

## Electronic structure of SiO<sub>2</sub>. I. Theory and sample calculations\*

Kwok Leung Yip<sup>†</sup> and W. Beall Fowler

Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015

(Received 4 February 1974)

An LCLO (linear combination of localized orbitals) cluster method using a small basis set is developed to calculate the electronic structure of SiO<sub>2</sub>. The localized orbitals are obtained by Kunz's approach to the Adams-Gilbert equation. The matrix elements of the Fock operator  $F_{\alpha\beta}$  are evaluated in Gilbert's version of extended Hückel theory, which involves expanding  $F_{\alpha\beta}$  in powers of overlap integrals and keeping only terms of first order. Molecular orbitals and energy levels for a chosen cluster representing the solid system are then calculated by solving a secular equation. This paper discusses our approach, which involves no disposable parameters, compares it with other recent modifications to extended Hückel theory, and presents results of sample calculations on H<sub>2</sub> and H<sub>2</sub>O molecules for the purpose of testing our method and computer programming.

### I. INTRODUCTION

This is the first of two papers on the electronic structure of SiO<sub>2</sub>. In this paper we discuss the theory involved in the calculation and give the results of sample calculations on H<sub>2</sub> and H<sub>2</sub>O molecules. In the following paper we shall present and discuss the results on SiO<sub>2</sub>; comparisons with other calculations and with various experiments will also be given.

We have developed a new technique in the form of an LCLO-MO [(linear combination of localized orbitals)-(molecular orbital)] model for calculating the electronic structure of complex solid systems such as SiO<sub>2</sub>. This method is based on Gilbert's version of extended Hückel (EH) theory,<sup>1</sup> called the "KO (kinetic-energy overlap) approximation," which is derived from an overlap expansion of the Fock matrix for localized orbitals obtained by solving the Adams-Gilbert equation.<sup>2,3</sup> Gilbert's version involves several significant improvements over the conventional EH theory<sup>4</sup>: (i) Localized orbitals (LO's) are used instead of the usual Slater-type atomic orbitals. The LO's, calculated in a crystalline environment, form a better basis set than do atomic orbitals. (ii) Matrix elements of the Fock operator are calculated directly, not by guessing. (iii) A certain amount of self-consistency is included in the calculation.

In Sec. II we briefly discuss the concept of localized orbitals and the Adams-Gilbert equation for the LO's and describe the method of solution of the equation. The Gilbert KO approximation is derived in Sec. III, where the matrix elements of the Fock operator are given explicitly. In Sec. IV we formulate the LCLO-MO method to calculate the MO energies and MO coefficients for polyatomic systems. In Sec. V we discuss the open-shell approximation made for the systems consisting of open-shell atoms such as H<sub>2</sub> and H<sub>2</sub>O molecules. The

results of calculations on these simple molecules are presented in Sec. VI. Finally, conclusions are given in Sec. VII.

### II. ADAMS-GILBERT EQUATION

Adams<sup>2</sup> and Gilbert<sup>3</sup> have shown that it is possible to derive a rigorous extension to the Hartree-Fock (HF) equation in order to obtain localized orbitals, which may be regarded as atomiclike orbitals associated with each of the constituent atoms in any polyatomic system of closed-shell atoms. In doing this, one can introduce a "localizing potential,"  $\rho U'_a \rho$ , in the HF equation to obtain the following pseudoeigenvalue equation, usually called the Adams-Gilbert equation

$$(F - \rho U'_a \rho) |ai\rangle = \epsilon_{ai} |ai\rangle, \quad (1)$$

where  $F$  is the Fock operator,  $\rho$  is the density operator,  $|ai\rangle$  are the localized orbitals associated with the  $a$ th nucleus,  $\epsilon_{ai}$  are the eigenvalues, and  $U'_a$  is an arbitrary one-electron operator, chosen to obtain localized orbitals. In Eq. (1),  $\rho$  is defined as

$$\rho = \sum_{ai, bj} |ai\rangle S_{ai, bj}^{-1} \langle bj|, \quad (2)$$

where the summation is over all occupied orbitals, and  $S^{-1} = [S_{ai, bj}^{-1}]$  is the inverse of the overlap matrix  $S = [S_{ai, bj}] \equiv [\langle ai|bj\rangle]$ . We can obtain  $S_{ai, bj}^{-1}$  by using the Löwdin expansion<sup>1</sup>

$$S_{ai, bj}^{-1} = 2\delta_{ai, bj} - S_{ai, bj} + \sum_{ck} (1 - \delta_{ca})(1 - \delta_{cb}) S_{ai, ck} S_{ck, bj} + \dots \quad (3)$$

In order to solve Eq. (1), we proceed as follows: We use Kunz's technique<sup>5</sup> to simplify Eq. (1) by expanding the localizing potentials  $\rho U'_a \rho$  in powers

of the interatomic overlaps and retaining only the lowest order terms:

$$\rho U'_a \rho |ai\rangle \simeq \sum_k \langle ak | U'_a | ai \rangle |ak\rangle. \quad (4)$$

The Fock operator is written as the sum

$$F = F_a + U_a, \quad (5)$$

where  $F_a$  is the Fock operator for the  $a$ th atom and  $U_a$  is the atomic environment potential.

With the choice of  $U'_a = U_a$  and the use of Eqs. (4) and (5), the Adams-Gilbert equation becomes

$$(F_a + U_a - \epsilon_{ai}) |ai\rangle \simeq \sum_k \langle ak | U_a | ai \rangle |ak\rangle, \quad (6)$$

in which

$$\begin{aligned} F_a = & -\frac{1}{2}\nabla^2 - Z_a/|\vec{r} - \vec{R}_a| \\ & + 2 \sum_j \int |\vec{r} - \vec{r}'|^{-1} |aj(\vec{r}')\rangle \langle aj(\vec{r}')| d\vec{r}' \\ & - \sum_j |aj(\vec{r}')\rangle \langle aj(\vec{r}')| |\vec{r} - \vec{r}'|^{-1}, \end{aligned} \quad (7)$$

$$\begin{aligned} \left( -\frac{1}{2}\nabla^2 - \frac{Z_a}{|\vec{r} - \vec{R}_a|} + 2 \sum_j \int \varphi_{aj}^2(\vec{r}') |\vec{r} - \vec{r}'|^{-1} d\vec{r}' - \sum_b' \frac{Z_b}{|\vec{r} - \vec{R}_b|} + 2 \sum_{bj}' \int \varphi_{bj}^2(\vec{r}') |\vec{r} - \vec{r}'|^{-1} d\vec{r}' - \epsilon_{ai} \right) \\ \times \varphi_{ai}(\vec{r}) - \sum_j \varphi_{aj}(\vec{r}) \int \varphi_{aj}^*(\vec{r}') \varphi_{ai}(\vec{r}') |\vec{r} - \vec{r}'|^{-1} d\vec{r}' \\ = \sum_k \varphi_{ak}(\vec{r}) \int \left[ \varphi_{ak}^*(\vec{r}') \varphi_{ai}(\vec{r}') \left( -\sum_b' \frac{Z_b}{|\vec{r} - \vec{R}_b|} + 2 \sum_{bj}' \int \varphi_{bj}^2(\vec{r}') |\vec{r} - \vec{r}'|^{-1} d\vec{r}' \right) \right] d\vec{r}'. \end{aligned} \quad (9)$$

This is the localized-orbital equation which we will solve iteratively for each atom at inequivalent sites in the polyatomic system.

Equation (9) is to be solved by the Roothaan analytic expansion method.<sup>6</sup> By taking only the spherically symmetric part of  $U_a$ , we may assume the one-electron solution to Eq. (9) to be of the form

$$|ai\rangle \equiv \varphi_{nlms}(\vec{r}) = R_{nl}(r) Y_l^m(\theta, \varphi) X(s), \quad (10)$$

where  $R_{nl}$ 's are radial functions,  $Y_l^m$ 's are spherical harmonics,  $X$ 's are spin functions, and  $(nlm)$ 's are quantum numbers.<sup>7</sup>

Then we assume the normalized radial functions,  $rR_{nl}(r)$  to be in analytic form

$$rR_{nl}(r) = \sum_j C_{jni} N_{ij} r^{l+1+A_{ij}} e^{-Z_{ij}r}, \quad (11)$$

where  $N_{ij}$  is a normalization constant and can be expressed in terms of the parameters  $A_{ij}$  and  $Z_{ij}$ ,

$$N_{ij} = [(2Z_{ij})^{2l+2A_{ij}+3}/(2l+2A_{ij}+2)!]^{1/2} \quad (12)$$

Given the values of  $A_{ij}$ 's and  $Z_{ij}$ 's, we can solve Eq. (9) self-consistently for  $C_{jni}$ 's and  $\epsilon_{ni}$ 's ( $\epsilon_{ni} \equiv \epsilon_{ai}$ ) by a matrix diagonalization technique. Instead of using a full variational method, we obtain  $A_{ij}$  and  $Z_{ij}$  from prior calculations.

and

$$\begin{aligned} U_a \simeq & -\sum_b' \frac{Z_b}{|\vec{r} - \vec{R}_b|} \\ & + 2 \sum_{bj}' \int |\vec{r} - \vec{r}'|^{-1} |bj(\vec{r}')\rangle \langle bj(\vec{r}')| d\vec{r}', \end{aligned} \quad (8)$$

where  $Z_a$  is the atomic number of the  $a$ th nucleus,  $\vec{r} - \vec{R}_a$  is the radial vector of the electron from the  $a$ th nucleus, and the prime on the sum indicates that the term  $a=b$  is omitted. Here we use atomic units in which  $e = m = \hbar = 1$ , the unit of length is the Bohr radius and the unit of energy is the Hartree. Eq. (8) contains only the essential terms of  $U_a$  which must be retained in Eq. (6) for consistency to first order in overlap.

With the explicit expressions for  $F_a$  and  $U_a$ , we may rewrite Eq. (6) as

### III. GILBERT'S KO APPROXIMATION

The first step in deriving the Gilbert KO approximation is to analyze the Fock operator  $F$  for a system which is composed of closed-shell atoms. If the total state of the system is nondegenerate,  $F$  is uniquely determined by the density operator  $\rho$  [Eq. (2)]:

$$\begin{aligned} F = & -\frac{1}{2}\nabla^2 + \sum_a \frac{-Z_a}{|\vec{r} - \vec{R}_a|} \\ & + 2 \int |\vec{r} - \vec{r}'|^{-1} \rho(\vec{r}', \vec{r}') d\vec{r}' - \rho(\vec{r}, \vec{r}')/|\vec{r} - \vec{r}'|. \end{aligned} \quad (13)$$

In Eq. (13),  $F$  consists of four terms: the kinetic energy, the Coulomb field of the nuclei, the electronic Coulomb potential, and the exchange potential, which will be denoted by  $T$ ,  $V^Z$ ,  $V^C[\rho]$ , and  $V^E[\rho]$ , respectively.

We then rewrite  $\rho$  as the sum

$$\rho = \sum_a \rho_a + \sum_a \delta\rho_a + \sum_{ab, a \neq b} \rho_{ab}, \quad (14)$$

where  $\rho_a$ ,  $\delta\rho_a$ , and  $\rho_{ab}$  are the atomic density operator, the intra-atomic overlap density operator, and a component of the interatomic overlap density operator, respectively, and are defined by the fol-

lowing equations:

$$\rho_a = \sum_i |ai\rangle\langle ai|, \quad (15)$$

$$\delta\rho_a = \sum_{ij} |ai\rangle(S_{ai}^{-1} - \delta_{ij})\langle aj|, \quad (16)$$

$$\rho_{ab} = \sum_{ij} |ai\rangle S_{ai, bj}^{-1} \langle bj|. \quad (17)$$

By using Eq. (3) for  $S_{ai, bj}^{-1}$  and by omitting terms of second order in the overlap, we can obtain the following expansions:

$$\delta\rho_a \approx - \sum_{ij}' |ai\rangle S_{ai, aj} \langle aj| = 0, \quad (18)$$

$$\rho_{ab} \approx - \sum_{ij} |ai\rangle S_{ai, bj} \langle bj|. \quad (19)$$

These expansions will be used to analyze the matrix elements of the Fock operator in terms of the powers of the overlap integral.

In order to evaluate the one-center matrix elements of the Fock operator, we make the same separation for  $F$  as before [Eq. (5)]

$$F = F_a + U_a.$$

For calculating two-center matrix elements, we may use the following separation:

$$F = F_a + F_b + U_{ab} - T, \quad (20)$$

where  $U_{ab}$  is the environment potential of the  $a$ th and the  $b$ th atoms (it includes the electronic Coulomb and exchange interactions between the two atoms).

Next we use the localized orbitals defined by the Adams-Gilbert equation to evaluate the matrix elements of the Fock operator. From Eq. (1) (with  $F = F_a + U_a$  and  $U'_a = U_a$ )

$$(F_a + U_a - \rho U_a \rho) |ai\rangle = \epsilon_{ai} |ai\rangle, \quad (21)$$

and the projection properties of  $\rho$  and  $\rho U_a \rho$

$$\rho |ai\rangle = |ai\rangle \quad (22)$$

$$\langle ai | \rho U_a \rho |bj\rangle = \langle ai | U_a |bj\rangle, \quad (23)$$

we obtain the following relations:

$$\langle ai | F_a |aj\rangle = \epsilon_{ai} \delta_{ij} \quad (24)$$

$$\langle ai | F_a |bj\rangle = \epsilon_{ai} S_{ai, bj} \quad (25)$$

$$\langle ai | F_b |bj\rangle = \epsilon_{bj} S_{ai, bj}. \quad (26)$$

Using Eqs. (5) and (24), the one-center matrix elements of the Fock operator between LO's may be written as

$$\langle ai | F |aj\rangle = \epsilon_{ai} \delta_{ij} + \langle ai | U_a |aj\rangle. \quad (27)$$

Similarly, using Eqs. (20), (25), and (26), the two-center matrix elements of  $F$  become

$$\begin{aligned} \langle ai | F |bj\rangle &= S_{ai, bj}(\epsilon_{ai} + \epsilon_{bj}) + \langle ai | U_{ab} |bj\rangle \\ &\quad - \langle ai | T |bj\rangle. \end{aligned} \quad (28)$$

The KO approximation consists of expanding  $\langle ai | U_a |aj\rangle$  and  $\langle ai | U_{ab} |bj\rangle$  in powers of overlap integrals and discarding terms of second and higher order in the overlap.

To evaluate  $\langle ai | U_a |aj\rangle$ , we rewrite Eq. (8) as

$$\begin{aligned} U_a &\approx \sum_b' \frac{N_b - Z_b}{|\vec{r} - \vec{R}_b|} \\ &\quad + \sum_{bj}' \int \frac{2|bj(\vec{r}')\rangle\langle bj(\vec{r}')| - N_b \delta(\vec{r}' - \vec{R}_b)}{|\vec{r} - \vec{r}'|} d\vec{r}' \\ &= V_a^{\text{PI}} + \sum_b' V_b^0, \end{aligned} \quad (29)$$

where  $N_b$  is the effective nuclear charge of the  $b$ th nucleus,  $V_a^{\text{PI}}$  is the Madelung potential of the system having the  $a$ th ion removed (the point-ion potential), and  $V_b^0$  is the screened Coulomb potential produced by the  $b$ th ion (or atom). In the case of ionic systems, where  $N_b \neq Z_b$ , the Madelung potential will be the dominant term. The matrix elements  $\langle ai | V_b^0 |ai\rangle$  and  $\langle ai | V_b^0 |aj\rangle$  can be shown to be of second order or higher in the overlap. Therefore, we obtain

$$\langle ai | U_a |aj\rangle \approx \langle ai | V_a^{\text{PI}} |aj\rangle. \quad (30)$$

for the one-center matrix elements of the atomic environment potential, and

$$\langle ai | F |aj\rangle = \delta_{ij} \epsilon_{ai} + \langle ai | V_a^{\text{PI}} |aj\rangle \quad (31)$$

for the one-center matrix elements of the Fock operator.

Similar analysis shows that there are only two terms in  $U_{ab}$  which can give first-order (in the overlap) contributions to the matrix elements of  $\langle ai | U_{ab} |bj\rangle$ , namely, the Madelung potential  $V_{ab}^{\text{PI}}$  of the system having the  $a$ th and  $b$ th ions removed, and the exchange interaction  $V_{ab}^E$  between the  $a$ th and  $b$ th atoms (or ions). By using the following relation for  $V_{ab}^E$ ,

$$V_{ab}^E = V^E[\rho_{ab}] = -\rho_{ab}(\vec{r}, \vec{r}')/|\vec{r} - \vec{r}'| \quad (32)$$

and the expansion (19) for  $\rho_{ab}$ , we obtain

$$\langle ai | V_{ab}^E |bj\rangle \approx S_{ai, bj}/|\vec{R}_a - \vec{R}_b|, \quad (33)$$

where  $\vec{R}_a$  and  $\vec{R}_b$  are the position vectors of the  $a$ th and the  $b$ th nuclei, respectively.

Therefore, we have

$$\langle ai | U_{ab} |bj\rangle \approx \langle ai | V_{ab}^{\text{PI}} |bj\rangle + S_{ai, bj}/|\vec{R}_a - \vec{R}_b| \quad (34)$$

for the two-center matrix elements of  $U_{ab}$ , and

$$\begin{aligned} \langle ai|F|bj\rangle &\simeq S_{ai,bj}(\epsilon_{ai} + \epsilon_{bj} + 1/|\vec{R}_a - \vec{R}_b|) \\ &+ \langle ai|V_{ab}^{\text{PI}}|bj\rangle - \langle ai|T|bj\rangle \end{aligned} \quad (35)$$

for the two-center matrix elements of the Fock operator.

For systems with ions at points of high symmetry, the matrix elements  $\langle ai|V_a^{\text{PI}}|aj\rangle$  and  $\langle ai|V_{ab}^{\text{PI}}|bj\rangle$  can be approximated by

$$\langle ai|V_a^{\text{PI}}|aj\rangle \simeq \delta_{ij} V_a^{\text{PI}}(\vec{R}_a), \quad (36)$$

$$\langle ai|V_{ab}^{\text{PI}}|bj\rangle \simeq S_{ai,bj} V_{ab}^{\text{M}}(\vec{R}_M), \quad (37)$$

where  $V_a^{\text{PI}}(\vec{R}_a)$  is the Madelung potential at the point  $\vec{R}_a$ , and  $V_{ab}^{\text{M}}(\vec{R}_M)$  is the Madelung potential at the midpoint  $\vec{R}_M$  between the two missing ions.

With Eqs. (36) and (37), the matrix elements of the Fock operator become

$$\langle ai|F|aj\rangle = \delta_{ij} [\epsilon_{ai} + V_a^{\text{PI}}(\vec{R}_a)], \quad (38)$$

$$\begin{aligned} \langle ai|F|bj\rangle &= S_{ai,bj}(\epsilon_{ai} + \epsilon_{bj} + 1/|\vec{R}_a - \vec{R}_b| + V_{ab}^{\text{M}}(\vec{R}_M)) \\ &- \langle ai|T|bj\rangle. \end{aligned} \quad (39)$$

These equations are usually called the Gilbert KO approximation because the only molecular integrals appearing are the kinetic energy and overlap integrals.

It should be noted that the matrix elements obtained in the KO approximation contain no adjustable parameters. This is in contrast with conventional EH theory.<sup>4</sup> For example, Wolfsberg and Helmholz<sup>8</sup> have proposed the following form for the elements  $\langle ai|F|bj\rangle$ :

$$\langle ai|F|bj\rangle = \frac{1}{2} K_{ai,bj} (\langle ai|F|ai\rangle + \langle bj|F|bj\rangle) S_{ai,bj} \quad (40)$$

with the quantity  $K_{ai,bj}$  set equal to 1.75. By equating the right-hand sides of Eqs. (39) and (40), we may compute effective values of the parameters  $K_{ai,bj}$  and compare them with the value 1.75.

Several authors have recently proposed alternatives to conventional EH theory.<sup>9-11</sup> In substance, these all involve calculation of the two-center kinetic-energy matrix elements and parametrization of the remainder. For example, Newton *et al.*<sup>9</sup> have proposed the form

$$\begin{aligned} \langle ai|F|bj\rangle &= \langle ai|T|bj\rangle \\ &+ \frac{1}{2} K' S_{ai,bj} (\langle ai|V|ai\rangle + \langle bj|V|bj\rangle), \end{aligned}$$

where the  $V$ 's are the potential-energy parts of the diagonal elements of  $F$ . It is found that the kinetic-energy elements do not scale well with overlap, while the potential-energy elements do; this permits a reasonable choice for  $K'$  to be made in one of several ways. Results obtained with these modifications have been encouraging.<sup>9-11</sup>

The Gilbert approach may be compared with these approaches, in that the total  $F$  element is not assumed to be proportional to overlap and that a kinetic-energy element is explicitly included. The chief difference is that the Gilbert approach is derived directly from Hartree-Fock theory with no disposable parameters, while the other alternatives<sup>9-11</sup> still involve parameters  $K'$ , whose values must be guessed, or estimated from more exact calculations on smaller systems. Some of the approximations made in the derivation of the Gilbert approach may be theoretically tested (such as expansion in powers of overlap); however, its application to open-shell systems requires empirical validation.

#### IV. LINEAR COMBINATION OF LOCALIZED ORBITALS (LCLO)

It is noted that in the Adams-Gilbert equation [Eq. (21)]

$$(F_a + U_a - \rho U_a \rho) |ai\rangle = \epsilon_{ai} |ai\rangle,$$

the localized orbitals  $|ai\rangle$  are eigenfunctions of the effective Hamiltonian  $F_a + U_a - \rho U_a \rho$ , but not eigenfunctions of the Fock operator  $F$  which is equal to  $F_a + U_a$ , and the eigenvalues  $\epsilon_{ai}$  have no direct physical meaning. In order to obtain the molecular orbitals and energy levels for a polyatomic system, we may construct the MO's  $|\psi_i\rangle$  from linear combinations of the localized orbitals associated with each atom in the system

$$|\psi_i\rangle = \sum_{\beta} C_{i\beta} |\beta\rangle, \quad (41)$$

where  $|\beta\rangle = |ai\rangle = \text{LO's}$ .

For each  $|\psi_i\rangle$ , the average energy  $E_i$  is calculated,

$$E_i = \langle \psi_i | F | \psi_i \rangle / \langle \psi_i | \psi_i \rangle \quad (42)$$

and the coefficients  $C_{i\beta}$  are varied to minimize  $E_i$ , so that  $\partial E_i / \partial C_{i\beta} = 0$ . This leads to a system of linear equations

$$\sum_{\beta} (F_{\alpha\beta} - E_i S_{\alpha\beta}) C_{i\beta} = 0, \quad (43)$$

where  $F_{\alpha\beta} = \langle \alpha | F | \beta \rangle$  and  $S_{\alpha\beta} = \langle \alpha | \beta \rangle$ , from which the  $C_{i\beta}$  are calculated. The condition that these equations are soluble provides the secular equation

$$|F_{\alpha\beta} - E_i S_{\alpha\beta}| = 0, \quad (44)$$

from which the energy levels  $E_i$  are obtained.

It is noted that the present LCLO-MO method is very similar to the conventional LCAO-MO method except that localized orbitals will be used as basis functions rather than the Slater-type atomic orbitals in forming the molecular orbitals.

## V. OPEN-SHELL APPROXIMATION

So far, the Adams-Gilbert equation and the Gilbert KO approximation are derived only for systems of closed-shell atoms or ions. Recently, Schlosser<sup>12</sup> has generalized the Adams-Gilbert approach for constructing localized orbitals to open-shell atomic systems. He then made use of the open-shell generalization of the Adams-Gilbert equation to derive the EH approximation for open-shell polyatomic systems.<sup>13</sup> These generalizations of the Adams-Gilbert equation and Gilbert's KO approximation to open-shell systems involve a more complex mathematical formulation and computational difficulties. From a mathematical point of view, they are not in a convenient form for practical calculation.

Alternatively, Kunz<sup>14</sup> has extended the Adams-Gilbert local-orbital theory to open-shell atomic systems using the symmetry and equivalence ideas introduced into atomic HF theory by Nesbet.<sup>15</sup> Basically, the method involves solving the same localized-orbital equation [Eq. (9), written in integrated form for the open  $l$  shell], for the open  $l$  shell for the atom as well as for the filled  $l$  shells. It is obvious that Kunz's technique is more computationally viable than Schlosser's generalization for solid-state calculations. Therefore, for systems of open-shell atoms such as SiO<sub>2</sub>, we shall use Kunz's open-shell approach to obtain the localized orbitals. Gilbert's KO approximation will then be used to calculate the matrix elements of the Fock operator. Finally, the LCLO-MO method will be employed to obtain the molecular orbitals and energy levels. Because in an *ab initio* treatment of the open-shell case there will be interaction terms which do not decrease as powers of overlap, the accuracy of the present approach is not easily assessed except by experience. In order to empirically test this open-shell approximation, then, we perform test calculations on H<sub>2</sub> and H<sub>2</sub>O molecules which consist of open-shell atoms. The results of these sample calculations, which are presented in the following section, will be used to help justify our open-shell approximation.

TABLE I. Values of  $A_{lj}$ ,  $Z_{lj}$ , and  $C_{jnl}$  for free H and for H in H<sub>2</sub>.<sup>a</sup> ( $l=0$  for the 1s level of the hydrogen atom.)

$j$	$A_{0j}$	$Z_{0j}$	Free hydrogen atom	
			$C_{10j}$	Hydrogen in H <sub>2</sub>
1	0	1.0	0.998 361	0.790 337
2	0	1.2	0.001 676	0.211 750

<sup>a</sup> $A_{lj}$ ,  $Z_{lj}$ , and  $C_{jnl}$  are defined in Sec. II.

VI. LCLO CALCULATIONS FOR H<sub>2</sub> AND H<sub>2</sub>OA. H<sub>2</sub> molecule

First, we use Roothaan's analytic expansion technique to solve the localized-orbital equation [Eq. (9)] for self-consistent localized orbitals. Using the Hartree notation,<sup>16</sup> we can transform the localized orbital equation into integral form. For the 1s orbital of hydrogen (H), we have

$$\epsilon_{1s} = K_{1s} + F^0(1s, 1s) - G^0(1s, 1s) + V_{1s}, \quad (45)$$

where  $V_{1s} = \langle 1s | U_a | 1s \rangle$ , and  $U_a$  is the atomic environment potential. For the free hydrogen atom  $U_a = 0$ , and for hydrogen in H<sub>2</sub>,

$$U_a \approx 2 \int \phi_{1s}^2(\vec{r}') | \vec{r} - \vec{r}' |^{-1} d\vec{r}'. \quad (46)$$

It is noted that only the spherically symmetric part of  $U_a$  will be used throughout the calculations.

Calculations were performed for the free hydrogen atom as well as for hydrogen in H<sub>2</sub>. The internuclear distance of H<sub>2</sub> was set equal to 1.5 bohr.<sup>17</sup> The values for  $A_{lj}$  and  $Z_{lj}$  defined in Sec. II were obtained from previous calculations.<sup>17</sup> In Table I, we specify the values of the parameters  $A_{lj}$  and  $Z_{lj}$ , and also give the self-consistent values of the  $C_{jnl}$  for the free hydrogen atom and for hydrogen in H<sub>2</sub>. In Table II, the one-electron eigenvalues  $\epsilon_{nl}$ , the expectation values of the atomic environment potential  $U_a$  and the Fock operator  $F$  are given for the systems

$$V_{nl} = \langle nl | U_a | nl \rangle, \quad (47)$$

$$\epsilon_{nl, n'l'} = \delta_{ll'} \langle nl | F | n'l' \rangle. \quad (48)$$

Next, we use the calculated localized orbitals and eigenvalues for H<sub>2</sub> to evaluate the corresponding matrix elements of the Fock operator by applying Gilbert's version of EH theory. The matrix elements  $\langle ai | U_a | aj \rangle$  given in Eq. (27) were calculated by using only the spherically symmetric part of  $U_a$  given in Eq. (46), and the matrix elements  $\langle ai | U_{ab} | bj \rangle$  given in Eq. (28) were obtained from Eq. (34) by neglecting the Madelung potential term  $\langle ai | V_{ab}^P | bj \rangle$ .

TABLE II. Values of  $\epsilon_{nl}$ ,  $V_{nl}$ , and  $\epsilon_{nl, n'l'}$  for free H and for H in H<sub>2</sub>.<sup>a</sup>

Energy parameters		
(Ry)	Free hydrogen atom	Hydrogen in H <sub>2</sub>
$\epsilon_{1s}$	-1.000 000	-0.998 257
$V_{1s}$	0.000 000	-0.190 152
$\epsilon_{1s, 1s}$	-1.000 000	-1.188 409

<sup>a</sup> $\epsilon_{nl}$ ,  $V_{nl}$ , and  $\epsilon_{nl, n'l'}$  are defined in Eqs. (45), (47), and (48), respectively.

TABLE III. Ground electronic state of  $H_2$  calculated by the LCLO method.

Molecule	MO Symmetry	Internuclear distance $R$ (bohr)	Matrix elements of the Fock operator (eV)		WH <sup>a</sup> Parameter $K$	Molecular energy $E$ (eV)	Normalized wave-function coefficients		Calculated dissociation energy $D_e$ (eV)	Experimental dissociation energy $D_e$ (eV)
			$F_{aa}$	$F_{ab}$			$C_a$	$C_b$		
$H_2$	$\sigma_g$	1.5	-16.1693	-11.7740	1.03 <sup>b</sup>	-16.3570	0.5410	0.5410	3.03	4.75 <sup>c</sup>

<sup>a</sup> Reference 8.<sup>b</sup> Obtained by Eq. (40).<sup>c</sup> From Ref. 18.

The LCLO-MO method is then employed to obtain the MO coefficients and MO energies. The results for the ground state of  $H_2$  are presented in Table III. In Table III, the ground state molecular orbital  $|\psi\rangle$  and energy level  $E$  for the  $H_2$  molecule are given by

$$|\psi\rangle = C_a |1s_a\rangle + C_b |1s_b\rangle, \quad (49)$$

$$E = \frac{F_{aa} + F_{ab}}{1 + S_{ab}}, \quad (50)$$

where  $|1s_a\rangle$  and  $|1s_b\rangle$  are the localized  $1s$  orbitals centered on the atoms  $a$  and  $b$  in the molecule, respectively.  $C_a$  and  $C_b$  are MO coefficients,  $F_{aa} = \langle 1s_a | F | 1s_a \rangle$ ,  $F_{ab} = \langle 1s_a | F | 1s_b \rangle$  and  $S_{ab} = \langle 1s_a | 1s_b \rangle$ . In calculating the corresponding dissociation energy  $D_e$  of the molecule, we have assumed that at  $R = \infty$ , where  $R$  is the internuclear distance, the total energy  $E_\infty$  of  $H_2$  is  $-2$  Ry such that

$$D_e = E_\infty - E_{\text{tot}}, \quad (51)$$

in which  $E_{\text{tot}}$  is the total energy of the system given by

$$E_{\text{tot}} = \sum_i [E_i + I(i, i)] + N, \quad (52)$$

where  $E_i$  is the molecular energy of the  $i$ th molecular orbital,  $I(i, i)$  is the corresponding one-electron integral, and  $N$  is the nuclear repulsion energy at the observed value of  $R$ .

It can be seen from Table III that the dissociation energy for the  $H_2$  molecule calculated by the present method (3.03 eV) is not in good agreement with the experimental data<sup>18</sup>; however, it is in fair agreement with the value 3.64 eV obtained by Hartree-Fock theory,<sup>19</sup> which is a more important comparison to make.

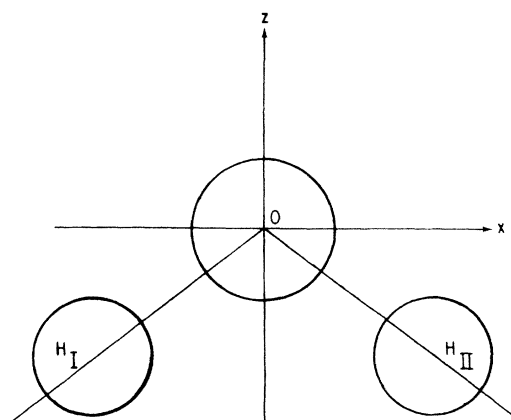


FIG. 1. Coordinate system for the water molecule. The  $y$  axis is perpendicular to the molecular plane (inward).

TABLE IV. Basis orbitals<sup>a</sup> used for the LCLO Calculation on H<sub>2</sub>O.

<i>j</i>	<i>A</i> <sub>0<i>j</i></sub>	<i>Z</i> <sub>0<i>j</i></sub>	For oxygen orbitals				For hydrogen orbital				
			<i>A</i> <sub>1<i>j</i></sub>	<i>Z</i> <sub>1<i>j</i></sub>	<i>C</i> <sub><i>j</i>10</sub>	<i>C</i> <sub><i>j</i>20</sub>	<i>C</i> <sub><i>j</i>21</sub>	<i>j</i>	<i>A</i> <sub>0<i>j</i></sub>	<i>Z</i> <sub>0<i>j</i></sub>	<i>C</i> <sub><i>j</i>10</sub>
1	0	7.66	0	2.21	0.997 391	0.248 513	0.967 507	1	0	1.27	0.116 337
2	1	2.25	0	2.275	0.011 092	-1.027 811	0.325 09	2	0	1.00	-1.113 609
$\epsilon_{1s} = -41.279 533^b$			$V_{1s} = -0.170 016$			$\epsilon_{1s,1s} = -41.449 549$			$\epsilon_{1s} = -0.999 066$		
$\epsilon_{2s} = -2.320 102$			$V_{2s} = -0.264 129$			$\epsilon_{2s,2s} = -2.584 231$			$V_{1s} = -0.412 903$		
$\epsilon_{2p} = -1.019 838$			$V_{2p} = -0.261 864$			$\epsilon_{2p,2p} = -1.281 702$			$\epsilon_{1s,1s} = -1.411 969$		

<sup>a</sup>*A*<sub>1*j*</sub>, *Z*<sub>1*j*</sub>, and *C*<sub>*j**nl*</sub> are defined in Sec. II.

<sup>b</sup> $\epsilon_{nl}$ , *V*<sub>*nl*</sub>, and  $\epsilon_{nl,nl}$  are in rydbergs.  $\epsilon_{nl}$  are defined by Eqs. (56)–(58); *V*<sub>*nl*</sub> and  $\epsilon_{nl,nl}$  are defined by Eqs. (47) and (48), respectively.

### B. H<sub>2</sub>O molecule

In the ground state, the water molecule has a triangular configuration in which the H-O-H angle is about 104.5° and the H-O bond length is 1.81 bohr. As in Fig. 1, we shall take the plane of the molecule to be the *zx* plane, the *z* axis being the bisector of the angle between the two O-H bonds, and the oxygen being at the origin. If we regard the *z* axis as an axis of rotation, the symmetry operations form the point group *C*<sub>2*v*</sub>.

By taking linear combinations of those symmetry orbitals which transform according to the same irreducible representation, we obtain the following set of molecular orbitals<sup>20</sup>:

$$|\psi_{a_1}\rangle = C_1|O 1s\rangle + C_2|O 2s\rangle + C_3|O 2p_z\rangle + C_4[2(1+S')]^{-1/2}(|H_I 1s\rangle + |H_{II} 1s\rangle), \quad (53)$$

$$|\psi_{b_1}\rangle = C_1|O 2p_x\rangle + C_2[2(1-S')]^{-1/2}(|H_I 1s\rangle - |H_{II} 1s\rangle), \quad (54)$$

$$|\psi_{b_2}\rangle = C_1|O 2p_y\rangle \quad (55)$$

where *C*'s are MO coefficients subject to conditions of normalization and orthogonality, and *S*' =  $\langle H_I 1s | H_{II} 1s \rangle$ . The basis orbitals |*O* 1*s*⟩, etc. in Eqs. (53)–(55) are localized orbitals which are obtained by solving the corresponding localized

orbital equations. For hydrogen, the localized orbital equation (in its integral form) for the 1*s* orbital is

$$\epsilon_{1s} = K_{1s} + F^0(1s, 1s) - G^0(1s, 1s) + V_{1s}, \quad (56)$$

and for oxygen, the corresponding equations for the 1*s*, 2*s* and 2*p* shells are

$$\begin{aligned} \epsilon_{ns} = & K_{ns} + 2F^0(ns, 1s) + 2F^0(ns, 2s) + 4F^0(ns, 2p) \\ & - G^0(ns, 1s) - G^0(ns, 2s) - \frac{2}{3}G^1(ns, 2p) + V_{ns}, \\ n = & 1, 2 \end{aligned} \quad (57)$$

$$\begin{aligned} \epsilon_{2p} = & K_{2p} + 2F^0(2p, 1s) + 2F^0(2p, 2s) + 4F^0(2p, 2p) \\ & - \frac{1}{3}G^1(2p, 1s) - \frac{1}{3}G^1(2p, 2s) - G^0(2p, 2p) \\ & - 0.30G^2(2p, 2p) + V_{2p}. \end{aligned} \quad (58)$$

The basis parameters *A*<sub>1*j*</sub> and *Z*<sub>1*j*</sub> used in solving these equations and the self-consistent solutions (*C*<sub>*j**nl*</sub> and  $\epsilon_{nl}$ ) to these equations, together with their corresponding energy parameters (*V*<sub>*nl*</sub> and  $\epsilon_{nl, nl}$ ) are given in Table IV. The values of *A*<sub>1*j*</sub> and *Z*<sub>1*j*</sub> for oxygen and hydrogen are obtained from Huzinaga<sup>21</sup> and from Ref. 18, respectively.

The molecular-orbital energies and molecular-orbital coefficients of the system are then obtained by solving the secular equation

$$|F_{\alpha\beta} - E_i S_{\alpha\beta}| = 0,$$

TABLE V. Results of MO calculation for H<sub>2</sub>O by the LCLO method.

MO symmetry	MO energy (Ry)	MO coefficients				Electronic configuration
		<i>C</i> <sub>1</sub>	<i>C</i> <sub>2</sub>	<i>C</i> <sub>3</sub>	<i>C</i> <sub>4</sub>	
1 <i>b</i> <sub>2</sub>	-1.2817	1.0	...	...	...	H <sub>I</sub> <sup>-0.3063</sup> (1s <sup>0.6937</sup> )
3 <i>a</i> <sub>1</sub>	-1.3530	0.0222	-0.1910	0.9079	0.1641	H <sub>II</sub> <sup>0.3063</sup> (1s <sup>0.6937</sup> )
1 <i>b</i> <sub>1</sub>	-1.6431	0.5358	0.5579	...	...	O <sup>-0.6127</sup> (1s <sup>2.025</sup> 1.92552 <i>p</i> <sub>x</sub> <sup>0.9082</sup> 2 <i>p</i> <sub>y</sub> <sup>2.025</sup> 2 <i>p</i> <sub>z</sub> <sup>1.7780</sup> )
2 <i>a</i> <sub>1</sub>	-2.5903	0.0051	0.9598	-0.0041	0.0378	Dipole moment: 1.72 debye units
1 <i>a</i> <sub>1</sub>	-41.4495	1.0000	-0.0002	-0.0001	0.0001	

TABLE VI. Summary of MO calculations for H<sub>2</sub>O.

Occupied MO's	MO Energies (Ry)						Experimental values <sup>f</sup>
	Ellison and Shull <sup>a</sup> (SCF)	Fink and Allen <sup>b</sup> (SCF)	Pitzer and Merrifield <sup>c</sup> (SCF)	Snyder and Basch <sup>d</sup> (SCF)	Allen and Russell <sup>e</sup> (EH)	LCLO	
1b <sub>2</sub>	-0.87	-0.95	-0.80	-1.01	-1.31	-1.28	-0.93 ± 0.01
3a <sub>1</sub>	-0.97	-1.05	-0.94	-1.13	-1.32	-1.35	-1.07 ± 0.02
1b <sub>1</sub>	-1.37	-1.31	-1.24	-1.43	-1.38	-1.64	-1.19 ± 0.02
2a <sub>1</sub>	-2.81	-2.59	-2.56	-2.72	-2.53	-2.59	...
1a <sub>1</sub>	-40.98	...	-41.12	-41.11	...	-41.45	...
Valence band width (Ry)	0.50	0.37	0.44	0.42	0.07	0.36	0.26
Dipole moment (debye unit)	1.51	2.57	1.92	2.68	...	1.72	1.85

<sup>a</sup>Reference 22.<sup>b</sup>Reference 23.<sup>c</sup>Reference 24.<sup>d</sup>Reference 25.<sup>e</sup>Reference 26.<sup>f</sup>Reference 27.

in which the matrix elements of the Fock operator are evaluated by the Gilbert approximation. The results of the MO calculation for H<sub>2</sub>O and the LCLO method are given in Table V. In Table VI we summarize some other self-consistent-field (SCF) and semiempirical MO calculations for H<sub>2</sub>O.

From the results given in Tables V and VI, it can be seen that our energies are all lower than experimental values and the best theoretical values. Considering relative energies, however, even for the more ionic system H<sub>2</sub>O the LCLO method works successfully and gives reasonable results consistent with the SCF-MO calculations and experimental data.

## VII. CONCLUSIONS

In this paper we have presented the LCLO-MO method used for calculating the electronic structure of polyatomic systems. This method is based on the use of localized orbitals<sup>28</sup> which are obtained by solving the Adams-Gilbert equation, as basis functions to construct the molecular orbitals for the system, and on the use of the Gilbert version of EH theory to evaluate the matrix elements of

the Fock operator directly without the *ad hoc* parametrization procedure. An open-shell approximation has been made in applying this method to systems which are composed of open-shell atoms (or ions). It has been noted that the Gilbert approach shares certain features with other improvements to EH theory which have been suggested. The sample calculations on the simple molecules H<sub>2</sub> and H<sub>2</sub>O which have given reasonable agreement with other calculations and experimental results help to justify the use of the LCLO-MO method to calculate the electronic structure of complex solid systems. In the next paper, we shall present the results of LCLO calculation in SiO<sub>2</sub>.

## ACKNOWLEDGMENTS

The authors wish to thank Dr. A. Barry Kunz for making available to them a copy of his computer program. Many helpful discussions with Dr. K. Klier, Dr. F. J. Feigl, and Dr. C. E. Jones, P. Hutta and P. Schneider are gratefully acknowledged. We thank Dr. T. L. Gilbert for his useful comments.

\*Research supported by the National Science Foundation, Grant No. GH-33759.

†Present address: Department of Physics, University of Illinois, Urbana, Ill. 61801.

<sup>1</sup>T. L. Gilbert, in *Sigma Molecular Orbital Theory*, edited by O. Sinanoglu and K. B. Wiberg (Yale U. P., New Haven, Conn., 1970), p. 249.

<sup>2</sup>W. H. Adams, *J. Chem. Phys.* **34**, 89 (1961); **37**, 2009 (1962).

<sup>3</sup>T. L. Gilbert, in *Molecular Orbitals in Chemistry, Physics and Biology*, edited by P. O. Löwdin (Academic,

New York, 1964), p. 405.

<sup>4</sup>R. Hoffman, *J. Chem. Phys.* **39**, 1397 (1963).

<sup>5</sup>A. B. Kunz, *Phys. Status Solidi* **36**, 301 (1969); *J. Phys. B* **6**, L47 (1973).

<sup>6</sup>C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951); **32**, 179 (1960).

<sup>7</sup>From a rigorous theoretical point of view, the (*nlm*)'s are not really good quantum numbers in the polyatomic systems; but, in general, it is more convenient to use them to classify the orbitals than by using group-theoretical notations.



- <sup>8</sup>M. Wolfsberg and L. Helmholz, *J. Chem. Phys.* **20**, 837 (1952).
- <sup>9</sup>M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.* **88**, 2353 (1966).
- <sup>10</sup>G. Blyholder and C. A. Coulson, *Theor. Chim. Acta (Berl.)* **10**, 316 (1968).
- <sup>11</sup>J. A. Tossell, *J. Phys. Chem. Solids* **34**, 307 (1973).
- <sup>12</sup>H. Schlosser, *J. Chem. Phys.* **55**, 5453 (1971).
- <sup>13</sup>H. Schlosser, *J. Chem. Phys.* **55**, 5459 (1971).
- <sup>14</sup>A. B. Kunz, *Phys. Status Solidi B* **46**, 385 (1971).
- <sup>15</sup>R. K. Nesbet, *Rev. Mod. Phys.* **33**, 28 (1961).
- <sup>16</sup>D. R. Hartree, *The Calculations of Atomic Structures* (Wiley, New York, 1957).
- <sup>17</sup>J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), Vol. 1.
- <sup>18</sup>I. N. Levine, *Quantum Chemistry, Quantum Mechanics and Molecular Electronic Structure* (Allyn and Bacon, Boston, 1970), Vol. 1.
- <sup>19</sup>R. Daudel, R. Lefebvre and C. Moser, *Quantum Chemistry, Method and Applications*, 2nd ed. (Interscience, New York, 1965), p. 426.
- <sup>20</sup>C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory* (Benjamin, New York, 1965).
- <sup>21</sup>S. Huzinaga, technical report (University of Alberta, 1971) (unpublished).
- <sup>22</sup>F. O. Ellison and H. Shull, *J. Chem. Phys.* **21**, 1420 (1953); **23**, 2348 (1955).
- <sup>23</sup>W. Fink and L. C. Allen, *J. Chem. Phys.* **46**, 2261 (1967).
- <sup>24</sup>Quoted in S. Aung, R. M. Pitzer, and S. I. Chan, *J. Chem. Phys.* **49**, 2071 (1968), from Ref. 18.
- <sup>25</sup>L. C. Snyder and H. Basch, *Molecular Wave Functions and Properties: Tabulated from SCF Calculations in a Gaussian Basis Set* (Wiley, New York, 1972).
- <sup>26</sup>L. C. Allen and J. D. Russell, *J. Chem. Phys.* **46**, 1029 (1967).
- <sup>27</sup>D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford U. P., New York and Oxford, 1969).
- <sup>28</sup>T. L. Gilbert and A. B. Kunz (unpublished) have recently examined some of the limitations associated with the formation and use of localized orbitals.