APPLICATION OF BONDING MOLECULAR ORBITALS TO

THE VALENCE BANDS OF DIAMOND

By

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NOMENCLATURE

a_O	lattice constant
$\vec{a}_i$	crystal basis vector
$\vec{b}_i$	reciprocal lattice basis vector
$b(\vec{k},\vec{r})$	Bloch sum
$C^n(\vec{k})$	variational coefficients
E	energy eigenvalues
$D(r)$	term used in calculation of $V(K)$
H	Hamiltonian
$H(\vec{k})$	Hamiltonian matrix
$\vec{k}$	wave vector
$\vec{K}$	reciprocal lattice vector
n	wave function index
N	number of unit cells in lattice
$Q(r)$	term used in calculation of $V(K)$
$\vec{r}$	position vector
R_{nl}	atomic wave function
$\vec{R}$	lattice vector
$S(\vec{k})$	overlap matrix
$\vec{t}_i$	sublattice position vector
V	crystal potential
V_{at}	atomic-like potential

V_{at}^{coul}	atomic-like Coulomb potential
V_{at}^{exc}	atomic-like exchange potential
W	variational function
Z	atomic number
α	orbital index
γ	hybridization parameter
δ	Kronecker delta
ϵ	phase factor
η	hybridized orbital
$\mu, \vec{\mu}$	vector of reciprocal lattice vector coefficients
$\nu, \vec{\nu}$	vector of direct lattice vector coefficients
ρ	charge density
ϕ	atomic-like wave function
ψ	crystal wave function
Ω	volume of primitive unit cell
∇^2	Laplacian operator

CHAPTER I

INTRODUCTION

Several methods are available for the study of the energy band structure of diamond-type crystals. Virtually all methods employ certain approximations to reduce the number and type of terms involved in the crystal potential. A common approximation is often used, the single-particle approximation, in which it is assumed that each particle experiences some sort of average field, $V(\vec{r})$, produced by all the other particles in the crystal. The equation to be solved is the Schroedinger equation, $H\psi_n = E_n\psi_n$, where ψ is the wavefunction, E is the energy, and H is the Hamiltonian, which takes the form

$$H = -\frac{\nabla^2}{2} + V(\vec{r}), \tag{1}$$

the units used being Hartree atomic units (Appendix A). A further approximation is often used, the Born-Oppenheimer approximation, in which it is assumed that the nuclei are fixed at the lattice points of the crystal, which considerably reduces the magnitude of the problem. A direct result of the fixed lattice of atoms and the corresponding translational symmetry is the Bloch condition. If $\psi(\vec{r})$ is the wave function, then

$$\psi(\vec{r} + \vec{R}) = \exp(i\vec{k}\cdot\vec{R})\ \psi(\vec{r}) \tag{2}$$

1

where $\vec{R}$ is a lattice vector of the Bravais lattice and $\vec{k}$ is a wave vector associated with the wave function.

Within these approximations, there has been considerable interest in attempting to describe the valence bands of diamond in terms of bonding molecular orbitals [1] [2] [3] [4]. A successful description of crystalline properties in terms of molecular orbitals would demonstrate the compatibility of these two apparently different pictures, although this compatibility is often dismissed as unrealistic [5]. The bond energy between two carbon atoms in a diamond crystal should not be expected to differ greatly from the high bond energy between carbon atoms in molecules [6]. The extremely large bulk modulus of the diamond crystal indicates that the electronic bonds are not easily deformed, and retain their molecular character even within the crystal. Such a molecular description of crystals, where valid, provides a natural method for dealing with a large variety of crystal defects. A systematic, ab initio treatment of the valence bands of diamond using bonding molecular orbitals in a manner permitting direct comparison to more conventional methods is highly desirable.

One choice for the method to be used, the method of orthogonalized plane waves (OPW), has been used successfully in band structure calculations [7] [8]. In this method, the basis set consists of plane waves constructed to approximate the nearly free outer electrons. The plane waves are made orthogonal to the atomic-like core states. This method puts no severe restrictions on the nature of the potential, works well for materials with well-defined core states, and the basis set portrays the delocalized nature of the electrons. The method of OPW is relatively fast for high symmetry points of the wave vector, $\vec{k}$, but has very

slow plane wave convergence for points of low symmetry. The secular

equation is usually quite large, especially in crystals like diamond

with so much structure to analyze in terms of plane waves.

Another method, the method of augmented plane waves (APW), has

also been used successfully to treat the diamond lattice (9). This

method uses as its basis functions atomic-like orbitals within spheres

centered about each atomic site, and plane waves in the regions between

spheres. As in OPW, this basis set portrays the delocalized nature of

the electrons. The method of APW is quite accurate for points of high

symmetry, and there is no limitation on the number of core states. How-

ever, the muffin-tin potential, in which the potential has an atomic-

like character within the spheres and a constant value in the intersti-

tial regions, is virtually the only choice for the crystal potential in

this method. For crystals like diamond with highly non-spherical atomic

environments, a muffin-tin potential is unrealistic.

The method of tight-binding, or linear combination of atomic orbi-

tals (LCAO), has enjoyed wide success in a large variety of problems

(10) (11) (12) (13) (14). This method works well for molecules, and so

should work even better for infinite crystals where boundary problems

are no drawback. The effect of delocalized electrons is produced by the

overlap between atomic orbitals. In the method of LCAO, Bloch sums are

constructed to be of the form

$$b(\vec{k},\vec{r}) = \sum_{\nu} \exp(i\vec{k}\cdot\vec{R}_{\nu}) \; \phi(\vec{r} - \vec{R}_{\nu}) \qquad (3)$$

where the ϕ are atomic-like wave functions and the R_{ν} are symmetry

translations of the lattice. That these Bloch sums satisfy the Bloch

condition of Equation (2) is easily demonstrated. The method of LCAO is conceptually satisfying in that the basis set reflects the physical nature of the crystal. The secular equations are smaller than OPW even at low symmetry points. Using a muffin-tin potential, LCAO is just as accurate as APW, yet is not as restricted in the choice of potential (12). Furthermore, LCAO does not need to rely on artificially construct-ed plane waves in the interstitial regions. The only major drawback to LCAO has been the necessity of evaluating many multi-center integrals, and this complication has been removed by recent numerical techniques (10) (11).

To use either OPW or APW to examine the bonding orbital descrip-tion would require projection techniques to project out the functions which would describe the molecular orbitals. Since LCAO is a very suc-cessful model and since it is easily adapted to molecular orbital basis functions, the method of LCAO has been used to examine the valence bands of diamond in terms of bonding molecular orbitals.

CHAPTER II

DIAMOND LATTICE

The atoms in a pure diamond crystal are located at the lattice points of two interpenetrating face-centered cubic (fcc) Bravais lattices. The axes of these lattices, referred to as sublattice one and sublattice two, are parallel, and sublattice two is displaced from sublattice one by a distance of one fourth the cube diagonal along the body diagonal. Let a_0 be the lattice constant for diamond. The basis vectors for the fcc lattice can then be written as

$$\vec{a}_1 = a_0 (1,1,0)/2$$

$$\vec{a}_2 = a_0 (1,0,1)/2 \qquad\qquad (4)$$

$$\vec{a}_3 = a_0 (0,1,1)/2 \; .$$

Now let the origin of the coordinate system be chosen midway between two neighboring carbon atoms in opposite sublattices. Vectors $\vec{t}_1$ and $\vec{t}_2$ are defined such that

$$\vec{t}_1 = - \vec{t}_2 = - a_0 (1,1,1)/8 \; . \qquad\qquad (5)$$

Then the position of any carbon atom can be described by a vector $\vec{v} = (v_1, v_2, v_3)$ which determines the lattice point, and by an index i which determines the sublattice. That is, there is a carbon atom at all positions

$$\vec{R}_\nu + \vec{t}_i = \vec{R}_\nu + \vec{t}_i = (\nu_1\vec{a}_1 + \nu_2\vec{a}_2 + \nu_3\vec{a}_3) + \vec{t}_i \tag{6}$$

where $i = 1,2$ and ν_j, $j = 1,2,3$, take on all integer values for an infinite crystal. The cubic cell of the fcc lattice is not a primitive unit cell; that is, the cubic cell contains more than one lattice point. The primitive unit cell for the fcc lattice may take on many forms, but the cell which best displays the symmetry of the lattice points is the Wigner-Seitz cell. The boundaries of the Wigner-Seitz unit cell are the planes which bisect perpendicularly the lattice vectors $\vec{R}_\nu$. The volume centered on a lattice point and enclosed by these planes is a dodecahedron, and is the Wigner-Seitz unit cell for the fcc lattice. There are two carbon atoms per primitive unit cell, the volume of which is $\Omega = a_O^3/4$.

It will be useful at this time to define the reciprocal lattice for diamond. The reciprocal lattice basis vectors are defined as

$$\vec{b}_1 = \frac{2\pi(\vec{a}_2 \times \vec{a}_3)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{b}_2 = \frac{2\pi(\vec{a}_3 \times \vec{a}_1)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \tag{7}$$

$$\vec{b}_3 = \frac{2\pi(\vec{a}_1 \times \vec{a}_2)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)},$$

and using the explicit form for $\vec{a}_i$ for the fcc lattice given in Equation (4),

$$\vec{b}_1 = 2\pi(1,1,-1)/a_0$$

$$\vec{b}_2 = 2\pi(1,-1,1)/a_0 \qquad (8)$$

$$\vec{b}_3 = 2\pi(-1,1,1)/a_0 \ .$$

These are simply the basis vectors for a body-centered cubic (bcc) Bravais lattice. Note that $\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{i,j}$. A vector $\vec{K}_\mu$ is defined analogous to the vector $\vec{R}_\nu$ in direct space:

$$\vec{K}_\mu = \vec{K}_{\vec{\mu}} = \mu_1\vec{b}_1 + \mu_2\vec{b}_2 + \mu_3\vec{b}_3 \ , \qquad (9)$$

where the μ_j, $j = 1,2,3$, take on all integer values. The set of all points $\vec{K}_\mu$ constitutes the reciprocal lattice. A translation of the reciprocal lattice by $\vec{K}_\mu$ leaves the reciprocal lattice invariant. Note also that $\exp(i\vec{K}_\mu \cdot \vec{R}_\nu) = 1$ for all values of μ,ν.

The first Brillouin zone for the diamond crystal is defined as the Wigner-Seitz primitive unit cell for the bcc reciprocal lattice. This unit cell is a truncated octahedron with volume $(2\pi)^3/\Omega$. There are N discrete values of the wave vector $\vec{k}$ within the Brillouin zone, where N is the number of unit cells in the crystal. As the size of the diamond crystal approaches an infinite crystal, $\vec{k}$ becomes continuous rather than discrete.

CHAPTER III

CRYSTAL POTENTIAL

In choosing a specific form for the crystal potential, the first consideration is that it have the periodicity of the Bravais lattice:

$$V(\vec{r} + \vec{R}_\nu) = V(\vec{r}) \ . \tag{10}$$

Any function with the periodicity of the crystal can be expressed as a Fourier series, and since the origin has been chosen such that inversion symmetry exists, the Fourier expansion can be written

$$V(\vec{r}) = \sum_\mu V(\vec{K}_\mu) \cos(\vec{K}_\mu \cdot \vec{r}) \tag{11}$$

or inversely,

$$V(\vec{K}_\mu) = (N\Omega)^{-1} \int_{N\Omega} V(\vec{r}) \cos(\vec{K}_\mu \cdot \vec{r}) \, d\vec{r} \ . \tag{12}$$

Now we express the crystal potential as a superposition of functions $V_{at}(\vec{r})$ centered about the positions of the carbon nuclei:

$$V(\vec{r}) = \sum_\nu \sum_i V_{at}(\vec{r} - \vec{R}_\nu - \vec{t}_i) \ . \tag{13}$$

Equations 12 and 13 can be combined to give

$$V(\vec{K}_\mu) = 2\Omega^{-1} \cos(\vec{K}_\mu \cdot \vec{t}_1) \int_{N\Omega} V_{at}(\vec{r}) \cos(\vec{K}_\mu \cdot \vec{r}) \, d\vec{r} \ . \tag{14}$$

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In considering a form for the function $V_{at}(\vec{r})$, the motivation is to approximate the crystal potential by a sum of free-atom potentials. This model is called the overlapping atomic potential (OAP) model, and uses the Slater approximation for exchange on each atomic charge separately (15) (16). We write

$$V_{at}(\vec{r}) = V_{at}^{coul}(\vec{r}) + V_{at}^{exc}(\vec{r}) \qquad (15)$$

where

$$V_{at}^{coul}(\vec{r}) = -\frac{Z}{r} + \frac{4\pi}{r} \int_0^r \rho(r')r'^2 dr' + 4\pi \int_r^\infty \rho(r')r' dr'$$

$$V_{at}^{exc}(\vec{r}) = -\frac{3}{2} \left[3\rho(r)/\pi \right]^{1/3} . \qquad (16)$$

The absolute value free-atom electronic charge density $\rho(r)$ is obtained from the Hartree-Fock self-consistent field (SCF) solutions for the ground state of carbon, $(1s)^2(2s)^2(2p)^2$, from Jucys (17), using the relationship

$$4\pi\rho(r) = 2\left[R_{1s}(\vec{r})\right]^2 + 2\left[R_{2s}(\vec{r})\right]^2 + 2\left[R_{2p}(\vec{r})\right]^2 . \qquad (17)$$

Now the Fourier coefficients can be written as

$$V(\vec{K}_\mu) = \frac{-8\pi}{\Omega K_\mu^2} \cos(\vec{K}_\mu \cdot \vec{t}_1) \{Z - K_\mu^{-1} \int_0^\infty Q(r)\sin(K_\mu r)dr$$

$$\qquad (18)$$

$$+ K_\mu \int_0^\infty D(r)\sin(K_\mu r)dr\}$$

where

$$Q(r) \quad = \quad 4\pi r \rho(r)$$

$$D(r) \quad = \quad \frac{3r}{2} \left[3\rho(r)/\pi \right]^{1/3}$$

and where Q and ε are approximated by a non-linear least-squares curve fit of exponential-type terms, and the integrals in Equation 18 are evaluated as in Woodruff (16). The choice of the ground state of carbon, $(1s)^2(2s)^2(2p)^2$, rather than the valence state, $(1s)^2(2s)(2p)^3$, was made to facilitate comparison with the results of earlier papers, as was the choice of a_O = 6.728 (8) (12).

CHAPTER IV

LINEAR COMBINATION OF ATOMIC ORBITALS

As the name implies, the Bloch sums of Equation 3 used in the LCAO method are constructed from atomic wave functions. The specific choice for the wave functions is the Hartree-Fock SCF atomic wave functions obtained by fitting the tabulated functions of Jucys (18) for the ^5S state of the $(1s)^2(2s)(2p)^3$ configuration. The results, from Chaney, Lin, and Lafon (12) are

$$\phi_{1s}(\vec{r}) = 1.79382 \exp(-8.33500r) + 6.00411 \exp(-5.28343r)$$

$$\phi_{2s}(\vec{r}) = 1.71115 \exp(-5.11268r) - 1.28779r \exp(-1.70623r) \qquad (19)$$

$$\phi_{2p_x}(\vec{r}) = x\{1.69606 \exp(-2.64212r) + 0.840266 \exp(-1.28884r)\}$$

and similarly for $\phi_{2p_y}(\vec{r})$ and $\phi_{2p_z}(\vec{r})$. The five Bloch sums corresponding to $\alpha = 1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$ are constructed for each sublattice $(i = 1,2)$:

$$b_\alpha^i(\vec{k},\vec{r}) = N^{-\frac{1}{2}} \sum_\nu \exp(i\vec{k}\cdot\vec{R}_\nu) \, \phi_\alpha(\vec{r} - \vec{R}_\nu - \vec{t}_i) \qquad (20)$$

Now a trial wave function is chosen of the form

$$\psi_n(\vec{k},\vec{r}) = \sum_\alpha \sum_i C_{\alpha,i}^n(\vec{k}) \, b_\alpha^i(\vec{k},\vec{r}) \qquad (21)$$

This ψ_n will satisfy the Bloch condition since the $\{b_\alpha^i\}$ do. We form the function

$$W\{\vec{c}^n(\vec{k})\} = \frac{\int \psi_n^*(\vec{k},\vec{r}) \, H\psi_n(\vec{k},\vec{r}) \, d\vec{r}}{\int \psi_n^*(\vec{k},\vec{r}) \, \psi_n(\vec{k},\vec{r}) \, d\vec{r}} \qquad (22)$$

and demand that the $\{\vec{c}^n(\vec{k})\}$ be chosen variationally such that

$$\frac{\partial \, W\{\vec{c}^n(\vec{k})\}}{\partial \, c_{\alpha,i}^n(\vec{k})} \Bigg|_{\vec{c}^n} = 0 \quad \text{for all } \alpha,i \,. \qquad (23)$$

The secular equation which must be solved is

$$[H(\vec{k}) - E_n(\vec{k})S(\vec{k})] \, \vec{c}^n(\vec{k}) = 0 \,, \qquad (24)$$

where the first term in Equation 24 is a square matrix (10 x 10) and the second term is the vector of variational coefficients. Equation 24 gives rise to the 10 x 10 secular equation

$$\left| H(\vec{k}) - E_n(\vec{k})S(\vec{k}) \right| = 0 \qquad (25)$$

where

$$H_{\alpha,i}^{\alpha',i'}(\vec{k}) = \int b_\alpha^{i\,*}(\vec{k},\vec{r}) \, H \, b_{\alpha'}^{i'}(\vec{k},\vec{r}) \, d\vec{r}$$

$$\qquad (26)$$

$$S_{\alpha,i}^{\alpha',i'}(\vec{k}) = \int b_\alpha^{i\,*}(\vec{k},\vec{r}) \, b_{\alpha'}^{i'}(\vec{k},\vec{r}) \, d\vec{r}$$

and where the one-electron Hamiltonian is of the form given in Equation 2. The secular equation has been solved, with the resultant band struc-

ture shown in Figure 1. Note that the effect of the choice of the trial wave function in Equation 21 essentially forces the electrons within this model to participate only in atomic-type orbitals.
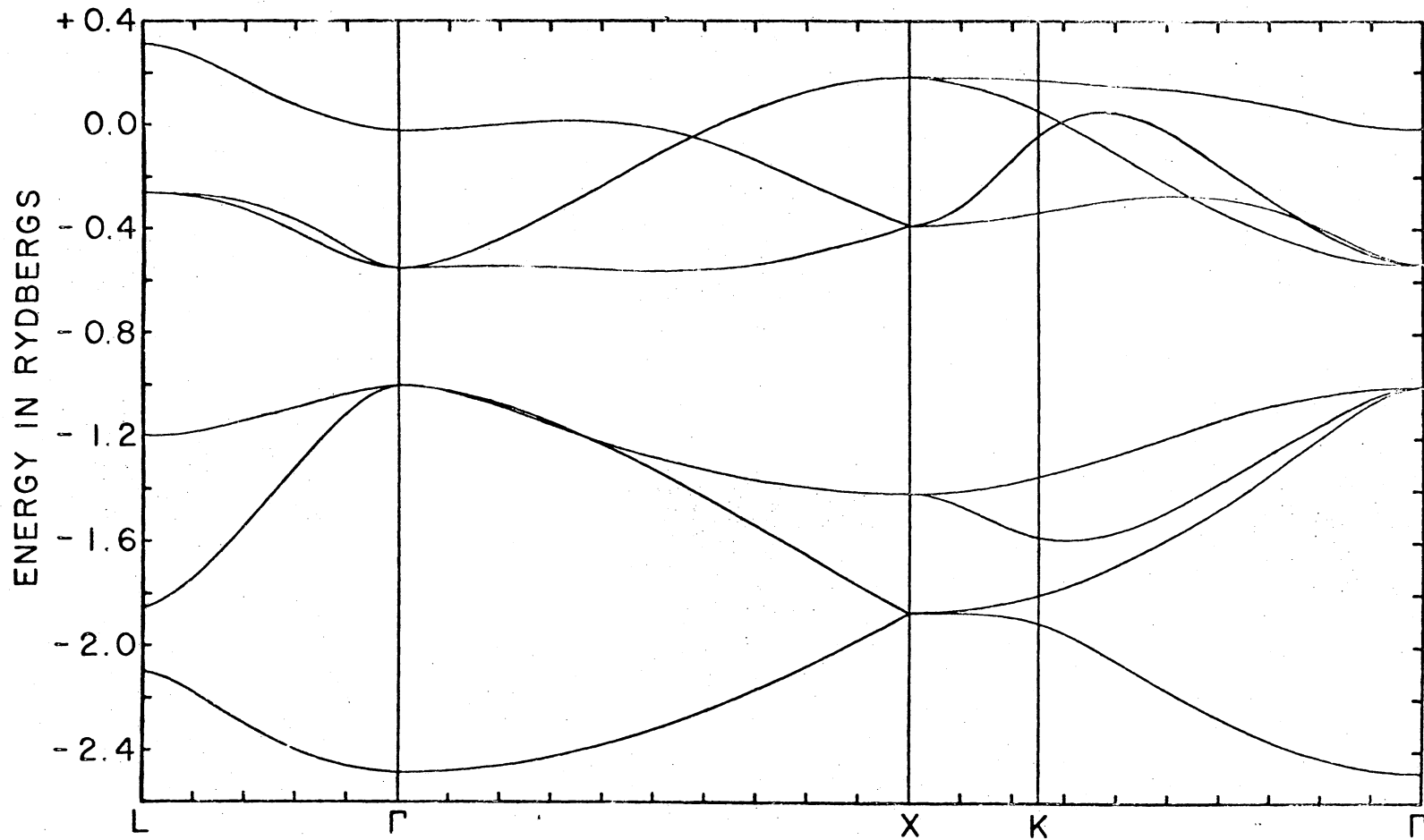
Figure 1.   Valence and Conduction Bands of Diamond Obtained From a Linear Combination of
Atomic Orbitals

CHAPTER V

LINEAR COMBINATION OF BONDING ORBITALS

As an alternative to the LCAO method, construct linear combinations of molecular orbitals (LCMO) which convey the character of the strong bonding between nearest neighbors in the diamond lattice. First we construct the hybridized orbitals

$$\eta_{111}(\vec{r}) = \frac{1}{2}\left[\gamma\phi_{2s}(\vec{r}) + \phi_{2p_x}(\vec{r}) + \phi_{2p_y}(\vec{r}) + \phi_{2p_z}(\vec{r})\right]$$

$$\eta_{1\bar{1}\bar{1}}(\vec{r}) = \frac{1}{2}\left[\gamma\phi_{2s}(\vec{r}) + \phi_{2p_x}(\vec{r}) - \phi_{2p_y}(\vec{r}) - \phi_{2p_z}(\vec{r})\right] \qquad (27)$$

$$\eta_{\bar{1}1\bar{1}}(\vec{r}) = \frac{1}{2}\left[\gamma\phi_{2s}(\vec{r}) - \phi_{2p_x}(\vec{r}) + \phi_{2p_y}(\vec{r}) - \phi_{2p_z}(\vec{r})\right]$$

$$\eta_{\bar{1}\bar{1}1}(\vec{r}) = \frac{1}{2}\left[\gamma\phi_{2s}(\vec{r}) - \phi_{2p_x}(\vec{r}) - \phi_{2p_y}(\vec{r}) + \phi_{2p_z}(\vec{r})\right]$$

for each atom in the first sublattice, and

$$\eta_{\bar{1}\bar{1}\bar{1}}(\vec{r}) = \eta_{111}(-\vec{r})$$

$$\eta_{\bar{1}11}(\vec{r}) = \eta_{1\bar{1}\bar{1}}(-\vec{r}) \qquad (28)$$

$$\eta_{1\bar{1}1}(\vec{r}) = \eta_{\bar{1}1\bar{1}}(-\vec{r})$$

$$\eta_{11\bar{1}}(\vec{r}) = \eta_{\bar{1}\bar{1}1}(-\vec{r})$$

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for each atom in the second sublattice. The hybridization constant, γ, is included to examine the effect of altering the strong overlap producing the bonding charge in the tetrahedral directions.

Bloch sums can then be constructed using these hybridized orbitals. The Bloch sums so created are defined by

$$b_0^{\pm}(\vec{k},\vec{r}) = N^{-\frac{1}{2}} \sum_{\nu} \exp(i\vec{k}\cdot\vec{R}_{\nu}) \left[\phi_{1s}(\vec{r} - \vec{R}_{\nu} - \vec{t}_1) \pm \phi_{1s}(\vec{r} - \vec{R}_{\nu} - \vec{t}_2)\right]$$

$$b_1^{\pm}(\vec{k},\vec{r}) = N^{-\frac{1}{2}} \sum_{\nu} \exp(i\vec{k}\cdot\vec{R}_{\nu}) \left[\eta_{111}(\vec{r} - \vec{R}_{\nu} - \vec{t}_1) \pm \varepsilon_1 \eta_{\bar{1}\bar{1}\bar{1}}(\vec{r} - \vec{R}_{\nu} - \vec{t}_2)\right]$$

$$b_2^{\pm}(\vec{k},\vec{r}) = N^{-\frac{1}{2}} \sum_{\nu} \exp(i\vec{k}\cdot\vec{R}_{\nu}) \left[\eta_{1\bar{1}\bar{1}}(\vec{r} - \vec{R}_{\nu} - \vec{t}_1) \pm \varepsilon_2 \eta_{\bar{1}11}(\vec{r} - \vec{R}_{\nu} - \vec{t}_2)\right] \quad (29)$$

$$b_3^{\pm}(\vec{k},\vec{r}) = N^{-\frac{1}{2}} \sum_{\nu} \exp(i\vec{k}\cdot\vec{R}_{\nu}) \left[\eta_{\bar{1}1\bar{1}}(\vec{r} - \vec{R}_{\nu} - \vec{t}_1) \pm \varepsilon_3 \eta_{1\bar{1}1}(\vec{r} - \vec{R}_{\nu} - \vec{t}_2)\right]$$

$$b_4^{\pm}(\vec{k},\vec{r}) = N^{-\frac{1}{2}} \sum_{\nu} \exp(i\vec{k}\cdot\vec{R}_{\nu}) \left[\eta_{\bar{1}\bar{1}1}(\vec{r} - \vec{R}_{\nu} - \vec{t}_1) \pm \varepsilon_4 \eta_{11\bar{1}}(\vec{r} - \vec{R}_{\nu} - \vec{t}_2)\right]$$

where

$$\varepsilon_i = \exp(i\vec{k}\cdot\vec{R}_i)$$

and where

$$\vec{R}_1 = (0,0,0)$$

$$\vec{R}_2 = (0,1,1)a_0/2 \qquad (30)$$

$$\vec{R}_3 = (1,0,1)a_0/2$$

$$\vec{R}_4 = (1,1,0)a_0/2 \; .$$

The $b_0^{\pm}$ are the core states and must be included for the core orthogonalization required by this variational approach. The b_i^{+}, $i = 1,2,3,4$, are

the bonding combinations of the hybridized valence orbitals, while the $\bar{b}_i$ are the antibonding combinations. The ε_i must be included as a phase factor since the atomic site in the second sublattice in Equation 29 is usually not in the same unit cell as the atomic site in the first sublattice.

The set of Bloch sums in Equation 29 span the same space identically as the Bloch sums of Equation 20; the energy eigenvalues are the same regardless of the basis set used in the secular equation. The eigenfunctions are also the same (or span the same subspace in the case of degenerate eigenvalues) although the coefficients $c^{\vec{n}}$ differ according to the different basis set. The new trial wave function is

$$\psi_n(\vec{k},\vec{r}) = \sum_j \sum_\pm c^n_{j,\pm}(\vec{k}), \; b^\pm_j(\vec{k},\vec{r}) \; , \tag{31}$$

and the new 10 x 10 secular equation differs only in the basis set used. For the reasons just stated, there is no need to actually solve this secular equation.

The problem of interest here, of course, is the effect on the band structure of including only Bloch sums of bonding combinations, plus the Bloch sums of core states for core orthogonalization. This set of Bloch sums will span only a subspace of the space spanned by all combinations of Bloch sums given in Equation 29. This reduced number of Bloch sums, and the trial wavefunction formed from this subset, effectively restricts the valence electrons to participation only in bonding molecular orbitals. Naturally, a 40% reduction in the size of the basis set yields less information about the band structure. The size of the secular equation for this linear combination of bonding orbitals (LCBO) for diamond

reduces from 10 x 10 complex to 6 x 6 complex, the solution of which involves a complex matrix formulation (Appendix B). The energy eigenvalues obtained in the solution to this secular equation give an upper bound (due to the variational method used) to the energies, within the formalism of the model under discussion. There is no guarantee that the upper bounds obtained are upper bounds to the valence band energies. The irreducible representations of the group of the wave vector, using the notation of Bouckaert, Smoluchowski, and Wigner (19), are given in Table I for some high symmetry points and lines in the Brillouin zone (20). Using this table and the transformation properties of the basis set, some predictions can be made concerning the energy levels at these symmetry points and lines. Look for example at the energies at the X point. If the bonding combinations included no X_4 symmetry, no information would be obtained about the energy level at X_4 in LCBO. Similarly, if the bonding combinations included X_3 symmetry, the energy levels obtained by LCBO would be an upper bound to the energy level at X_3 in the conduction band. The energy level at X_1 in the valence band will almost certainly rise from the LCAO approach to the LCBO approach, since mixing between valence and conduction bands is possible. It is therefore possible to obtain poor results at the X point. In fact, this is not the case. The results of the solution of the 6 x 6 secular equation are shown in Figure 2 for $\Upsilon = 1$. The effect of Υ on the energy levels of high symmetry points in the Brillouin zone is shown in Table II, along with the results for the 10 x 10 LCAO secular equation for comparison. The amount by which the various points and lines are raised by omission of the antibonding combinations is an indication of the degree of breakdown of the molecular description. Notice that the level of the X_4 point

TABLE I

IRREDUCIBLE REPRESENTATIONS FOR HIGH SYMMETRY POINTS
AND LINES OF THE BRILLOUIN ZONE OF DIAMOND

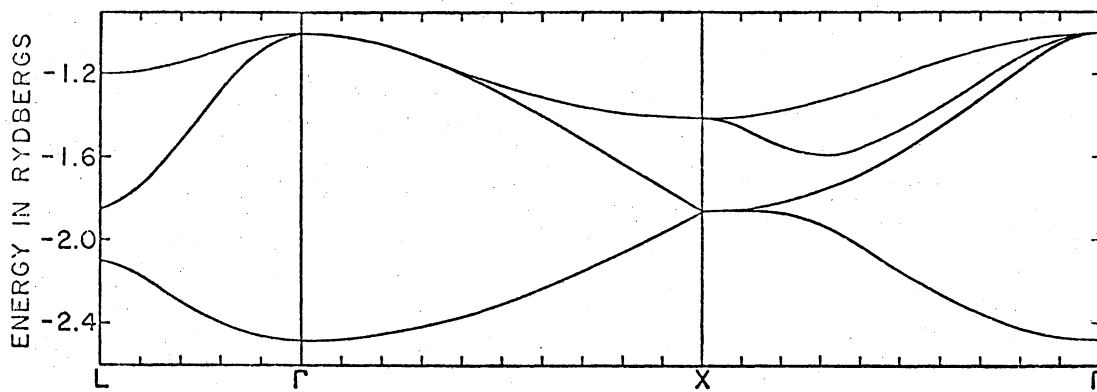|	Γ	L	X	Γ-L	Γ-X	K-X	Γ-K
CONDUCTION BAND	Γ_{15}	L_1	X_1	Λ_1	Δ_1	S_1	Σ_1
	$\Gamma_{2'}$	$L_{2'}$	X_3	Λ_3	$\Delta_{2'}$	S_3	Σ_3
		L_3			Δ_5	S_4	Σ_4
VALENCE BAND	$\Gamma_{25'}$	L_1	X_1	Λ_1	Δ_1	S_1	Σ_1
	Γ_1	$L_{2'}$	X_4	Λ_3	$\Delta_{2'}$	S_2	Σ_2
		L_4			Δ_5	S_3	Σ_3

Figure 2. Valence Band of Diamond Obtained From a Linear Combination of Bonding Molecular Orbitals

TABLE II

TABULAR COMPARISON OF LCAO AND LCBO CALCULATIONS OF THE VALENCE BAND
OF DIAMOND FOR SEVERAL CHOICES OF THE HYBRIDIZATION
PARAMETER (ENERGIES IN a.u.)

	LCAO	LCBO $\gamma = 1$	LCBO $\gamma = .995$	LCBO $\gamma = .90$
Γ_1	-1.2434	-1.2434	-1.2434	-1.2434
$\Gamma_{25'}$	-0.5028	-0.5028	-0.5028	-0.5028
X_1	-0.9379	-0.9315	-0.9313	-0.9284
X_4	-0.7073	-0.7073	-0.7073	-0.7073
$L_{2'}$	-1.0516	-1.0452	-1.0451	-1.0423
L_1	-0.9273	-0.9251	-0.9251	-0.9240
L_4	-0.5980	-0.5980	-0.5980	-0.5980

is unchanged, implying that the antibonding combinations, which were omitted, did not include X_4 symmetry. Although the X_1 point did raise somewhat, the difference is quite small. The bonding molecular orbital description is obviously quite good in the case of diamond.

Notice that the hybridization parameter of 1 gives equal or lower values for the energies than the other choices of γ. Since for a particular model, the variational method yields an upper bound for the energy, the lower energies corresponding to $\gamma = 1$ imply more accurate energies. This corresponds to sp^3 hybridization.

Note also that the variation between LCAO and LCBO valence band structure is very small, and in some instances there is no discrepancy at all. Very little information about the valence band of diamond is omitted by neglecting antibonding combinations.

CHAPTER VI

CONCLUSION

The excellent agreement between LCAO and LCBO for the valence band of diamond is compelling evidence for the bonding molecular orbital description in this model. It is apparent that for diamond, with a very open structure due to strong tetrahedral bonding, the valence electrons indeed occupy primarily hybridized molecular bondong orbitals in a pure crystal. Moreover, within this model, the optimum bonding orbitals are constructed from sp^3 hybridized orbitals. This concept provides a straight-forward mechanism for treating a wide variety of problems where the molecular bonds maintain their identity to a great extent in the crystal structure. It is evident that poor results for this molecular orbital picture in the past were caused, not by a breakdown in the physical concept, but by poor mathematical approximations.

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APPENDIX A

HARTREE ATOMIC UNITS

Unit of length   The Bohr radius for a fixed
                                  nucleus H-atom

Unit of charge   The charge on an electron

Unit of mass   The mass of an electron

Unit of angular momentum $h/(2\pi)$

Unit of energy   Twice the ionization energy for
                                  a fixed nucleus H-atom (21)

APPENDIX B

TREATMENT OF COMPLEX MATRICES

One result of this research has been the development of methods to
handle certain computations of complex matrices, specifically a method
to find the inverse of a complex matrix, and a method to determine the
eigenvalues and eigenvectors of a complex Hermitian matrix. The approach
used is to analyze these matrices in terms of real matrices rather than
develop new programs to handle complex matrices. These methods use a
real matrix with four times the storage requirements of the original
complex matrix, but have the advantage that they may be used easily on
a computer with no complex number facilities.

We write the n x n complex Hermitian matrix, C, as a sum of two
n x n real matrices, one containing the real part of C and the other
containing the imaginary part of C:

$$C = R + iI \ .$$ (1)

Now we form a real matrix, 2n x 2n, of the form

$$X = \left(\begin{array}{c|c} R & -I \\ \hline I & R \end{array} \right)$$ (2)

The eigenvalues and eigenvectors of C, as well as the inverse of C, may
be computed by performing analogous manipulations of the real matrix X.
Note that if C is Hermitian, that is, if $C^+ = C$, then from Equation 1,

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$$R^T - iI^T = R + iI \qquad (3)$$

which implies that

$$R^T = R$$
$$I^T = -I \qquad (4)$$

Equation 4 indicates that X is a symmetric matrix.

The inverse of C is written as

$$C^{-1} = R' + iI' \qquad (5)$$

Combining Equations 1 and 5:

$$C^{-1}C = (R' + iI')\ (R + iI)$$
$$= (R'R - I'I) + i(R'I + I'R) \qquad (6)$$

which means that

$$R'R - I'I = 1$$
$$R'I + I'R = O \qquad (7)$$

where 1 is the identity matrix and O is the null matrix. Now we form the matrix Y:

$$Y = \left(\begin{array}{c|c} R' & -I' \\ \hline I' & R' \end{array} \right) \qquad (8)$$

and form the produce YX, using Equations 2 and 8.

$$YX = \left(\begin{array}{c|c} R' & -I' \\ \hline I' & R' \end{array} \right) \left(\begin{array}{c|c} R & -I \\ \hline I & R \end{array} \right)$$
$$= \left(\begin{array}{c|c} R'R - I'I & -R'I - I'R \\ \hline I'R + R'I & -I'I + R'R \end{array} \right) \qquad (9)$$

and using Equation 7, the product YX can be written

$$YX = \left(\begin{array}{c|c} 1 & 0 \\ \hline 0 & 1 \end{array}\right) = 1 \qquad (10)$$

The matrix Y is the inverse of X; since X has one and only one inverse, $Y = X^{-1}$. Therefore, to find the inverse of C:

- The real matrix X is formed according to Equation 2.

- The inverse of X is determined, call it Y.

- The matrices R' and I' are determined from Y using Equation 8.

- The matrix C^{-1} is formed using Equation 5.

To determine the eigenvalues and eigenvectors of C, the following eigenvalue equation must be solved:

$$C \vec{u}_n = \lambda_n \vec{u}_n \qquad (11)$$

where $\vec{u}_n$ and λ_n are the associated eigenfunctions and eigenvectors. The related secular equation which must be solved is

$$\left| C - \lambda 1 \right| = 0 \qquad (12)$$

First decompose $\vec{u}_n$ into its real and imaginary parts,

$$\vec{u}_n = \vec{u}_n^R + i\vec{u}_n^I , \qquad (13)$$

and substituting Equation 1 into Equation 11,

$$\begin{aligned}
C \vec{u}_n &= (R + iI)(\vec{u}_n^R + i\vec{u}_n^I) \\
&= (R\vec{u}_n^R - I\vec{u}_n^I) + i(R\vec{u}_n^I + I\vec{u}_n^R) \qquad (14) \\
&= \lambda \vec{u}_n \\
&= \lambda \vec{u}_n^R + i\lambda \vec{u}_n^I
\end{aligned}$$

That is,

$$R\vec{u}_n^R - I\vec{u}_n^I = \lambda\vec{u}_n^R$$

(15)

$$R\vec{u}_n^I + I\vec{u}_n^R = \lambda\vec{u}_n^I$$

Equation 15 can be written in matrix notation as

$$\left(\begin{array}{c|c} R & -I \\ \hline I & R \end{array}\right)\left(\begin{array}{c} \vec{u}_n^R \\ \vec{u}_n^I \end{array}\right) = \lambda\left(\begin{array}{c} \vec{u}_n^R \\ \vec{u}_n^I \end{array}\right)$$

(16)

This corresponds to a secular equation of the form

$$\left|X - \lambda 1\right| = 0$$

(17)

Therefore, to find the eigenvalues and associated eigenfunctions of C:

- The real matrix X is formed as in Equation 2.

- The eigenvalues and associated eigenfunctions of X are determined, using the secular Equation 17. Note that the eigenvalues of X must be doubly degenerate with respect to the eigenvalues of C, since C is of order n while X is of order 2n. Because C is Hermitian, its eigenvalues are real.

- The eigenvectors of C are formed using Equations 13 and 16.

VITA 2

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