Electron Band Structure of Solid Methane: *Ab Initio* Calculations*

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The band structure of crystalline methane has been calculated in a linear-combination-of-molecular-orbitals approximation. In this molecular tight-binding method the Bloch sums are built up of Hartree–Fock orbitals of the free molecules. Interactions between the states of different molecules are calculated directly from molecular integrals without reducing the exchange interaction to an exchange potential. The approximations involved are shown to be well justified for a crystal made of closed-shell units. The band structure is obtained by solving secular equation in 400 points along the relevant symmetry lines. The calculated bands are relatively narrow, less than 2.5 eV wide, around the molecular levels. The band-to-band gap in solid methane is 24.5 eV. This value has the same order of magnitude as in solid rare gases.

I. INTRODUCTION

Molecular crystals are periodic structures built up by stable and tightly bound units, linked together by forces of much weaker character. Their one-electron electronic states, as solutions of the Hartree–Fock (HF) problem in a periodic lattice, can be described in terms of a band structure. Owing to the dominant presence of exciton effects, the spectroscopic data near the absorption edge are not directly interpretable as transitions from valence to conduction bands, as in the standard theory of optical properties of metals and semiconductors.[1] The usual approach for molecular crystals is that of Frenkel excitons in the Davydov-type model where the band structure is approximated with the corresponding molecular levels.[2] Because of the weakness of the interaction between the individual molecules in a molecular crystal, in fact the energy bands are expected to be relatively narrow, centered on the HF energies of the isolated molecules.

In the past few years a lot of experimental work has been done on molecular solids, especially in view of their biological interest. The calculations of band structures and HF electronic states are basic toward a better understanding of a number of physical properties and specifically the optical ones. In fact molecular crystals are in some respect similar to rare-gas solids and alkali halides—they all are built up of closed-shell units—for which the band-structure approach has proved to be a powerful tool for the interpretation of the optical spectra.[3-6] Moreover, the valence-band structure describes the HF fundamental state of the crystal and can be closely related to experimental data. Very recently, for instance, much direct information on the valence-band structure has been obtained by electron-spectroscopy-for-chemical-analysis (ESCA)[7] and x-ray-photoemission-spectro-scopy (XPS)[8] experiments in solids.

Practical band-structure calculations in molecular solids by the usual methods[9] are not expected to give reliable results; the main difficulties that arise can in fact be restated as follows, as has been pointed out recently by Coulson[10]: (a) The interaction between atoms in the same molecule must be treated differently from the interaction between molecules. Self-consistency is required at least in the domain of each molecule. (b) The directional forces that determine the crystal structure, as long as we do not consider nuclear-spin interaction, are dominated by repulsive exchange forces between atoms that are nearest neighbors in adjacent molecules, and the usual local-exchange approximations are unsuitable.

Some aspects of the possible advantages of a molecular tight-binding approach with respect to usual methods of calculation were briefly considered by Bassani,[11] extending the early work of Gubanov and Nran' Yan and of Coulson *et al.*[12] Very recently Pastori-Parravicini and Resca[13] and Bassani *et al.*[14] calculated the valence-band structures of cubic ice and solid hydrogen fluoride by a molecular tight-binding method. This method was developed in close analogy to the usual tight-binding "atomic" type method in solids,[9] and the Bloch sums of atomic orbitals were in this case substituted by Bloch sums built up of molecular orbitals. These molecular orbitals are solutions of the HF problem in the isolated molecule, possibly obtained by a self-consistent-field (SCF) calculation, and thus condition (a) above is fulfilled. This approximation of crystal wave functions as linear combinations of molecular orbitals (LCMO) is justified by the weakness of the interaction between different molecules in the solid. We wish to point out that for these same reasons atomic tight-binding calculations have in the past given good results in rare-gas solids[3] and alkali halides,[15-17] at

least for the valence-band structure.

We show in this paper, following the early work of Löwdin[15] and Howland[16] on ionic crystals, that the HF Hamiltonian of a crystal made up of closed-shell molecules can be well approximated in terms of the HF Hamiltonians of the isolated units, providing the exchange operator is used in its original nonlocal form. The molecular tight-binding method, as developed throughout this work, presents in comparison with the usual "atomic" one some computational complications, due essentially to the lack of spherical symmetry of the molecular orbitals and potentials and to the fact that two-center integrals in the molecular sense can involve computationally a large number of four-center integrals of an atomic type. The availability of high-speed computers, together with the advancement of molecular programs, makes possible nowadays the evaluation of such a large number of intergrals.

We present in this paper the theory of the molecular tight-binding method, in the sense sketched above, and a system of programs we have developed at C.E.C.A.M. to perform this type of molecular tight-binding calculation. A detailed band-structure calculation is presented for the case of solid methane in phase I. All the monoelectronic and bielectronic integrals needed for the calculation, actually several thousands, were generated by a molecular program, originally written by Stevens for SCF calculations.[18]

In Sec. II we develop the theory of the molecular tight-binding method and in Sec. III we analyze the structure of the matrix elements involved. Section IV is devoted to a discussion of the crystallographic structure of solid methane. In Sec. V we present our band-structure calculation for solid methane as given in phase I. In Sec. VI we discuss the results.

II. MOLECULAR TIGHT-BINDING METHOD

We extend the tight-binding method as described by Howland[16] to the case of molecular crystals explicitly including nonlocal exchange. For simplicity in notation, we consider only the case of one molecule per unit cell, as in the structure we assume for solid methane; the general case is not substantially different. The equations for the one-electron functions and energies in the LCMO approximation are obtained as follows. Let the crystal contain N unit cells and $2M$ electrons; because of translational symmetry we can write the HF LCMO wave function for the ith band and wave vector $\vec{k}$ as

$$\psi_i(\vec{k}, \vec{r}) = \sum_m c_{im}(\vec{k}) \, b_m(\vec{k}, \vec{r}), \qquad (1)$$

where $b_m(\vec{k}, \vec{r})$ is the following Bloch sum:

$$b_m(\vec{k}, \vec{r}) = \frac{1}{N^{1/2}} \sum_g e^{i\vec{k}\cdot\vec{R}_g} u_m(\vec{r} - \vec{R}_g), \qquad (2)$$

and $u_m(\vec{r} - \vec{R}_g)$ is the HF molecular orbital of quantum number m centered on the molecule at lattice site $\vec{R}_g$. The electronic Hamiltonian for the $2M$-electron crystal is

$$\mathcal{H} = \sum_j F_j + \sum_{\substack{j,j' \\ j \neq j'}} G_{jj'}, \qquad (3)$$

where F_j is the one-electron operator for electron j (kinetic energy and Coulomb interaction with nuclei), and $G_{jj'}$ is the two-electron operator for electrons j, j' (Coulomb repulsion). HF solutions in the crystal satisfy the following set of equations:

$$F_1 \psi_i(\vec{k}, \vec{r}) + 2 \int G_{12} \, \psi_i(\vec{k}, \vec{r}_1) \rho(\vec{r}_2, \vec{r}_2) \, dv_2$$

$$- \int G_{12} \psi_i(\vec{k}, \vec{r}_2) \rho(\vec{r}_2, \vec{r}_1) \, dv_2$$

$$= E_i(\vec{k}) \psi_i(\vec{k}, \vec{r}_1), \qquad (4)$$

where $E_i(\vec{k})$ is the band-structure energy and $\rho(\vec{r}_2, \vec{r}_1)$ is given by

$$\rho(\vec{r}_2, \vec{r}_1) = \sum_{i'\vec{k}'} \psi_{i'}^*(\vec{k}', \vec{r}_2) \psi_{i'}(\vec{k}', \vec{r}_1). \qquad (5)$$

According to a general result of Löwdin,[15,16] $\rho(\vec{r}_2, \vec{r}_1)$ in our case can be written in a way which does not involve the coefficients $c_{im}(\vec{k})$ of (1). In fact if we indicate the $M \times M$ matrix of all the molecular overlap integrals as

$$\Delta(m\vec{R}_g, n\vec{R}_{g'}) = \int u_m^*(\vec{r} - \vec{R}_g) u_n(\vec{r} - \vec{R}_{g'}) \, dv, \qquad (6)$$

Löwdin's theorem yields

$$\rho(\vec{r}_2, \vec{r}_1) = \sum_{m,n} \sum_{g,g'} \Delta^{-1}(m\vec{R}_g, n\vec{R}_{g'})$$

$$\times u_m^*(\vec{r}_2 - \vec{R}_g) u_n(\vec{r}_1 - \vec{R}_{g'}). \qquad (7)$$

This result is valid under the following hypothesis: (i) The Bloch functions $\psi_i(\vec{k}, \vec{r})$ are mutually orthonormal. (ii) The functions u are linearly independent. (iii) The number of occupied Bloch functions ψ is the same as the number of starting functions u. The third condition limits the application of the theorem to valence-band structures built up from closed-shell units; it has been used in the literature for ionic crystals,[15,16] but it is applicable also for solid rare gases, and for the present molecular tight-binding approach in solid methane.

Substitution in (4) yields

$$F_1 \psi_i(\vec{k}, \vec{r}) + \sum_{m,n,g,g'} \Delta^{-1}(m\vec{R}_g, n\vec{R}_{g'})$$

$$\times \left(2 \int G_{12} \psi_i(\vec{k}, \vec{r}_1) u_n^*(\vec{r}_2 - \vec{R}_{g'}) u_m(\vec{r}_2 - \vec{R}_g) \, dv_2 \right.$$

$$-\int G_{12}\,\psi_i(\vec{k},\,\vec{r}_2)u_n^*(\vec{r}_2-\vec{R}_{g'})u_m(\vec{r}_1-\vec{R}_g)dv_2\bigg)$$

$$=E_i(\vec{k})\,\psi_i(\vec{k},\,\vec{r}_1). \qquad (8)$$

Owing to the smallness of the overlap between orbitals centered on different molecules, the matrix $\hat{\Delta}$ is very close to the unit matrix

$$\Delta\,(m\vec{R}_g,\,n\vec{R}_{g'}) \approx \delta_{mn}\,\delta_{gg'}, \qquad (9)$$

and its inversion can be done by a power-series expansion.

In the zeroth-order approximation the molecular tight-binding approach is not self-consistent over the crystal, and the crystal potential is written as the sum of molecular potentials centered on lattice sites. In this case we rewrite the one-electron Hamiltonian of the left-hand side of (8) as

$$H=\frac{p^2}{2m}+\sum_g\,[\,V_N(\vec{r}-\vec{R}_g)+2J\,(\vec{r}-\vec{R}_g)-K(\vec{r}-\vec{R}_g)]. \qquad (10)$$

Here V_N, J, and K are, respectively, the nuclear, Coulombic, and exchange HF SCF potentials for the single molecule; while V_N and J are local potentials, K is a nonlocal operator. In terms of their definition,

$$J(\vec{r}_1)=\int G_{12}\sum_m\,|u_m(\vec{r}_2)|^2 dv_2, \qquad (11)$$

$$K[\,\varphi\,]\,(\vec{r}_1)=\int G_{12}\,\varphi(\vec{r}_2)\sum_m u_m(\vec{r}_1)u_m^*(\vec{r}_2)dv_2, \qquad (12)$$

and the sum is done over all the occupied molecular orbitals u_m.

Now the eigenvalue problem

$$H\psi_i\,(\vec{k},\,\vec{r})=E_i(\vec{k})\,\psi_i(\vec{k},\,\vec{r}) \qquad (13)$$

over the LCMO basis is easily reduced to a secular equation,

$$|\langle m\vec{k}|H-E(\vec{k})|n\vec{k}\rangle|=0, \qquad (14)$$

where $|n\vec{k}\rangle$ indicates the general Bloch sum. If we symbolize with $|m\vec{R}_g\rangle$ the molecular orbitals, we can write using translational symmetry

$$\langle m\vec{k}|n\vec{k}\rangle=\sum_g e^{i\vec{k}\cdot\vec{R}_g}\,\Delta(m0,\,n\vec{R}_g), \qquad (15)$$

$$\langle m\vec{k}|H|n\vec{k}\rangle=\sum_g e^{i\vec{k}\cdot\vec{R}_g}\,\langle m0|H|n\vec{R}_g\rangle. \qquad (16)$$

Now using the fact that we have started from the molecular orbitals which are solutions of the HF equations in the isolated molecule, we can use the equation

$$[\,p^2/2m+V_N(\vec{r})+2J(\vec{r})-K(\vec{r})]\,|m0\rangle=\epsilon_m|m0\rangle, \qquad (17)$$

where ϵ_m represents the eigenvalue of the molecular state. We also obtain

$$\langle m\vec{k}|H|n\vec{k}\rangle=\sum_g e^{i\vec{k}\cdot\vec{R}_g}\,\bigg\{\epsilon_m\,\Delta(m0,\,n\vec{R}_g)$$

$$+\sum_{g'\neq0}\,\langle m0|\,[\,V_N(\vec{r}-\vec{R}_{g'})+2J(\vec{r}-\vec{R}_{g'})$$

$$-K(\vec{r}-\vec{R}_{g'})]\,|n\vec{R}_g\rangle\bigg\}. \qquad (18)$$

The second term in curly brackets contains two- and three-center integrals, in the molecular sense; in the following sections of this paper we neglect the three-center ones. Although this can be inadequate in a generical tight-binding calculation, [19] in molecular crystals the approximation is particularly good, because of the smallness of the overlap integrals between different molecules. With straightforward manipulation we arrive at the final form

$$\langle m\vec{k}|H|n\vec{k}\rangle=\epsilon_n\,\delta_{mn}$$

$$+\sum_{g\neq0} e^{i\vec{k}\cdot\vec{R}_g}\,\langle m0|\epsilon_m+\epsilon_n-p^2/2m|n\vec{R}_g\rangle$$

$$+\sum_{g\neq0}\,\langle m0|\,V_N(\vec{r}-\vec{R}_g)+2J(\vec{r}-\vec{R}_g)$$

$$-K(\vec{r}-\vec{R}_g)|n0\rangle. \qquad (19)$$

The three terms in the right-hand member can be recognized, respectively, as (i) the isolated-molecule Hamiltonian (diagonal on this basis), (ii) the interaction matrix, and (iii) the crystal-field matrix. The structure of the matrix elements will be investigated in Sec. III; it is useful to note here, that the interaction-matrix elements are built up only from monoelectronic integrals, while the Coulombic and exchange parts in the crystal-field matrix are built up from bielectronic integrals. We note explicitly that in the calculation there is no need for a local-exchange approximation, when we are able to compute the monoelectronic and bielectronic integrals involved.

The approximations made are then as follows: (i) choice of a finite LCMO basis over which we expand the crystal wave functions; (ii) neglect of three-center contributions in a molecular sense (i.e., of matrix elements involving three different molecules); (iii) self-consistency only over the range of the molecules, and not over the whole crystal. Self-consistency corrections for the whole crystal can be evaluated by the Löwdin method. If we write the molecular overlap matrix $\hat{\Delta}$ as

$$\hat{\Delta}=\hat{1}+\hat{S}, \qquad (20)$$

the Löwdin correction can be shown to be of the order of $\hat{S}^2$. Also the three-center corrections are of the order of $\hat{S}^2$, so we can say that approximations (ii) and (iii) arise from an expansion of the molecular overlap matrix up to the first order.

How good it is numerically clearly depends upon the specifical crystal. For solid methane the molecular overlap matrix is tabulated in Table II. The largest matrix elements of $\hat{S}$ are actually about 10^{-2}, and this shows the validity of the two-center approximation.

III. COMPUTATION OF MATRIX ELEMENTS

The molecular orbitals of formula (2) are in general well approximated as linear combinations of atomic orbitals (LCAO), and the coefficients of these combinations are the result of SCF calculations on the isolated molecule. So we can write

$$u_m(\vec{r}) = \sum_j a_{jm} \varphi_j(\vec{r} - \vec{d}_j), \tag{21}$$

where $\vec{d}_j$ is the position of the atom inside the molecule and φ_j is the suitable atomic-type orbital. The "atomic" index j describes the quantum number as well as the center. We actually use Slater-type orbitals (STO's) for the atomic functions φ_j and we obtain the coefficients a_{jm} by the Stevens program,[18] which also yields the orbital energies ϵ_m of the isolated molecule. For the secular equation [Eq. (14)] we need five different kinds of matrix elements between molecular orbitals, as can be easily seen from Eqs. (15) and (19).

In details, the matrix elements needed are as follows:

(i) Overlap:

$$\Delta(m0, n\vec{R}_g) = \langle m0 | n\vec{R}_g \rangle$$

$$= \sum_{i,j} a_{im} a_{jn} \int \varphi_i(\vec{r} - \vec{d}_i) \, \varphi_j(\vec{r} - \vec{d}_j - \vec{R}_g) \, dv. \tag{22}$$

(ii) Kinetic:

$$\langle m0 | \frac{p^2}{2m} | n\vec{R}_g \rangle = \sum_{i,j} a_{im} a_{jn}$$

$$\times \int \varphi_i(\vec{r} - \vec{d}_i) \frac{p^2}{2m} \varphi_j(\vec{r} - \vec{d}_j - \vec{R}_g) \, dv. \tag{23}$$

(iii) Nuclear: We indicate with $z(\vec{d}_k)$ the nuclear charge present at the atomic site $\vec{d}_k$,

$$\langle m0 | V_N(\vec{r} - \vec{R}_g) | n0 \rangle = \sum_{ij} a_{im} a_{in}$$

$$\times \int \varphi_i(\vec{r} - \vec{d}_i) \, \varphi_j(\vec{r} - \vec{d}_j) \sum_{\vec{d}_k} \frac{-e^2 z(\vec{d}_k)}{|\vec{r} - \vec{d}_k - \vec{R}_g|} \, dv, \tag{24}$$

and the inner sum is obviously over the atomic sites of a molecule.

(iv) Coulombic:

$$\langle m0 | J(\vec{r} - \vec{R}_g) | n0 \rangle = \sum_{i,j} a_{im} a_{jn}$$

$$\times \int \varphi_i(\vec{r}_1 - \vec{d}_i) \, \varphi_j(\vec{r}_1 - \vec{d}_j) J(\vec{r}_1 - \vec{R}_g) dv_1. \tag{25}$$

Substituting for the expression given by (11), and using (21), we obtain

$$\langle m0 | J(\vec{r} - \vec{R}_g) | n0 \rangle = \sum_{h,k,i,j} a_{im} a_{jn} \sum_s a_{hs} a_{ks}$$

$$\times \int \frac{e^2}{r_{12}} \varphi_i(\vec{r}_1 - \vec{d}_i) \, \varphi_j(\vec{r}_1 - \vec{d}_j) \, \varphi_h(\vec{r}_2 - \vec{d}_h - \vec{R}_g) \, \varphi_k(\vec{r}_2 - \vec{d}_k - \vec{R}_g) dv_1 dv_2. \tag{26}$$

We note that h, k, i, j run over the atomic orbitals, but s runs over the molecular occupied orbitals.

(v) Exchange: They can be expressed as the matrix elements of the nonlocal-exchange operator, using (12) and (21). We obtain

$$\langle m0 | K(\vec{r} - \vec{R}_g) | n0 \rangle = \sum_{h,k,i,j} a_{im} a_{jn} \sum_s a_{hs} a_{ks}$$

$$\times \int \frac{e^2}{r_{12}} \varphi_i(\vec{r}_1 - \vec{d}_i) \, \varphi_h(\vec{r}_1 - \vec{d}_h - \vec{R}_g) \, \varphi_j(\vec{r}_2 - \vec{d}_j) \, \varphi_k(\vec{r}_2 - \vec{d}_k - \vec{R}_g) dv_1 dv_2. \tag{27}$$

So we can see that the two-center matrix elements between molecular orbitals involve in the general case [and only for types (iv) and (v)] four-center integrals between atomic orbitals. In any case the matrix elements are constructed from the monoelectronic and bielectronic integrals between atomic orbitals familiar in molecular problems, but involving always a pair of molecules. The number of different geometries needed, (i.e., the number of nonequivalent $\vec{R}_g$ involved) depends obviously on the symmetry present in the specific problem and on the number of neighbors relevant in the interaction. In solid methane we need only a geometry for each order of neighbors. For the computation of the described integrals we make a run of the Stevens program for the system of two molecules. This time, however, we are not interested in a SCF calculation, and we only generate on a magnetic tape unit all the monoelectronic and bielectronic integrals of the system. Another program rearranges these integrals and computes the sums needed for the five types of matrix elements.
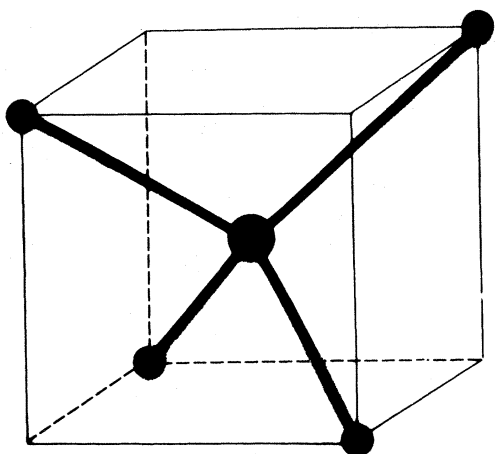
FIG. 1. Orientation of the methane molecules with respect to the crystallographic axes, as assumed throughout this work.

Although the numerical values of the integrals, as given by the Stevens program, can be very accurate (one part in 10^6), we had to overcome some numerical difficulties: In fact the nuclear potential and the electronic Coulombic-matrix-elements one are not small, but they combine to give a small potential (multipolar at large distances). So cancellation of significant figures may be of importance. This is specifically the case for solid methane: In fact the potential is only octupolar and in our geometry the centers of the surrounding molecules are in the direction of the zero octupolar field. Consequently, for some purposes it can be better to substitute the matrix elements of $V_N + 2J$ with the ones of a suitable multipole potential, in order to reduce cancellation by a direct calculation.

Our program also does a Mulliken analysis of a single molecule and so evaluates the matrix elements of $V_N + 2J$ directly by the Mulliken charge model for a multipolar potential.[20] Whether the matrix elements computed by the Mulliken model or those obtained by the standard method are more appropriate will depend on the particular crystal. For the reason explained before, in solid methane the use of Mulliken analysis is compulsory, while if the potential is only dipolar or the geometry is not very symmetrical the results by the normal way are more reliable. This was checked with test runs on solid hydrogen fluoride and cubic ice.[13,14]

IV. SOLID-METHANE CRYSTAL STRUCTURE

The ordinary methane CH_4 crystallizes at 89 °K in the fcc system.[21] While the lattice position of C atoms has been detected early to a very good accuracy, the position of hydrogen cannot be detected with great accuracy, even with neutron-diffraction

techniques. In addition, directional forces between the different molecules in the crystal are very weak, and rotations of molecules around their centers are possible with an extremely small energy difference. Much work has recently been developed on solid methane and its deuterated forms $CH_{4-m}D_m$. Phase transitions due to different orientations of molecules appear in the crystal, and their behavior strongly depends on the nuclear spins involved. The orientations most probable in each phase have been investigated theoretically on the basis of a James–Keenan model[22] and in other ways.[23] The electronic spectrum of a solid film of methane in the far ultraviolet up to 11 eV has been measured by Lombos et al.[24] It does not appear very different from the spectrum of the gaseous phase. except for a large bathocromic shift (about 4200 cm^{-1}). Very accurate results of neutron crystallography on CD_4 have been published by Press.[25] From these it appears that the higher-temperature phase (the one best known) is characterized by nearly free rotations of the single molecules around their centers. Strictly speaking, solid methane in phase I is not a "true" crystal, because only the carbon atoms have a periodic array. Of course we must fix the position of the nuclei, in order to preserve the transational symmetry. In particular, we fix the molecules in the position of maximum symmetry, giving to the whole crystal the T_d symmetry, the same as the isolated molecule. With this choice the orientation of each molecule with respect to the crystallographic axes of the fcc lattice is shown in Fig. 1. Other choices could be useful for solid methane in Phase I only in view of more accurate Born–Oppenheimer-type calculations.[9]

In this paper we present only the calculation for the T_d symmetry orientation, which is the more similar to the reality for solid methane in phase I. The lattice parameter as used throughout the present calculation is 5.90 Å (one molecule per cell).[21,25] The Brillouin zone is given in Fig. 2 with the usual symbols for the symmetry points. As noted before, symmetry is the same for the whole crystal and for the isolated molecule; so no splitting of the molecular levels is expected at the Γ point of the Brillouin zone. In the fundamental state of the isolated molecule the ten valence electrons completely fill the two totally symmetric states Γ_1 of degeneracy 1 and a state Γ_{15} of degeneracy 3 (a_1 and t_2, respectively, in molecular notations). Symmetry analysis and compatibility relations between the states at Γ and other points of the Brillouin zone are the same in the zinc-blende structure and are reported in the review article by Koster.[26]

V. CALCULATION OF ELECTRONIC STATES

We use for the molecular wave function the minimal basis set in STO's with the optimized exponents

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TABLE I. Results of SCF calculation on the methane molecule. Energies are in atomic units, C-H length is 2.0665 a.u. Exponents given by Pitzer, Ref. 21.

	Occupied			Virtual		STO
	$1a_1$	$2a_1$	$1t_{2x}$	$3a_1$	$2t_{2x}$	exponents
			Molecular-orbital coefficients			
H $1s$	−0.004600	0.186801	0.318616	0.632214	−0.607253	1.17
C $1s$	0.994732	−0.215501	0	0.241923	0	5.68
C $2s$	0.025330	0.606010	0	−1.594926	0	1.76
C $2p_x$	0	0	0.552731	0	1.098865	1.76
			Orbital energies (a.u.)			
	−11.205974	−0.920892	−0.535156	0.652771	0.656772	

Total energy is −40.128128 a.u.

given by Pitzer,[27] and we assume for the C-H distance the value 2.0665 a.u. Results of the SCF calculation obtained with the Stevens program, including virtual levels, are given in Table I. In the methane molecule the minimal basis set is a particularly good one, because of the high symmetry. In fact, the computed total energy turns out to be actually about 99.7% of the HF limit.

All matrix elements needed for the calculation of the band structure were evaluated as described in Sec. III. We report in Table II the overlap matrix elements between molecular orbitals for first and second neighbors. This shows the goodness of the tight-binding approximation in this case and shows why it is not necessary to go beyond the second-neighbor interaction. Since the largest element of the overlap matrix for the second neighbor is less than 6×10^{-4}, they always give a small contribution and further neighbors can be neglected. Calculations were performed on the IBM 370/165 instal-

lation available at C.E.C.A.M. in Orsay. Evaluation of all the integrals by the Stevens program took about 21 min for each geometry. All the other calculations needed for the present work were much faster. The secular equation of the molecular tight-binding method was solved in 400 points of the Brillouin zone on the relevant symmetry directions. The resulting valence-band structure is reported in Fig. 3. The scale is absolute and it refers to the vacuum. All bands are, as expected, very narrow around the corresponding molecular level. The core band Γ_1 originating from the $1s$ state of carbon is not reported here, since it coincides with the molecular level and its width is less than 10^{-3} a.u. The two highest valence bands stick together for symmetry reasons on the Λ and Δ line, but they have a small splitting in other symmetry directions. The total width of the highest valence bands corresponding to the Γ_{15} molecular state is 0.06 a.u. and the maximum is at Γ.

We also give the calculation of the conduction band based on virtual molecular states. In this case Löwdin's[15,16] theorem is not valid, and furthermore the tight-binding approximation is not as
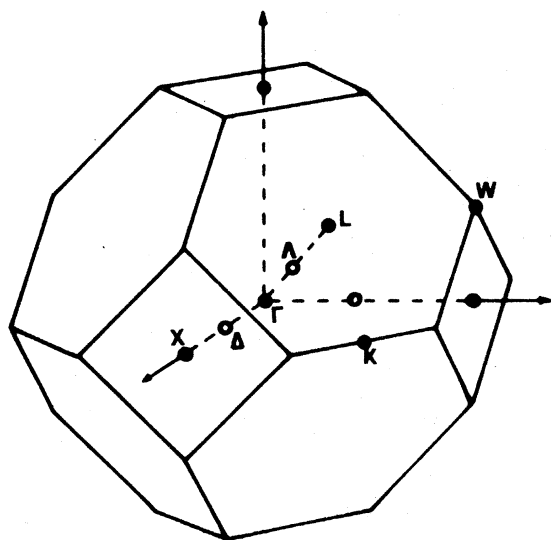

FIG. 2. Brillouin zone of solid methane in phase I. The symbols are those given by Koster, Ref. 26.

TABLE II. (a) Overlap matrix elements between molecular orbitals. The ordering of states is $1a_1$, $2a_1$, $1t_{2x}$, $1t_{2y}$, and $1t_{2z}$. The first neighbor is in the position $\frac{1}{2}a(1,1,0)$. (b) Overlap matrix elements between molecular orbitals. The ordering of states is $1a_1$, $2a_1$, $1t_{2x}$, $1t_{2y}$, and $1t_{2z}$. The second neighbor is in the position $\frac{1}{2}a(2,0,0)$.

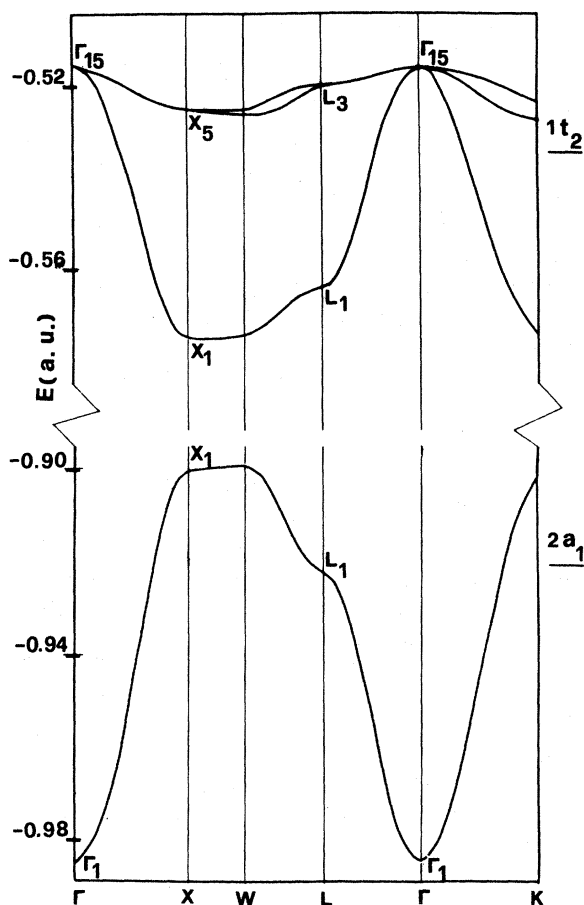| (a) First neighbor				
−0.000005	0.000051	−0.000095	−0.000095	0.000081
0.000051	0.009003	−0.010065	−0.010065	0.006499
0.000095	0.010065	−0.010779	−0.012089	0.008040
0.000095	0.010065	−0.012089	−0.010779	0.008040
0.000081	0.006499	−0.008040	−0.008040	0.007138
(b) Second neighbor				
0	−0.000002	0.000001	0	0
−0.000002	0.000310	−0.000427	0	0
−0.000001	0.000427	−0.000582	0	0
0	0	0	0.000050	0
0	0	0	0	0.000050

FIG. 3. Valence-band structure of solid methane. The HF levels for the isolated methane molecule are also shown.

good as for the valence band. Our starting molecular states are thus not the true Hartree–Fock excited states, but the virtual states resulting from

TABLE III. Hartree–Fock calculations on methane molecule, STO's. Energies are in atomic units. (a) Minimal basis set, optimized exponents given by Pitzer, Ref. 21. (b) Extended basis set with 39 STO's; calculated by Stevens, Ref. 22. In both cases C-H distance is 2.0665 a.u.

	Minimal basis set (a)	Extended basis (b)
Occupied		
$1a_1$	−11.20597	−11.20522
$2a_1$	−0.92089	−0.93880
$1t_1$	−0.53516	−0.54246
Virtual		
$3a_1$	0.65277	0.45534
$2t_2$	0.65677	0.44097
Total energy (ground state)		
	−40.12813	−40.21416

the closed-shell calculation. According to the theorem of Koopmans, they are a good approximation for the states of the negative molecular ion. Unfortunately, the energies of these states are strongly dependent on the choice of the basis. We compare in Table III the results obtained with our minimal basis set and the ones of an extended-basis calculation by Stevens.[28] We see that while agreement is very good for the occupied states, it is indeed very bad for virtual ones. Also, the ordering of the virtual levels is inverted. The conduction band we present is obtained in a mixed way, perturbating the best values of the HF energies with the interaction resulting from the minimal basis set. The resulting conduction band is given in Fig. 4. The width of the lower conduction band is 0.04 a.u. and the minimum is at X. The energy values for high-symmetry points are reported in Table IV for all bands. The gap between the top valence state Γ_{15} and the bottom conduction state X_5 is 24.5 eV. The direct gap between the states at X is 24.75 eV.
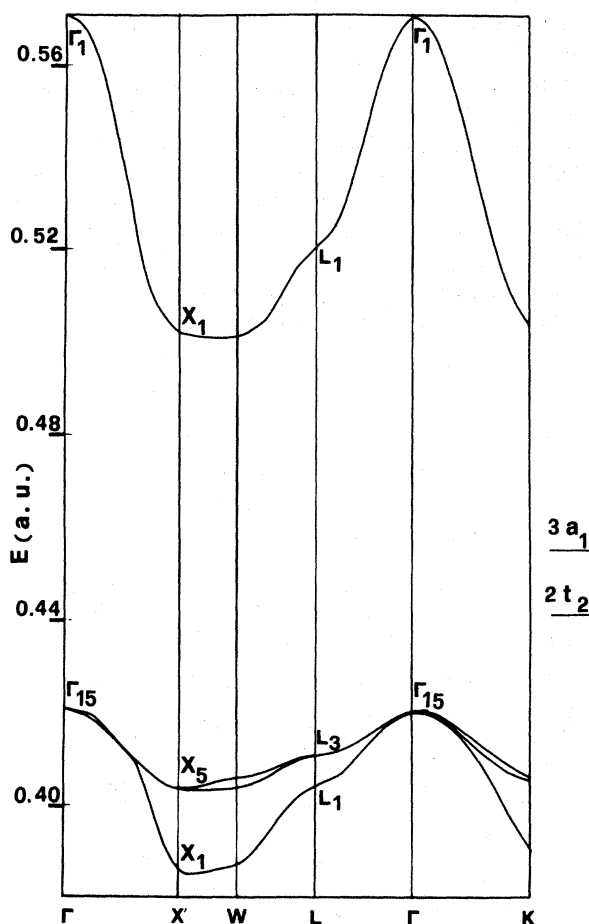

FIG. 4. Conduction band of solid methane. The virtual HF levels for the isolated methane molecule are also shown.

TABLE IV. Crystal energies at high-symmetry points (atomic units).

Γ	X	L
−11.2053	−11.2062	−11.2060
−0.9847	−0.9000	−0.9223
−0.5164	−0.5752	−0.5646
	−0.5254	−0.5202
0.4203	0.3848	0.4042
	0.4033	0.4108
0.5700	0.5016	0.5202

VI. DISCUSSION AND CONCLUSION

The *ab initio* calculation of the electronic structure of a molecular solid presented in this paper gives eigenvalues and eigenfunctions which are expected to be quite reliable as a picture of the HF fundamental state. The LCMO approximation is in fact very good for the valence bands and the neglect of molecular three-center integrals and the lack of self-consistency "*in toto,*" are shown to be a valid approximation. The overlap matrix elements between molecular orbitals are in fact small as shown in Table II. The band structure reported in Fig. 3 could then be directly compared with eventual experiments of the ESCA[7] or XPS[8] type.

Quite a different situation exists for the conduction band because the STO's minimal basis set we have chosen is not a very accurate representation of the eigenstates of an extra electron in presence of a closed-shell unit. In a physical case, in many respects analogous to molecular solids (namely, the solid rare gases), Knox and Bassani[3] realized early that an orthogonalized-plane-wave (OPW) calculation is much more reliable for conduction-band structure.

We also wish to point out that the conduction band computated here represents the HF virtual levels of the crystal, i.e., the energies of an extra electron put in the crystal, according to the theorem of Koopmans. This is not to be compared directly with the excitation by optical means, because the interaction with the hole strongly lowers the energy of the configuration and therefore

the optical transition energy. This effect is present in all closed-shell configurations and must be accounted for very carefully in the interpretation of the excitation spectrum.[6] In molecular crystals the electron-hole interaction is particularly strong because both the hole and the electron are localized in the unit cell so that the exciton can appear in the middle of the gap. An estimate of the energy of the excited singlet configuration could be obtained either by shifting the conduction band by $J_{vc} - 2K_{vc}$, where J_{vc} and K_{vc} are the Coulombic and exchange matrix elements between the valence and conduction bands, or shifting the starting energy of the molecular excited level, as done by Pastori-Parravicini and Resca.[13]

As noted above, there is close analogy between solid rare gases and molecular crystals. Both theoretical and experimental[4,5,29] works have shown that correlation effects beyond the HF scheme are also important and lower the band-to-band gap. We think that a similar situation occurs in molecular crystals, and correlation could be accounted for along lines similar to those of Refs. 4 and 5.

The HF gap of 24.5 eV of this calculation in solid methane is of the same order of magnitude as in various HF calculations in solid rare gases.[4,5] Another common feature is that the gap is larger than the ionization energy of the isolated molecule or atom.

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[1]F. Bassani, *International School of Physics "Enrico Fermi,"* *Course XXXIV* (Academic, New York, 1966).

[2]A. S. Davydov, *Theory of Molecular Excitons* (McGraw-Hill, New York, 1962).

[3]R. S. Knox and F. Bassani, Phys. Rev. **124**, 652 (1961).

[4]N. O. Lipari and W. B. Fowler, Phys. Rev. B **2**, 3354 (1970).

[5]L. Dagens and F. Perrot, Phys. Rev. B **5**, 641 (1972).

[6]F. Bassani and E. S. Giuliano, Nuovo Cimento 8B, 193 (1972).

[7]W. Gudat, E. E. Koch, P. Y. Yu, M. Cardona, and C. M. Penchina, Phys. Status Solidi B **52**, 505 (1972).

[8]L. Ley, S. Kowalczyk, R. Pollak, and D. A. Shirley, Phys.

Rev. Lett. **29**, 1088 (1972); R. A. Pollak, L. Levy, S. Kowalczyk, D. A. Shirley, J. D. Johannopoulos, D. J. Chadi, and M. L. Cohen, Phys. Rev. Lett. **29**, 1103 (1972).

[9] J. Ziman, Solid State Phys. **26**, 1 (1971); G. C. Fletcher, *Electron Band Theory of Solids* (North-Holland, Amsterdam, 1971); F. Bassani and G. Pastori-Parravicini, *Electronic States and Optical Properties of Crystals* (Pergamon, Oxford, to be published).

[10] C. A. Coulson, at the International Conference on Band Structure in Solids, Exeter, 1972 (unpublished).

[11] F. Bassani, in *Semiconductors and Semimetals*, edited by R. K. Williardson and A. C. Beer (Academic, New York, 1966), Vol. 1, p. 21.

[12] A. I. Gubanov and A. A. Nran'Yan, Fiz. Tverd. Tela **1**, 1044 (1959) [Sov. Phys.-Solid State **1**, 956 (1959)]; C. A. Coulson, L. B. Redei, and D. Stocker, Proc. R. Soc. A **270**, 357 (1962).

[13] G. Pastori-Parravicini and L. Resca, J. Phys. C **4**, L301 (1971). G. Pastori-Parravicini and L. Resca (unpublished).

[14] F. Bassani, L. Pietronero, and R. Resta (unpublished).

[15] P. O. Löwdin, thesis (Upsala, 1948) (unpublished).

[16] L. P. Howland, Phys. Rev. **109**, 1927 (1958).

[17] A. B. Kunz and J. Van Sciver, Phys. Rev. **142**, 462 (1966).

[18] R. M. Stevens, J. Chem. Phys. **52**, 1397 (1970); R. M. Stevens, Quantum Chemistry Program Exchange, Program 161.

[19] E. E. Lafon and C. C. Lin, Phys. Rev. **152**, 579 (1966).

[20] See, for instance, F. L. Pilar, *Elementary Quantum Chemistry* (McGraw-Hill, New York, 1968), p. 499.

[21] A. Schallamach, Proc. R. Soc. A **171**, 569 (1939).

[22] H. M. James and T. A. Keenan, J. Chem. Phys. **31**, 12 (1959); S. Alexander and M. Lerner-Naor (unpublished).

[23] S. Kimel, A. Ron, and D. F. Hornig, J. Chem. Phys. **40**, 3351 (1964); H. P. Hopkins, J. V. V. Kasper, and K. S. Pitzer, J. Chem. Phys. **46**, 218 (1967).

[24] B. A. Lombos, P. Sauvageau, and C. Sandorfy, Chem. Phys. Lett. **1**, 382 (1967).

[25] W. Press, J. Chem. Phys. **56**, 2597 (1972).

[26] G. F. Koster, Solid State Phys. **5**, 174 (1957).

[27] R. M. Pitzer, J. Chem. Phys. **46**, 4871 (1967).

[28] R. M. Stevens. SCF calculation with 39 STO's basis functions (unpublished).

[29] G. Baldini, Phys. Rev. **128**, 1562 (1962).

Equivalence of the Projection-Operator, Laplace-Transform, and Green's-Function Approaches to Harmonic Lattices[*]

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The recently derived projection-operator approach to lattice dynamics in the harmonic approximation is compared with the Laplace-transform and Green's-function methods in such a manner as to obtain the equivalence between the three approaches.

INTRODUCTION

In a recent publication Deutch and Silbey[1] made use of projection-operator techniques to obtain an exact equation of motion for the momentum of a special (mass-defect) particle selected from a one-dimensional harmonic-oscillator chain of equal-mass particles. They found that the so-obtained generalized Langevin equation,[2] involving the "random" force $F^*(t)$, simplified greatly for this harmonic system. The projection operator which appears in the definition of the random force disappears from the expression for the force on the selected particle to yield just the force as calculated in some reference system. These results were extended by Wada and Hori[3] to apply to a mass-disordered lattice. Here the reference system is some arbitrary mass-disordered lattice and one particle's mass is chosen to deviate from this reference system.

We wish to demonstrate the complete equivalence between this recent projection-operator approach and two previously derived approaches to harmonic-oscillator dynamics. These are the Green's-func-tion method set forth by Montroll[4] and further developed by Maradudin,[5] and the Laplace-trans-form method developed by Rubin in a series of articles.[6] We present the equivalences between these approaches in the simplest context of the one-mass-defect, classical, one-dimensional, har-monic chain since the generalizations to any cubic Bravais lattice, the quantum-mechanical case, and any "reference" system are immediate. In addition, the fact that this discussion is in the language of solids, and as such, phonons, is not essential. As long as one deals with a Hamiltonian which is quadratic in the generalized coordinates, all the results will be applicable. Thus one could discuss spin waves or certain radiation problems with the same techniques.

We first sketch the projection-operator develop-ment and cast it in a form which is most suited for comparison with the other approaches.

PROJECTION-OPERATOR DERIVATION

Consider a one-dimensional chain of $N+1$ har-monic oscillators of momenta p_k, coordinates q_k (expressed as deviations from equilibrium) with