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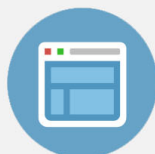
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Study of Electron Correlation in the  $H_6$  Ring, Using a Novel Approximation\*

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Studies on electron behavior in finite model systems provide information relevant to electrons in lattices. Approximate schemes for testing electron correlation may be tested by such model calculations. We report here the results of a study on the  $^1T_1$  ground state of the  $H_6$  hexagonal ring, using a novel type of wavefunction containing both valence bond and molecular orbital components. The method has a number of significant advantages and gives results as good as those of the simple alternant molecular orbital (AMO) method. Possible implications of these results for molecular and solid-state electron behavior are discussed briefly.

## I. INTRODUCTION

**T**HIS paper presents the results of a study of many-electron behavior in the ground state of a model system, a six-membered ring of one-electron atoms. Such studies are of interest because they may provide information about the effects of electron correlation on the wavefunctions not only of finite systems but of infinite lattices. The band theory of electronic structure in solids, in spite of its wide use, has serious defects because of its failure to give any account of the spatial correlation of electrons due to mutual repulsion. These defects become obvious if one examines the behavior of the ground-state wavefunction of a lattice, as a function of the lattice parameter  $R$  for a system containing one electron per atom. At small lattice spacings, the Bloch molecular orbital description (band model) is correct and the ground state is obviously that of a "metal"; but at very large spacings, the Bloch description leads to an energy far above that of the true ground state, since it corresponds to dissociation into ions as well as atoms, as  $R \rightarrow \infty$ ; the true ground state at  $R \rightarrow \infty$  is clearly that of neutral atoms, each with its localized electron and the simple Bloch model is incapable of describing such correlation. The nature of the transition, as a function of lattice spacing  $R$ , from the "localized electron" structure valid at large  $R$ , to the "metallic electron" structure at small  $R$ , has been the subject of much discussion. It has been suggested<sup>1</sup> that there is a critical spacing  $R_c$  at which the wavefunction changes, essentially discontinuously, from "localized" to "metallic" character. Unfortunately, critical examination of such questions for the infinite lattice is still computationally impractical. Attention has been given to finite model systems, with two aims: (a) Behavior of the model system may resemble that of the infinite one; (b) The accuracy of various approximate schemes in the model can be compared to "exact" calculations. With this in mind, co-workers of Slater have examined

the hexagonal ring of one-electron atoms.<sup>2,3</sup> [Since interest centers on the collective aspects of the system, rather than on the quantitative polarization of individual atomic orbitals, the model basis set includes only a single orbital ( $1s$  hydrogenic) on each atom.] Mattheiss<sup>2</sup> carried out a full configuration-interaction study of all the energy levels arising for this system. This calculation may be regarded as the "exact" solution to the model, and approximate treatments can be judged by comparison with it. Mattheiss also studied the use of second-order perturbation theory on the Bloch basis and forms of limited configuration interaction; he found that these were not adequate to describe the system. Moskowitz<sup>3</sup> did a calculation based on the alternant molecular orbital method (AMO) discussed by Löwdin.<sup>4</sup> The AMO method gives a qualitatively correct description of ground-state electron behavior at all values of  $R$ , and is moderately successful quantitatively. Neither the AMO nor exact calculation shows any sharp change in the electron structure as a function of  $R$ , the transition being very gradual. This result does not support the arguments of Mott,<sup>1</sup> if the  $H_6$  ring is a relevant model. We present some qualitative arguments later which suggest that it is not.

Another approach to the spatial correlation of electrons is that of the valence bond theory. At large  $R$ , the ground-state wavefunction should be well represented by resonance of all possible valence bond structures, with singlet pair bonds between nearest neighbors. For tractable calculation, Wannier functions, rather than the simple atomic orbitals, must be employed to construct the bond pair singlet functions; but since overlap is required to have binding, a (variable) amount of ionic character in the bond pairs is necessary. The term "VB wavefunction" always refers to wavefunctions constructed from such sophisticated pair singlets. In general, the structures with bonds only between nearest-neighbor atoms do not exhaust the list of canonical valence bond structures, but the "long-bond"

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<sup>1</sup> N. F. Mott, *Can. J. Phys.* **34**, 1356 (1956); *Phil. Mag.* **6**, 287 (1961).

<sup>2</sup> L. F. Mattheiss, *Phys. Rev.* **123**, 1209 (1961); thesis, Physics Department, MIT 1960.

<sup>3</sup> J. W. Moskowitz, *J. Chem. Phys.* **38**, 677 (1963).

<sup>4</sup> P.-O. Löwdin, *Phys. Rev.* **97**, 1509 (1955); *Rev. Mod. Phys.* **34**, 80 (1962); R. Pauncz, J. de Heer, and P.-O. Löwdin, *J. Chem. Phys.* **36**, 2247 (1962).

structures have not been included in the appropriate treatment of this study. For H<sub>6</sub> (or for any 2*n*-membered ring) the two "Kekulé" structures suffice, and for the ground singlet state, which always belongs to the invariant representation <sup>1</sup>Γ<sub>1</sub>, only their symmetrical sum appears.

This VB wavefunction, with the disposable parameter λ representing ionic character in the bond pairs, gives an adequate description of the ground state over a rather wide range of *R*, except at the shorter distances, where the Bloch theory is valid. In order to obtain a description of the system ground state at all *R*, we added the molecular orbital ground state wave-function. Although this component is not orthogonal to the VB components, it is independent of them. Such a two-component wavefunction, which we abbreviate as the "MO-VBλ" scheme, suffices to give a good description of the model ground state at all distances. The binding energy obtained is essentially the same as that of the one-parameter AMO calculation at all distances, though not identical to it.

Like the one-parameter (simple) AMO method, the MO-VBλ scheme can be extended to larger systems as an approximate treatment. In this connection, it has a number of interesting features, which constitute the main reasons we present the results of this study:

(1) The amount of labor involved in computation appears to be comparable to that of the AMO method. Most of this labor is involved in the calculation of interaction matrix elements between "MO" and "VBλ" components.

(2) The AMO method appears useful only for "alternant" (two-sublattice) structures, while no such restriction holds for the MO-VBλ scheme. In connection with applications to chemical systems (cyclic polyenes, etc.) this flexibility may be useful.

(3) In some cases, the MO-VBλ method may predict a different ground state than does the AMO method; a particular example we have in mind is that of the 4*n*-membered rings, where the AMO ground state is a triplet, while the MO-VBλ ground state appears to be a singlet, at least at distances larger than some critical one. Exploration of differences between the two theories may be valuable.

(4) As the results of this study show, the peculiar behavior of the parameters of the MO-VBλ scheme clearly reveals the transition from localized electron structure to metallic structure as a function of lattice parameter. In Sec. 3 we advance an hypothesis concerning the nature of this transition in two- and three-dimensional lattices, compared to its character in one dimension. The MO-VBλ scheme is well suited for testing this hypothesis on some model systems.

The next section describes the MO-VBλ method; the third one presents the results of calculations on the H<sub>6</sub> system, and a discussion of pertinent questions raised by the study.

## II. DESCRIPTION OF METHOD

### A. System and Basis

Consider a regular array of identical atomic centers *i*, each having associated to it a basis orbital *u<sub>i</sub>(r)* describing an electron bound to this center. We assume that one electron is contributed by each atom, so that altogether the number both of centers and of electrons is 2*N* (we take an even number for convenience). Further, assume the existence of a group *G* of geometrical symmetry operations on the array which interchange identical atoms without distinguishably altering the array. It follows that the 2*N* orbitals {*u<sub>i</sub>*} span a representation of *G* which can be broken down into its irreducible components by transforming to a new basis set {*ψ<sub>k</sub>*} which transform irreducibly. Although the functions *u<sub>i</sub>* are not mutually orthogonal, the {*ψ<sub>k</sub>*} are; the transformation {*u<sub>i</sub>*} → {*ψ<sub>k</sub>*} is not unitary. We shall suppose that the *ψ<sub>k</sub>* are so defined as to be normalized to unity. The *ψ<sub>k</sub>* are the *molecular orbitals* or *Bloch orbitals*. From the nonunitary transformation matrix for {*u<sub>i</sub>*} → {*ψ<sub>k</sub>*} a related unitary one can be constructed, whose inverse transforms {*ψ<sub>k</sub>*} into a new orthonormal set of functions {*φ<sub>i</sub>*}, the *orthogonal atomic orbitals* or *Wannier functions*. We regard either {*ψ<sub>k</sub>*} or {*φ<sub>i</sub>*} as proper basis sets for the problem, but all computations must eventually express matrix elements involving these basis functions in terms of the fundamental basis {*u<sub>i</sub>*}, a routine task.

In the system actually treated, the array is a regular hexagon; the point symmetry *D*<sub>6</sub> more than suffices to reduce the representation spanned by {*u<sub>i</sub>*}. The intended analogy between the sixfold rotation *C*<sub>6</sub><sup>(1)</sup> and the elementary translation in an infinite one-dimensional chain is clear if we accept the validity of the Born-von Karman condition for the latter. The *ψ<sub>k</sub>* are given by

$$\psi_k = \mathfrak{N}_k \sum_{j=1}^6 u_j(\mathbf{r}) \exp[\pi i k j / 3], \quad k = 0, \pm 1, \pm 2, 3; \quad (1)$$

$$\mathfrak{N}_k^{-2} = 6[1 + 2S_{12} \cos(k\pi/3) + 2S_{13} \cos(2k\pi/3) + S_{14} \cos k\pi]. \quad (2)$$

Numbering *k* with positive and negative values agrees with the usual Brillouin zone notation; *k* = ±1, ±2-span doubly degenerate irreducible representations. *S*<sub>1*l*</sub> is an overlap integral (three distinct ones exist):

$$S_{1l} = \int u_l(\mathbf{r}) u_l(\mathbf{r}) d\mathbf{r}^3. \quad (3)$$

The Wannier functions *φ<sub>j</sub>* are given by

$$\varphi_j = [1/(6)^{1/2}] \sum_k \psi_k \exp[-\pi i k j / 3]. \quad (4)$$

### B. MO Wavefunction

In the MO method the molecular orbitals *ψ<sub>k</sub>* are used to build up a suitable many-electron wavefunction. The

method works well if one-electron SCF effects dominate, rather than pair correlation effects. Many-electron wavefunctions must satisfy the Pauli principle and spin and space symmetry requirements. Antisymmetrized products of spin-orbital functions (with  $\psi_k$ 's as orbitals) satisfy the Pauli principle, and simple, symmetry-determined linear combinations of these determinants satisfy spin and space symmetry requirements. Such wavefunctions do not give any correlation of electrons except through the Pauli principle. In many cases (filled shell configurations) a single Slater determinant suffices.

For the six-membered ring, the MO ground configuration is a closed shell,  $(0)^2(1)^2(\bar{1})^2$ , giving rise to a  ${}^1\Gamma_1$  state. For small  $R$ , this single Slater determinant is a good description of the ground state. Under the same conditions the low-lying excited states arise from configurations in which an electron with  $k=\pm 1$  is excited to  $k'=\pm 2$ . In our study of the ground state, we use only the MO ground-state component:

$$\Psi^{\text{MO}}({}^1\Gamma_1) = A(6) \{ \psi_0(1)\alpha(1)\psi_0(2)\beta(2)\psi_1(1)\alpha(3) \\ \times \psi_1(4)\beta(4)\psi_1(5)\alpha(5)\psi_1(6)\beta(6) \}; \quad (5)$$

the antisymmetrizer  $A(6)$  is, as usual,

$$A(6) \equiv [1/(6!)]^{\frac{1}{2}} \sum_P (-1)^P P, \quad (6)$$

where the sum is over all permutations  $P$  of the six electrons.

### C. Valence Bond Wavefunctions

The valence bond method attempts to give explicit account of spatial correlation of electrons.

Let us define a *pair singlet* function, representing a bond pair for two orbitals  $i, j$ , as:

$${}^1\chi(i, j; 1, 2) = 1/(2[1+\lambda^2])^{\frac{1}{2}} \{ \varphi_i(1)\varphi_j(2) + \varphi_j(1)\varphi_i(2) \\ + \lambda\varphi_i(1)\varphi_i(2) + \lambda\varphi_j(1)\varphi_j(2) \} \alpha(1)\beta(2). \quad (7)$$

Since the space part of  ${}^1\chi(i, j)$  is symmetric with respect to permutation of Electrons 1 and 2, the action of an antisymmetrizer on functions containing it can only generate a spin singlet from it. Any many-electron function which is an antisymmetrized product of such pair functions is a singlet, and, if no two pairs share a common orbital, as we always require, may be represented by a simple bond diagram in which a line connects the centers  $i, j$  for each bond pair.<sup>5</sup>

Representation of states of higher multiplicity is easy if the state of maximum  $M_s$  is considered; unpaired electrons are simply represented by suitable one-electron functions, associated with  $\alpha$ -spins. Their failure to be explicitly correlated with each other is compensated by

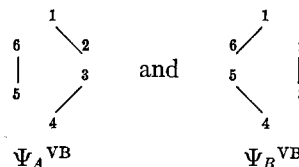
<sup>5</sup> Such a wavefunction is of the form proposed by A. C. Hurley, J. Lennard-Jones, and J. A. Pople [Proc. Roy. Soc. (London) **A220**, 446 (1953)] for applications to saturated systems.

the Pauli principle. Unpaired electrons may be represented on a bond diagram by dots.

To each bond diagram there is associated, then, a corresponding VB wavefunction, an antisymmetrized product of pair singlets and unpaired electron functions. Such a wavefunction satisfies both the proper spin multiplicity and the Pauli principle, by construction. To meet space symmetry requirements, one observes that all bond diagrams fall into sets whose members transform into each other under the symmetry operations of the array. Each such set spans a reducible representation of  $G$  and combinations of the VB wavefunctions may be chosen which transform irreducibly.

The number of independent VB diagrams is limited to the famous canonical set for  $\lambda=0$ ; the more relevant case  $\lambda \neq 0$  is more complicated but limits still exist. However, for the actual problem and for all useful applications of the formalism we present here, we consider a still more limited set than even the canonical set: the bond diagrams in which all bonds are between nearest neighbors only. A physical assumption is involved in this limitation, namely, that if bond pair correlation is important in the ground state, it is of predominantly short range. With this assumption, the additional assumption of a single parameter  $\lambda$  common to all pair functions in every diagram is obvious and proper.

In the six-membered ring, there are only two bond diagrams for the ground singlet, the Kekulé structures:



The linear combination

$$\Psi^{\text{VB}}({}^1\Gamma_1) = C[\Psi_A^{\text{VB}} + \Psi_B^{\text{VB}}] \quad (8)$$

is a  ${}^1\Gamma_1$  state.

The "MO-VB $\lambda$ " approximation consists simply in finding the best variational function of the form

$$\Psi = C_{\text{MO}}\Psi^{\text{MO}}({}^1\Gamma_1) + C_{\text{VB}}\Psi^{\text{VB}}({}^1\Gamma_1). \quad (9)$$

The energy is minimized with respect to  $\lambda$  and the coefficients of Eq. (9). Although  $\Psi^{\text{MO}}$  and  $\Psi^{\text{VB}}$  are not orthogonal, they are independent and offer rather different descriptions of electron behavior regardless of the value of  $\lambda$ . This fact is strikingly illustrated by the results for the six-membered ring (in the section following this one); the common cliché that "molecular-orbital-with-configuration-interaction" calculations are *equivalent to* "valence-bond-with-ionic-character" calculations must be severely qualified.

### D. Matrix Elements

Matrix elements of the Hamiltonian  $H$  and the identity  $1$  must be computed between the three funda-

mental components ( $\Psi_A^{VB}$ ,  $\Psi_B^{VB}$ , and  $\Psi^{MO}$ ). We discuss these briefly.

(1)  $\langle \Psi^{MO} | 1 | \Psi^{MO} \rangle = 1$ ;  $\langle \Psi^{MO} | H | \Psi^{MO} \rangle$  is given by

$$H_{MO-MO} = 2 \sum_{k \text{ occ}} \langle \psi_k(1) | h(1) | \psi_k(1) \rangle + 2 \sum_{k, \text{occ}} \sum_{k', \text{occ}} \langle \psi_k(1) \psi_{k'}(2) | e^2/r_{12} | \psi_k(1) \psi_{k'}(2) \rangle - \sum_{k, \text{occ}} \sum_{k', \text{occ}} \langle \psi_k(1) \psi_{k'}(2) | e^2/r_{12} | \psi_k(2) \psi_{k'}(1) \rangle, \quad (10)$$

where  $h(1)$  is the one-electron Hamiltonian, representing the kinetic energy of an electron and its potential energy of interaction with  $2N$  atomic centers,  $J$ :

$$h(1) = -(\hbar^2/2m)\nabla_1^2 - \sum_{J=1}^{2N} V(r_{1J}). \quad (11)$$

(2) Diagonal VB elements. Because of the orthonormality of the Wannier functions  $\{\varphi_j\}$  and therefore also of the pair singlets without common atoms, the following results may easily be proved for the matrix elements of a single bond diagram:

$$\langle \Psi_A^{VB} | 1 | \Psi_A^{VB} \rangle = \langle \Psi_B^{VB} | 1 | \Psi_B^{VB} \rangle = 1; \quad (12a)$$

$$\langle A | H | A \rangle = \langle B | H | B \rangle$$

$$H_{AA} = \sum_{\text{pairs}(ij)} \{ 2 \langle {}^1\chi_{ij}(1, 2) | h(1) | {}^1\chi_{ij}(1, 2) \rangle + \langle {}^1\chi_{ij}(1, 2) | e^2/r_{12} | {}^1\chi_{ij}(1, 2) \rangle \} + \frac{1}{2} \sum_{(ij)} \sum_{(kl) \neq (ij)} \{ 4 \langle {}^1\chi_{ij}(1, 2) {}^1\chi_{kl}(3, 4) | e^2/r_{13} | {}^1\chi_{ij}(1, 2) {}^1\chi_{kl}(3, 4) \rangle - 2 \langle {}^1\chi_{ij}(1, 2) {}^1\chi_{kl}(3, 4) | e^2/r_{13} | {}^1\chi_{ij}(3, 2) {}^1\chi_{kl}(1, 4) \rangle \}. \quad (12b)$$

(3) Interaction of two VB structures. The problem of computing interaction matrix elements for two VB structures can best be understood by examining the diagram produced by superposition of the two bond diagrams. Such a superposition diagram consists of a number of superposed bonds (bond coincides in both structures) and a number of "islands," whose perimeters are formed by chains of noncoincident bonds in the two structures. The matrix elements can be characterized totally by the contributions of the islands. In the case of the six-membered ring there is only one island and the results are quite simple.

$$\text{Overlap} \quad \langle A | 1 | B \rangle = (1+\lambda^6)/4(1+\lambda^2)^3. \quad (13a)$$

The energy of interaction  $H_{AB}$  should be compared to the quantity

$$H_{AB}^0 \equiv \frac{1}{2} \langle A | 1 | B \rangle [H_{AA} + H_{BB}] \quad (13b)$$

the resonance energy depends only on the difference  $H_{AB} - H_{AB}^0$ .  $H_{AB}$  is the sum of two terms,  $F_{AB} + G_{AB}$ ;

$F_{AB}$  is the matrix element of the one-electron operators and reduces to

$$F_{AB} = 6 \langle A | 1 | B \rangle \{ \langle 1 | h(1) | 1 \rangle + 2\lambda [(1+\lambda^4)/(1+\lambda^6)] \langle 1 | h(1) | 2 \rangle - 2\lambda^3(1+\lambda^6)^{-1} \langle 1 | h(1) | 4 \rangle \}, \quad (13c)$$

where the numbers in the brackets refer to orbitals  $\varphi_i$ .  $G_{AB}$ , the matrix element of the electron interactions, is also a polynomial in  $\lambda$ , whose form may be derived systematically; for brevity's sake we do not quote it here. More details about these expressions and their derivation is available on request [Ref. (6)].

(4) Interaction of MO and VB components. These matrix elements are the most difficult to evaluate; a brief outline of procedure is as follows: Consider the matrix element of a spinless linear operator  $\Theta$  (symmetric to permutations of electrons) between  $\Psi_A^{VB}$  and  $\Psi^{MO}$  (results here are specialized to the case of the six-membered ring); this is equal to the expression

$$\langle \Psi_A^{VB} | \Theta | \Psi^{MO} \rangle = \sum_P (-1)^P \langle \prod_{\mu=1}^3 [{}^1\chi_{\mu}(i_{\mu}, j_{\mu}; 2\mu-1, 2\mu)] | \Theta | P \prod_{\nu=1}^3 [\psi_{k_{\nu}}(2\nu-1) \psi_{k_{\nu}}(2\nu) \alpha(2\nu-1) \beta(2\nu)] \rangle, \quad (14)$$

where the index  $\mu$  specifies  $(i_{\mu}, j_{\mu})$  and  $k_{\nu}$  takes on the values 0, +1, -1 as specified in Eq. (5). The product of pair functions can be expanded,

$$\prod_{\mu=1}^3 [{}^1\chi_{\mu}(i_{\mu}, j_{\mu}; 2\mu-1, 2\mu)] = [2(1+\lambda^2)]^{-3} \sum_{\tau} \left(\frac{\lambda}{2}\right)^{p_{\tau}} X_{\tau}, \quad (15a)$$

\* E. G. Larson, thesis, Chemistry Department, MIT 1964.

with

$$X_\tau = \left\{ \prod_{\mu=1}^3 [1 + T_\mu^{ab}] \varphi_{a\tau\mu}(2\mu-1) \varphi_{b\tau\mu}(2\mu) \alpha(2\mu-1) \beta(2\mu) \right\}, \quad (15b)$$

where  $T_\mu^{ab}$  is an operator that permutes the orbital indices  $a\tau\mu$  and  $b\tau\mu$ , and  $p_\tau$  is the number of pairs  $\mu$  for which  $a\tau\mu$  and  $b\tau\mu$  are the same. This can be written as

$$X_\tau = \left\{ \sum_{r=1}^8 Q_r \left[ \prod_{\mu=1}^3 \varphi_{a\tau\mu}(2\mu-1) \varphi_{b\tau\mu}(2\mu) \alpha(2\mu-1) \beta(2\mu) \right] \right\}; \quad (15c)$$

the operators  $Q_r$  are just the terms in the expansion of the operator product

$$\prod_{\mu=1}^3 [1 + T_\mu^{ab}].$$

Expansion of the molecular orbitals  $\psi_{k_\nu}$  in Wannier functions by the inverse of Eq. (6) is also performed with the result

$$\begin{aligned} & \prod_{\nu=1}^3 [\psi_{k_\nu}(2\nu-1) \psi_{k_\nu}(2\nu) \alpha(2\nu-1) \beta(2\nu)] \\ &= 6^{-3} \sum_{a_1', a_2', a_3'} \sum_{b_1', b_2', b_3'} \prod_{\nu=1}^3 \exp\left[\frac{1}{3}(i\pi k_\nu)(a_\nu' + b_\nu')\right] \varphi_{a_\nu'}(2\nu-1) \varphi_{b_\nu'}(2\nu) \alpha(2\nu-1) \beta(2\nu). \end{aligned} \quad (16)$$

The matrix element can now be written

$$\begin{aligned} & \langle \Psi_A^{VB} | \Theta | \Psi^{MO} \rangle = [72(1+\lambda^2)]^{-3} \sum_\tau \left(\frac{1}{2}\lambda\right)^{p_\tau} \sum_{a_1', a_2', a_3'} \sum_{b_1', b_2', b_3'} \sum_r \sum_P (-1)^P \\ & \times \langle Q_r \prod_{\mu=1}^3 \{ \varphi_{a\tau\mu}(2\mu-1) \alpha(2\mu-1) \varphi_{b\tau\mu}(2\mu) \beta(2\mu) \} | \Theta | P \prod_{\nu=1}^3 \{ \exp\left[\frac{1}{3}(i\pi k_\nu)(a_\nu' + b_\nu')\right] \varphi_{a_\nu'}(2\nu-1) \alpha(2\nu-1) \varphi_{b_\nu'}(2\nu) \beta(2\nu) \} \rangle. \end{aligned} \quad (17)$$

Here  $P$  permutes the electron coordinates (1, ...6) in the expression to the right of it. From Eq. (15c) we recall that  $Q_r$  involves permutations of the pairs of orbital indices ( $a\tau\mu$ ,  $b\tau\mu$ ) in the left-hand part of the bracket. Since  $\Theta$  is a spinless operator, nonvanishing integrals can only arise from those permutations  $P$  which are products of permutations  $P_\alpha$  of odd-numbered electrons and permutations  $P_\beta$  of even-numbered electrons. Integrating over spin coordinates, we obtain

$$\langle Q_r \prod_{\mu=1}^3 \{ \varphi_{a\tau\mu}(2\mu-1) \varphi_{b\tau\mu}(2\mu) \} | \Theta | P_\alpha P_\beta \prod_{\nu=1}^3 \{ \exp\left[\frac{1}{3}(i\pi k_\nu)(a_\nu' + b_\nu')\right] \varphi_{a_\nu'}(2\nu-1) \varphi_{b_\nu'}(2\nu) \} \rangle \quad (18a)$$

for the element in angular brackets in Eq. (17). Since the spin has been removed, the permutations  $Q_r$  of orbital index pairs ( $a\tau\mu$ ,  $b\tau\mu$ ) are equivalent to permutations  $Q_r$  of electron coordinate pairs ( $2\mu-1$ ,  $2\mu$ ), in the left-hand part of the bracket. Since the integration variables are dummies, right and left hand parts may be multiplied through by  $Q_r^{-1}(=Q_r)$  so that (18a) is equal to

$$\left\langle \prod_{\mu=1}^3 [\varphi_{a\tau\mu}(2\mu-1) \varphi_{b\tau\mu}(2\mu)] | \Theta | \prod_{\nu=1}^3 \exp\left[\frac{1}{3}(i\pi k_\nu)(a_\nu' + b_\nu')\right] Q_r P_\alpha P_\beta \{ \varphi_{a_\nu'}(2\nu-1) \varphi_{b_\nu'}(2\nu) \} \right\rangle. \quad (18b)$$

We can rewrite (18b)

$$\prod_{\nu=1}^3 \exp\left[\frac{1}{3}(i\pi k_\nu)(a_\nu' + b_\nu')\right] \left\langle \prod_{\mu=1}^3 [\varphi_{a\tau\mu}(2\mu-1) \varphi_{b\tau\mu}(2\mu)] | \Theta | \prod_{\nu=1}^3 [\varphi_{a_\nu''}(2\nu-1) \varphi_{b_\nu''}(2\nu)] \right\rangle, \quad (18c)$$

if by the symbols ( $a_\nu''$ ,  $b_\nu''$ ) we mean that particular ordering of the original set ( $a_\nu'$ ,  $b_\nu'$ ) which is achieved by the variable permutation  $Q_r P_\alpha P_\beta$ , followed by ordering the functions according to their variables. For each ordered set ( $a_\nu''$ ,  $b_\nu''$ ) and each operator  $Q_r P_\alpha P_\beta$  there exists one and only one set ( $a_\nu'$ ,  $b_\nu'$ ) which is so related. By proper definition of inverse permutations  $\bar{P}_\beta^{-1} \bar{P}_\alpha^{-1} \bar{Q}_r^{-1}$  which work on the ordered indices in the exponential, (18c) can be written

$$\left[ \bar{P}_\beta^{-1} \bar{P}_\alpha^{-1} \bar{Q}_r^{-1} \prod_{\nu=1}^3 \{ \exp\left[\frac{1}{3}(i\pi k_\nu)(a_\nu'' + b_\nu'')\right] \} \right] \left\langle \prod_{\mu=1}^3 [\varphi_{a\tau\mu}(2\mu-1) \varphi_{b\tau\mu}(2\mu)] | \Theta | \prod_{\nu=1}^3 [\varphi_{a_\nu''}(2\nu-1) \varphi_{b_\nu''}(2\nu)] \right\rangle. \quad (18d)$$

The reader may easily verify the one-to-one correspondence between operators  $Q_r P_\alpha P_\beta$  and operators  $\bar{P}_\beta^{-1} \bar{P}_\alpha^{-1} \bar{Q}_r^{-1}$ . Matrix element (17) can then be written:

$$\langle \Psi_{\mathbf{A}}^{\text{VB}} | \theta | \Psi^{\text{MO}} \rangle = [72(1+\lambda^2)]^{-3} \sum_{\tau} (\lambda/2)^{p\tau} \sum_{\alpha_1', \alpha_2', \alpha_3'} \sum_{b_1', b_2', b_3'} \left[ \sum_{\tau} D^{\alpha}(Q_r) D^{\beta}(Q_r) \right] \\ \times \left\langle \prod_{\mu=1}^3 [\varphi_{a_{\tau\mu}}(2\mu-1) \varphi_{b_{\tau\mu}}(2\mu)] | \theta | \prod_{\nu=1}^3 [\varphi_{a_{\nu}}(2\nu-1) \varphi_{b_{\nu}}(2\nu)] \right\rangle, \quad (19)$$

where  $D^{\alpha}(Q_r')$  and  $D^{\beta}(Q_r')$  are determinants of  $3 \times 3$  matrices as follows:

$$D^{\alpha} = \begin{vmatrix} 1 & \exp(\pi i \alpha_1/3) & \exp(-\pi i \alpha_1/3) \\ 1 & \exp(\pi i \alpha_2/3) & \exp(-\pi i \alpha_2/3) \\ 1 & \exp(\pi i \alpha_3/3) & \exp(-\pi i \alpha_3/3) \end{vmatrix};$$

$D^{\beta}$  equivalently with (18')

$\beta_1, \beta_2, \beta_3$  and the numbers  $(\alpha_1, \alpha_2, \alpha_3; \beta_1, \beta_2, \beta_3)$  are generated from the numbers  $(a_1', a_2', a_3'; b_1', b_2', b_3')$  by the permutations  $Q_r$  which are the eight terms in the expansion of the operator product

$$\prod_{\nu=1}^3 [1 + T_{\nu}^{a/b'}].$$

Symmetries of various kinds permit extensive reduction of the task of computing these determinants; only a very few distinct ones exist, in this case four. In addition, by no means all of the integrals in Eq. (17) are nonzero. At most two indices in the set  $(a_{\nu}', b_{\nu}')$  may differ from their counterparts  $(a_{\tau\nu}, b_{\tau\nu})$ , for the case of the two-electron operators, one index for one-electron operators, and none for the overlap integral. For the sake of brevity we shall not further describe the calculation of these elements. The scheme is readily adaptable for machine computation; a machine algorithm which computes the coefficient of each power of  $\lambda$  in Eq. (17) may be devised for the  $2N$ -membered ring, the only practical limit being the size of the determinants  $D^{\alpha}(Q_r)$  as  $N$  increases.

### III. RESULTS OF CALCULATIONS

Computations were performed for interatomic distances of 1.0, 2.0, 3.0, and 5.0 Bohr radii. Integrals between atomic orbitals were computed by Mattheiss.<sup>2</sup> Nuclear repulsion energies must be included to obtain binding energies. A number of comparison calculations, made either by us or by others, are listed, together with the results of the MO-VB $\lambda$  method, in Table I. Energies are in atomic units (hartrees). At  $R \rightarrow \infty$  the true energy is  $-3.000$  a.u. The rows labeled VB $\lambda$  and MO refer to calculations using, respectively, the trial forms of Eqs. (8) and (5). In the cases of VB $\lambda$  and MO-VB $\lambda$  calculations the optimum value of  $\lambda$  is given in parentheses below the energy, for comparison. AMO refers to the calculation of Moskowitz,<sup>3</sup> while the row

labeled "exact" refers to the full configuration interaction study of Mattheiss.<sup>2</sup> The AMO and MO-VB $\lambda$  results are quite comparable in accuracy, the latter being a little better, as may be expected, at larger  $R$ , while the AMO method is slightly better at small  $R$ . We do not know exactly the amount of overlap between these two wavefunctions but they appear very similar in many respects. The MO-VB $\lambda$  form is not specific to alternant (two-sublattice) structures, as the AMO form is, a fact which suggests some differences between them.<sup>7</sup>

Table II shows the optimal parameters of the MO-VB $\lambda$  eigenfunction. Taking account of the non-orthogonality of  $\Psi^{\text{VB}}$  and  $\Psi^{\text{MO}}$ , we define the "fractional MO character" of the eigenfunction, as follows: Define  $\phi_0$ , the angle between  $\Psi^{\text{VB}}$  and  $\Psi^{\text{MO}}$ , by

$$\cos \phi_0 = | \langle \Psi^{\text{VB}} | \Psi^{\text{MO}} \rangle |, \quad 0 \leq \phi_0 \leq \frac{1}{2}\pi; \quad (20)$$

define  $\phi$ , the angle between the MO-VB $\lambda$  solution and  $\Psi^{\text{VB}}$ , by

$$\cos \phi = | \langle \Psi(\text{MO-VB}\lambda) | \Psi^{\text{VB}} \rangle |; \quad (21)$$

then the fractional MO character  $x$  is given by  $(\phi/\phi_0)$ . Some interesting results are displayed in Table II. The behavior of  $\lambda$  is quite different as a function of  $R$  from that for the VB $\lambda$  function alone (cf. Table I). It reaches a limiting value of about 0.4 as  $R$  decreases and thereafter the further "dissociation into ions" is accounted for by rapid growth in the MO character

TABLE I. Total energy of the hexagonal H<sub>6</sub> ring in various approximations. [Energies in atomic units (hartrees) as a function of lattice spacing,  $R$ , in  $a_0$ ]  $E(\infty) = -3.000$  a.u.

Method	$R=1.0$	$R=2.0$	$R=3.0$	$R=5.0$
MO (ground configuration)	-1.567 <sub>2</sub>	-3.181 <sub>2</sub>	-3.000 <sub>4</sub>	-2.527 <sub>7</sub>
VB $\lambda$ (value of $\lambda$ )	-0.760 <sub>4</sub> (0.90) <sub>2</sub>	-2.970 <sub>0</sub> (0.72) <sub>7</sub>	-3.062 <sub>2</sub> (0.50) <sub>2</sub>	-3.005 <sub>0</sub> (0.14) <sub>7</sub>
MO-VB $\lambda$ (value of $\lambda$ )	-1.578 <sub>8</sub> (0.49) <sub>8</sub>	-3.218 <sub>2</sub> (0.45) <sub>5</sub>	-3.115 <sub>6</sub> (0.38) <sub>5</sub>	-3.005 <sub>2</sub> (0.14) <sub>4</sub>
AMO [Ref. (3)]	-1.579 <sub>7</sub>	-3.222 <sub>0</sub>	-3.115 <sub>6</sub>	-3.003 <sub>9</sub>
Exact [Ref. (2)]	-1.601 <sub>0</sub>	-3.249 <sub>6</sub>	-3.146 <sub>2</sub>	-3.008 <sub>5</sub>

<sup>7</sup> We have made a reduction of the MO-VB $\lambda$  wavefunction in terms of coefficients of fundamental spin-orbital atomic configurations. We feel this information is not of sufficient interest for the space required to list it here, but it is available in Ref. 5 or on request from us.

TABLE II. Parameters of the MO-VB  $\lambda$  eigenfunction.

Parameter	$R=1.0$	2.0	3.0	5.0
$\lambda$ (ionic character in VB pairs)	0.49 <sub>8</sub>	0.45 <sub>6</sub>	0.38 <sub>3</sub>	0.14 <sub>4</sub>
$\cos \phi_0$ (MO-VB overlap)	0.640	0.614	0.565	0.375
$(\phi/\phi_0)$	0.929	0.778	0.436	0.003

parameter  $x$ ,  $\lambda$  remaining roughly constant. In the VB $\lambda$  method  $\lambda$  tends to 1.0 as  $R \rightarrow 0$ , in an attempt to simulate delocalization as much as possible. The VB $\lambda$  energy shows how inadequate such simulation is. The change in  $\cos \phi_0$  as a function of  $R$  is sufficiently gradual that we feel justified in saying that  $x$  can be interpreted as a direct index of "metallic" character in the electron wavefunction. The growth in  $x$  at intermediate  $R$  is gradual, even though the growth behavior of  $\lambda$  levels off at about 0.4. This supports the earlier conclusion of Mattheiss (2) that there is no sharp "critical distance" at which  $x$  changes rapidly, in the six-membered ring.

The MO and VB $\lambda$  descriptions are rather different accounts of electronic structure. The VB $\lambda$  wavefunction contains ionic character in a certain correlated sense. Limited configuration interaction in the MO scheme gives a very different sort of wavefunction. The claim that "both methods are equivalent" is clearly fallacious at this level of computational difficulty. This conclusion should be important to the theory of  $\pi$  electrons in aromatic systems (spin-density calculations, etc.).

The MO-VB $\lambda$  scheme enjoys a certain flexibility compared to the AMO method, because it does not require a two-sublattice system to be effective. This means that it can be applied to more general problems with the hope of giving useful results.

For the case of one-dimensional lattices (rings of atoms, applications to cyclic polyenes) it has long been noticed that there is a difference between those with  $4n+2$  and those with  $4n$  atoms. The latter systems have a triplet ground state, according to MO theory and also in AMO theory; but at least on a cursory examination it seems evident that the VB $\lambda$  ground state is a singlet. The comparison of the lowest MO-VB $\lambda$  triplet and singlet states for the  $4n$  system would make a worthwhile study.

It is clear that a minor modification of the MO-VB $\lambda$  scheme provides an elegant framework for studying bond alternation in cyclic polyenes, though the role of the  $\sigma$ -electrons in that problem seems to be a crucial one.<sup>8</sup>

The importance of valence bonds between nearest neighbor atoms at larger lattice spacings leads us to

<sup>8</sup> H. C. Longuet-Higgins and L. Salem, Proc. Roy. Soc. (London) **A251**, 172 (1959).

make the following conjectural remarks about the behavior of electrons in infinite lattices: Let us suppose the transition from "metallic" to "localized" electron structure<sup>9</sup> to be described by a shift from "MO"-like to "VB $\lambda$ "-like components, depicted in our scheme by the movement of  $x$  from 1 as  $R \rightarrow 0$ , to 0 as  $R \rightarrow \infty$ . All of the VB structures are interacting with each other and with the MO wavefunction, and as  $R$  increases the downward movement of  $x$  reflects the growing stability of the resonating VB structures, relative to the MO component. For the six-membered ring, this transition is gradual, and therefore it at least does not show the behavior suggested by Mott.<sup>1</sup> In our opinion, the same result will be true of any  $2N$ -membered ring, regardless of the value of  $N$ ; it is a characteristic of a *one-dimensional* lattice. We believe that in 2- and 3-dimensional lattices, on the other hand, sharp transitions of the type suggested by Mott can occur. The valence bond model suggests clearly that this is so; only the structures with nearest-neighbor-pair bonds are important. In the one-dimensional lattices, only the *two* "K $\ddot{u}$ kul $\acute{e}$ " structures thus contribute. By comparison, the number of important VB structures increases rapidly with the number of atoms in the two- and three-dimensional lattices. We have begun studies on finite models of the two-dimensional lattices, viz., the cube (eight atoms) and the icosahedron (12 atoms). For eight atoms the number of canonical singlet valence bond structures is 14 and the number of nearest-neighbor bond structures in the cube is 9; for 12 atoms the number of canonical singlets is 132 and in the icosahedron 125 of these have only nearest-neighbor bonds. The greater number of important structures makes it possible to have a sharp change in the form of the true solution as a function of  $R$ , given a set form for the behavior of any *one* VB $\lambda$  wavefunction with respect to the MO component. We hope to demonstrate this phenomenon for the case of the cube. Thus our conjecture is, that while in a one-dimensional lattice the wavefunction changes gradually from metallic to localized electron structure, in two- and three-dimensional lattices this change may be quite sharply defined at a critical spacing  $R_c$ , for reasons similar to those which make statistical phase transitions possible (as functions of  $T$ ) in two- and three-dimensional systems, but not in normal one-dimensional systems.

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<sup>9</sup> A common misconception about the language of "localized" versus "delocalized" electrons is that they are equivalent descriptions of a system. This is essentially true, as long as only the properties of the one-electron density matrix are considered; but the distinction is a crucial one for the correlation properties given by the two-electron density matrix.