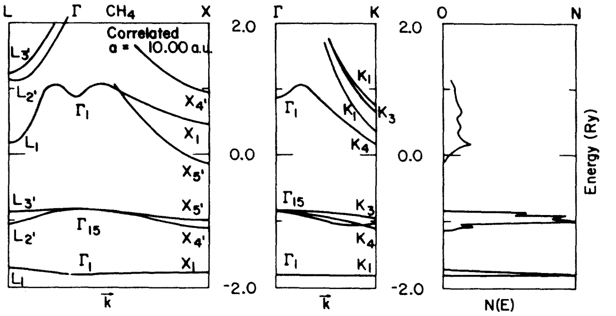

FIG. 4. Correlated band structure and density of states of solid CH_4 for a lattice parameter of 10.00 a.u. are given.

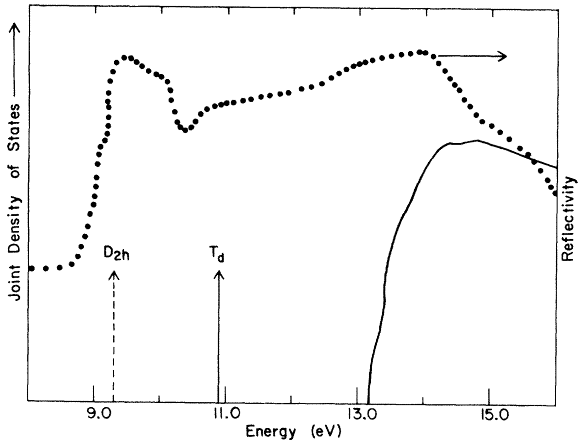

FIG. 5. Optical joint density of states is shown for solid CH_4 along with the T_d geometry exciton position and probable D_{2h} geometry exciton. The optical reflectivity of Ref. 22 is also shown.

joint density of states in comparison with the measured reflectance spectrum shown in Fig. 5.[22] 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. Owing 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.[17] If one assumes that 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 Fig. 5. 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.[7] It is hoped to enhance the available techniques to include computation of dipole-forbidden spectral regions in the future.

As stated earlier in this article, the basis set for the individual CH_4 unit was chosen for its ability to represent solid-state effects. Thus the CH_4 basis need not be useful for isolated molecular studies. The chief differences lie in the fact that solid-state effects such as bandwidths are largely determined by the long-range part of the wave function, whereas for the isolated molecule, total-energy accuracy is a property of the wave function near the nuclei. Therefore, the present basis set places far heavier emphasis on the diffuse basis-set members than would be the case in an equivalent-size basis set for an isolated molecular study. These is a second constraint imposed on the basis set by the nature of a solid. In a free atom or molecule, the wave function of bound states far from the nucleus must decay exponentially with distance. In the case of a solid with periodic boundary conditions this is no longer so. Therefore, the basis set on a molecule in such a solid need only span the physical space to the midpoint of a nearest-neighbor distance, since past this point the basis set on the neighbor takes over. Thus the diffuse part of a solid basis set need often be less diffuse than the basis set for an isolated atom or molecule and have greater variational freedom in the diffuse region.

The present basis set was chosen by solid-state criteria and need not provide an excellent description of the isolated CH_4 molecule. Calculations on the ground states of CH_4 were performed using the basis set shown in Table I. These results are compared there with the results of various available molecular CH_4 studies.[23] As is seen from Table IV, the results with the solid-state basis set for total energy are in fair agreement with the best available molecular studies, and in quite good agreement with respect to the one-electron energy parameters. This latter point is

TABLE III. The Hartree-Fock and correlated direct and indirect band gaps for solid CH_4 are given as a function of lattice constant.

	$a = 11.14$ a.u.	$a = 10.50$ a.u.	$a = 10.00$ a.u.
H-F direct gap (eV)	15.3	14.3	14.9
H-F indirect gap (eV)	15.0	13.0	13.1
Correlated direct gap (eV)	13.3	12.1	12.4
Correlated indirect gap (eV)	13.0	10.8	10.6

TABLE IV. The total energy of the isolated CH_4 molecule and the one-electron energy parameters are shown. The present study is obtained using the basis set of Table I, and the unrestricted Hartree-Fock (atomic structure) codes written by the author. The comparative other results are cited in Ref. 23. The term OCE refers to a one-center expansion calculation, LGTO to a calculation employing Gaussian lobe basis functions, and GTO to a Gaussian spherical harmonic type basis set. All energies are in hartree (1 hartree ≈ 27.2 eV).

Calculation	Basis set	E_T	ϵ_{1a_1}	ϵ_{2a_1}	ϵ_{1f_2}
Present	GTO	-40.13	-11.21	-0.94	-0.54
Moccia	OCE	-39.87			
Deutsch and Kunz	LGTO	-40.15	-11.21	-0.93	-0.53
Deutsch and Kunz	OCE	-39.52	-11.10	-0.88	-0.44
Bagus *et al.*	GTO	-40.21	-11.20	-0.94	-0.55
Meyer	GTO	-40.21			
Krauss	GTO	-40.17			

most essential, in that the energy bands are largely a property of these one-electron energies.

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 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, orbital 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 mass of H one need also be prepared to include Jahn-Teller distortion if one is to be fully quantitative. Finally, one sees that the band structure of such a weakly bonded molecular system is a sensitive function of lattice parameter.

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