0.0005 M with respect to TlCl, but in which the solvent was water mixed with various proportions of methanol, ethanol, or propanol, were measured. In all cases the maximum of the absorption band was moved toward higher wavelength by increasing alcohol content of the solvent, as illustrated by Table III.

The dielectric constants of 50% CH_3OH solution

and 50% C_2H_5OH solution are 60 and 53 respectively,[8] so that it is to be expected that the equilibrium concentrations of the ions and complexes in the two solutions would be about the same. This is borne out by the data of the table.

[8] Calculated from data given by International Critical Tables VI, 100.

Electronic Population Analysis on LCAO-MO Molecular Wave Functions.* I

R. S. MULLIKEN

Laboratory of Molecular Structure and Spectra, Department of Physics, The University of Chicago, Chicago 37, Illinois

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With increasing availability of good all-electron LCAO MO (LCAO molecular orbital) wave functions for molecules, a systematic procedure for obtaining maximum insight from such data has become desirable. An analysis in quantitative form is given here in terms of breakdowns of the electronic population into partial and total "gross atomic populations," or into partial and total "net atomic populations" together with "overlap populations." "Gross atomic populations" distribute the electrons almost perfectly among the various AOs (atomic orbitals) of the various atoms in the molecule. From these numbers, a definite figure is obtained for the amount of promotion (e.g., from $2s$ to $2p$) in each atom; and also for the gross charge Q on each atom if the bonds are polar. The total overlap population for any pair of atoms in a molecule is in general made up of positive and negative contributions. If the total overlap population between two atoms is positive, they are bonded; if negative, they are antibonded.

Tables of gross atomic populations and overlap populations, also gross atomic charges Q, computed from SCF (self-consistent field) LCAO-MO data on CO and H_2O, are given. The amount of s-p promotion is found to be nearly the same for the O atom in CO and in H_2O (0.14 electron in CO and $0.15e$ in H_2O). For the C atom in CO it is $0.50e$. For the N atom in N_2 it is $0.26e$ according to calculations by Scherr. In spite of very strong polarity in the π bonds in CO, the σ and π overlap populations are very similar to those in N_2. In CO the total overlap population for the π electrons is about twice that for the σ electrons. The most easily ionized electrons of CO are in an MO such that its gross atomic population is 94% localized on the carbon atom; these electrons account for the (weak) electron donor properties of CO. A comparison between changes of bond lengths observed on removal of an electron from one or another MO of CO and H_2, and corresponding changes in computed overlap populations, shows good correlation. Several other points of interest are discussed.

1. INTRODUCTION

R ECENT progress in the accurate determination of molecular electronic wave functions in the approximation of Roothaan's SCF LCAO-MO method[1] and related methods makes it desirable to examine the types of information which can be obtained from such wave functions. The values of various physical properties of molecules (e.g., dipole moments, quadrupole moments) can be computed fairly readily and with some degree of reliability once SCF-LCAO-MO wave functions are available, and a few such calculations are on hand. Rather accurate molecular ionization potentials are obtained concomitantly with SCF-LCAO-MO wave functions. Significant though less accurate calculations of certain molecular excitation energies can also be made. Refinement of the SCF-LCAO-MO method will make possible increasingly accurate calculations.

The reliable computation of dissociation energies will probably remain for some time a hard nut to crack,

mainly because of the difficulty in knowing how much the errors differ in the two large quantities (atomic and molecular energies) whose computed values must be subtracted in order to obtain dissociation energies. Nevertheless, much new insight into the bonding and antibonding characteristics and the polarities of the MOs of the electrons in a molecule can be obtained from inspection of SCF-LCAO-MO wave functions.

The study of *overlap populations*, computed from the LCAO coefficients, shows more, since these give quantitative figures which may be taken as measures of bonding and antibonding strengths. Further, again by computation from the LCAO coefficients, statistics concerning the distribution of electronic population among the atoms in a molecule, and among the different orbitals in each atom, can be obtained. From these statistics, values of gross charges on atoms, and of amounts of promotion, can be obtained. It seems probable that all these results may be fairly reliable even without great refinement in the SCF-LCAO calculations. The present paper deals mainly with the determination of atomic and overlap populations, illustrated by two examples taken from among a few mole-

[1] C. C. J. Roothaan, Revs. Modern Phys. 23, 69 (1951).

cules for which fairly complete SCF-LCAO-MO wave functions have recently become available.

2. POPULATION BREAKDOWNS

First consider any normalized MO ϕ of a diatomic molecule, written in approximate form as a linear combination of normalized AOs χ_r and χ_s of the two respective atoms k and l:

$$\phi = c_r \chi_r + c_s \chi_s. \tag{1}$$

Each AO may be either a pure or a hybrid one. If the MO ϕ is occupied by N electrons (usually $N=2$), this population may be considered as divided into three sub-populations whose detailed distributions in space are given by the three terms in the following expression:

$$N\phi^2 = Nc_r^2(\chi_r)^2 + 2Nc_rc_sS_{rs}(\chi_r\chi_s/S_{rs}) + Nc_s^2(\chi_s)^2, \tag{2}$$

where S_{rs} is the overlap integral $\int_\infty \chi_r\chi_s dv$. The function ϕ, and likewise each of the three functions χ_r^2, $\chi_r\chi_s/S_{rs}$, and χ_s^2, is a *normalized* distribution. Hence, on integration of each term in Eq. (2) over all space, one obtains the following breakdown of N into three parts[2]:

$$N = Nc_r^2 + 2Nc_rc_sS_{rs} + Nc_s^2. \tag{3}$$

The sub-populations Nc_r^2 and Nc_s^2 will be called the *net atomic populations* on atoms k and l, and $2Nc_rc_sS_{rs}$ will be called the *overlap population*.

The three sub-populations may be likened to those of two cities (k and l) and of a (joint) suburb which lies between them. However, it should be noticed that the three distributions χ_r^2, $\chi_r\chi_s/S_{rs}$, and χ_s^2 are not entirely mutually nonoverlapping like those of the cities and their suburb. This peculiarity of the present population breakdown, although it hinders giving a simple physical meaning to the three sub-populations, does not impair the real usefulness of the breakdown.

In general, any molecule contains electrons in several MOs, to each of which Eqs. (1)–(3) are applicable. Let the several MOs be called ϕ_i. Further, if either or both of χ_r and χ_s in Eq. (1) are *hybrid* AOs, they may (*if* desired) each be replaced by linear combinations of (two or sometimes more) pure AOs. Finally, the molecule may be polyatomic. In the general case, Eqs. (1) and (3) are replaced by the following:

$$\phi_i = \sum_{rk} c_{irk}\chi_{rk}, \tag{1'}$$

$$N(i) = N(i)\sum_{rk} c_{irk}^2 + 2N(i)\sum_{l>k} c_{irk}c_{isl}S_{rksl}. \tag{3'}$$

In Eq. (3'), $N(i)$ is most often 2.

In the subsequent application of Eqs. (1') and (3'),

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[2] Breakdowns of the total charge into overlap and "net" atomic populations have been in use for some time, e.g., R. S. Mulliken, Phys. Rev. **41**, 66 (1932); J. Chem. Phys. **3**, 573 (1935), Eqs. (38), (39), (42).

the following symbolism will be used:

$$n(i; r_k s_l) = 2N(i)c_{irk}c_{isl}S_{rksl};$$

$$n(i; k,l) = \sum_r \sum_s n(i; r_k, s_l);$$

$$n(r_k, s_l) = \sum_i n(i; r_k, s_l);$$

$$n(k,l) = \sum_r \sum_s n(r_k, s_l);$$ $$\tag{4}$$

$$n(i) = \sum_{rk, sl} n(i; r_k, s_l);$$

$$n = \sum_i n(i) = \sum_{k,l} n(k,l) = \sum_{rk, sl} n(r_k, s_l).$$

The quantities $n(i; r_k, s_l)$, $n(r_k, s_l)$, and so on, are partial and subtotal *overlap* populations[3] corresponding to various degrees and kinds of breakdown of a total overlap population n. In general any of the n's may have negative values. Positive and negative n's for a given pair of atoms correspond respectively to net bonding or antibonding between them (see paper II of this series for a detailed discussion).

Further quantities

$$n(i; r_k) = N(i)c_{irk}^2;$$

$$n(r_k) = \sum_i n(i; r_k); \quad n(k) = \sum_r n(r_k) \tag{5}$$

can also be defined for partial and sub-total *net atomic populations*; $n(k)$ is the *total* net atomic population on atom k. However, these quantities will not be used in the applications below.[4]

The foregoing equations are applicable only when the molecular wave function is one that corresponds to a single LCAO-MO electron configuration. Their extension to wave functions which include configuration interaction should be fairly straightforward, but will not be considered here.

Equations for a similar breakdown of the electronic population into AO and overlap populations would also be of interest for wave functions of the Heitler-London type. In addition, breakdowns into two-electron distribution functions [Eq. (3') is based on one-electron functions only] would be of interest. But these further types of electronic population analysis, which have been considered by McWeeny in unpublished work, will not be developed here.

The net atomic and the overlap populations defined in the foregoing for single-configuration LCAO-MO wave functions, and the gross atomic populations de-

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[3] The first of Eqs. (4) in general form was given by R. McWeeny, J. Chem. Phys. **19**, 1614L (1951) and **20**, 920 (1952); what is here called "overlap population" he called "bond charge." The former term is preferred here because it is more accurately, or at least more unambiguously, descriptive.

[4] The first of Eqs. (5) is given in reference 3, where $n(i; r_k)$ is called the "atom charge."

fined in Sec. 3, have a property of invariance without which their usefulness would be questionable—namely, those populations which represent sums over all MOs [e.g., $n(r_k)$, $n(k)$, $n(r_k,s_l)$, $n(k,l)$, n, but *not* $n(i;r_k)$, $n(i;r_k,s_l)$, etc.] are invariant quantities (like the energy and other molecular properties[1]) with respect to any orthogonal transformation among the *occupied* LCAO MOs (in particular, among those of any one group-theoretical species) in the given configuration. Proofs are given by Scherr in an accompanying paper,[5] and an example is discussed in paper III of this series.

3. GROSS ATOMIC POPULATIONS AND CHARGES; AMOUNTS OF PROMOTION

A particularly useful type of breakdown is one which allocates the whole population among the atomic centers only. Here it may first be noted [see Eq. (3) or (3′)] that the total population is a sum of net atomic populations and (positive or negative) overlap populations. Referring back to the simplest two-center case [see Eq. (3)], it is seen that the overlap term is related completely symmetrically to the two centers, even if these are unlike and the coefficients c_r and c_s therefore unequal. Hence it appears necessary to assign exactly half of the overlap population, plus, of course, the appropriate net atomic population, to each center. The same reasoning holds in the general case of Eq. (3′).

Applying the indicated procedure to Eq. (3), one obtains for the *gross atomic populations* $N(k)$ and $N(l)$ on atoms k and l the expressions:

$$N(k)=N(c_r{}^2+c_rc_sS_{rs}); \quad N(l)=N(c_rc_sS_{rs}+c_s{}^2). \quad (6)$$

The sum of $N(k)$ and $N(l)$ is just N [see Eq. (3)].

In the general case one has[6,7]:

$$N(i;r_k)=N(i)c_{ir_k}(c_{ir_k}+\sum_{l\neq k}c_{is_l}S_{r_ks_l}), \quad (6')$$

$$N(i;k)=\sum_r N(i;r_k);$$

$$N(k)=\sum_i N(i;k)=\sum_r N(r_k);$$

$$N(i)=\sum_{r_k} N(i;r_k)=\sum_k N(i;k); \quad (7)$$

$$N(r_k)=\sum_i N(i;r_k);$$

$$N=\sum_i N(i)=\sum_{r_k} N(r_k).$$

$N(i;r_k)$ is the partial gross population in MO ϕ_i and

AO χ_{r_k}; $N(i;k)$ is the subtotal in MO ϕ_i on atom k. $N(k)$ is the total gross population on atom k. $N(i)$ is the total population (necessarily an integer) in MO ϕ_i. $N(r_k)$ is the total gross population in AO χ_{r_k}. N is the over-all total population (necessarily an integer) of electrons in the molecule. $N(r_k)$, $N(k)$, and N are invariant with respect to orthogonal transformations of the occupied LCAO MOs.[5]

Ideally, the definition of $N(i;r_k)$ by Eq. (6′) would be such that no $N(i;r_k)$ would ever be less than zero. Actually, very small negative values[8] occasionally occur (see Table V, first row and column, and footnote). Likewise, if $N(r_k)$ corresponded ideally to the population of the AO χ_{r_k} in atom k, its value for a non-degenerate or a single individual AO (e.g., $1s$, $2s$, or $2p\sigma$) should never exceed the number 2.00 of electrons in a closed atomic sub-shell. Actually, $N(r_k)$ in some instances does very slightly exceed 2.00 (again see Table V and its footnote). The reason why these slight but only slight imperfections exist is obscure. But since they *are* only slight, it appears that the gross atomic populations calculated using Eq. (6′) may be taken as representing rather accurately the "true" populations in various AOs for an atom in a molecule. It should be realized, of course, that fundamentally there is no such thing as an atom *in* a molecule except in an approximate sense.

If definitions (6′) and (7) are accepted, one can at once define[9] the "gross charge," $Q(r_k)$, in any AO, or that, $Q(k)$, on any atom:

$$Q(r_k)=N_0(r_k)-N(r_k); \quad Q(k)=N_0(k)-N(k), \quad (8)$$

where $N_0(r_k)$ is the number of electrons in the AO χ_r and $N_0(k)$ the total number of electrons in the ground state of the free neutral atom k. The Q's in Eqs. (8) are in units of $+e$. Some examples of the application of Eq. (8) are given in Tables IV and V.

If the quantities $N(r_k)$ are known for the atoms in a molecule, a population summary or effective electron configuration for any atom can be written down. Comparison between this and the configuration of the free atom in its ground state shows, in general, differences, namely the quantities $Q(r_k)$. In the event that there is no gross charge $Q(k)$ on the atom, these differences can be expressed in terms of *amounts of promotion*. In case the promotion involves no increase in valence (isovalent promotion[10]), its amount may be identified with amount of *gross hybridization*. The same quantities can still be defined if there is a gross charge on the atom, although only at the cost of some arbitrariness. An example will make these matters clearer.

According to SCF-LCAO-MO calculations (see Table IV), the effective electron configurations for the two atoms in CO are as follows:

$$1s_C{}^{2.00}2s_C{}^{1.49}2p\sigma_C{}^{1.40}2p\pi_C{}^{1.02}; \quad 1s_O{}^{2.00}2s_O{}^{1.86}2p\sigma_O{}^{1.25}2p\pi_O{}^{2.98},$$

[5] C. W. Scherr, J. Chem. Phys. **23**, 569 (1955). See Appendix II for invariance theorems. Scherr has used the methods and notation of the present paper, which was prepared some time ago in preliminary form, in discussing his results on N_2.

[6] R. S. Mulliken, J. chim. phys. **46**, 675 (1949), Sec. 21. The present $N(i;r_k)$ is there called F_{ri}: see Eq. (139) there.

[7] B. H. Chirgwin and C. A. Coulson, Proc. Roy. Soc. (London) **201A**, 196 (1950), who speak of "formal charges" for what are here called "gross populations." Also reference 3.

[8] Reference 6, footnote 73.

[9] Reference 2, Eq. (39).

[10] R. S. Mulliken, J. Phys. Chem. **56**, 295 (1952).

TABLE I. Computed SCF-LCAO MOs for CO (by R. C. Sahni, reference 12).

ϕ_i \ χ_r	$2s_O$	$2p\sigma_O$	$2s_C$	$2p\sigma_C$	$2p\pi_O$	$2p\pi_C$	calc $-\epsilon_i(ev)$	obs $I_i(v)$
2σ	0.675	0.231	0.270	0.227			43.37	
4σ	0.718	−0.607	−0.493	−0.168			20.01	19.70
1π					0.8145	0.4162	15.97	16.58
5σ	0.187	−0.189	0.615	−0.763			13.37	14.01

or briefly,

$$1s_C^{2.00}2s_C^{1.49}2p_C^{2.42}; \quad 1s_O^{2.00}2s_O^{1.86}2p_O^{4.23},$$

as compared with

$$1s_C^{2.00}2s_C^{2.00}2p_C^{2.00}; \quad 1s_O^{2.00}2s_O^{2.00}2p_O^{4.00}$$

in the ground states of the two atoms. It is evident that in CO there has been promotion out of $2s$ for both atoms, but also there has been a charge transfer of $-0.09e$ from C to O. One might ask, how much of this transfer has been out of $2s_C$ and how much out of $2p_C$, and how much has been into $2s_O$ and how much into $2p_O$? These questions appear to have no definite answer, if indeed they have any real meaning. One may, however, reason that most of the charge transfer has been out of $2p_C$ and into $2p_O$, because the net $2s$ promotions which exist in CO, both out of $2s_C$ into $2p\sigma_C$ and out of $2s_O$ into $2p\sigma_O$, must have arisen mainly as a response to the possibility of gains in stability by hybridization; and if so, the extent of these promotions should be relatively independent of loss or gain of charge in, say, the $2p$ AOs.

In any event, one may arbitrarily *define* the amounts of promotion in the atoms in CO on the basis that charge transfer involves only the $2p$ AOs. One can then say that, in units of $-e$, the amount of $2s{\to}2p\sigma$ promotion is 0.51 in the C and 0.14 in the O atom.

4. EXAMPLES AND APPLICATIONS: SURVEY

The first successful computations by the LCAO-SCF method considered π electrons only, in an assumed Goeppert-Mayer-Sklar field representing the remaining electrons. Next Mulligan[11] (CO_2) and recently Sahni[12] (CO) have published results of LCAO-SCF calculations including all but the $1s$ electrons explicitly in the calculations, although the values of many of the integrals were approximated instead of computed. Meantime Fischer[13] carried out an approximately SCF LCAO treatment on LiH and BeH^+ in which all integrals were evaluated exactly. Higuchi[14] gave an SCF-LCAO treatment of several electronic states of CH, but did not include the carbon $1s$ electrons in the calculations. Duncan treated SF_6 including valence electrons only, and has recently treated HF with all electrons included.[15]

Ellison and Shull[16] have published an LCAO-SCF treatment of H_2O with some of the integrals approximated, but with *all* electrons included. Sahni[17] has carried out a complete treatment of BH, and Scherr[5] a complete treatment of N_2, in which all electrons were included and all integrals computed exactly. A preliminary report of a similar complete treatment of NH_3 has also appeared.[18] The work of Ellison and Shull, and of Scherr, show that the explicit inclusion of inner-shell (here $1s$) electrons in the SCF procedure is very important. All calculations thus far made, except some of those of Fischer and of Higuchi have been based exclusively on Slater-type AOs with essentially Slater's values of the effective nuclear charges, and have been made only for the equilibrium internuclear distances. However, Ellison and Shull made calculations for several values of the bond angle in H_2O. Configuration interaction has not been taken into account in most of the papers mentioned except for $2s-2p$ hybridization. Higuchi considered configuration interaction rather extensively for CH.

The use of the methods of population analysis described in preceding sections of this paper will now be illustrated by applying them to the approximate LCAO-SCF wave functions obtained by Sahni for CO and by Ellison and Shull for H_2O. Although these wave functions are subject to some revision, they are doubtless sufficiently accurate for the present illustrative purpose. In another paper, Scherr[5] has applied the present methods to his exact LCAO-SCF N_2 wave functions.

The electron configuration of CO (equilibrium interatomic distance 1.128 A) is

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2.$$

The MOs 1σ and 2σ were approximated by Sahni as $1s_O$ and $1s_C$ respectively. The LCAO coefficients (see Eq. (1′)) as determined by Sahni for the remaining MOs, all normalized and orthogonal, are reproduced in Table I. The $2p\sigma$ AOs are here defined in such a way that the positive lobe of each points toward the other atom. The computed orbital energies ϵ are also given in Table I, and compared with the observed ionization

[11] J. F. Mulligan, J. Chem. Phys. **19**, 347 (1951).
[12] R. C. Sahni, Trans. Faraday Soc. **49**, 1 (1953).
[13] I. Fischer, Arkiv Fysik **5**, 349 (1952).
[14] J. Higuchi, J. Chem. Phys. **22**, 1339 (1954).
[15] A. B. F. Duncan, J. Chem. Phys. **20**, 951 (1952); J. Am. Chem. Soc. **77**, 2107 (1955).

[16] F. O. Ellison and H. Shull, J. Chem. Phys. **21**, 1420(L) (1953) and later full paper.
[17] R. C. Sahni (to be published).
[18] H. Kaplan, on p. 30 of Quarterly Progress Report for October 15, 1954 of the Solid-State and Molecular Theory Group at the Massachusetts Institute of Technology, Cambridge, Massachusetts.

Table II. Computed SCF-LCAO MOs for H_2O (by Ellison and Shull, reference 16).

ϕ_i \ χ_r	$1s_O$	$2s_O$	$2p\pi_O$	$a_1(H_2)$	$2p\gamma_O$	$b_2(H_2)$	$2p\chi_O$	calc $-\epsilon_i(ev)$	obs $I_i(v)$
$1a_1$	1.0002	0.0163	0.0024	−0.0039				557.3	
$2a_1$	−0.029	0.845	0.133	0.208				36.2	
$1b_2$					0.543	0.613		18.6	16.2
$3a_1$	−0.026	−0.461	0.827	0.393				13.2	14.5
$1b_1$							1.000	11.8	12.56

potentials, with which[19] they should approximately agree.

The electron configuration of H_2O (symmetry C_{2v}, apex angle 105°, O-H equilibrium distance 0.958 A; z axis bisecting apex angle, x axis taken perpendicular to the molecule plane) is

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2.$$

The LCAO MOs are here best expressed as linear combinations of O atom AOs and the following two normalized GOs (group orbitals) of the H_2 group:

$$a_1(H_2) = (1s_a + 1s_b)/[2(1+S)]^{\frac{1}{2}},$$
$$b_2(H_2) = (1s_a - 1s_b)/[2(1-S)]^{\frac{1}{2}}, \tag{9}$$

where $1s_a$ and $1s_b$ refer to $1s$ AOs on the two H atoms, and $S = \int 1s_a 1s_b dv$. The coefficients of the AOs and GOs as determined by Ellison and Shull for the various normalized MOs are reproduced in Table II, together with the corresponding computed ϵ_i's and observed I_i's.

For convenience of reference, values of various overlap integrals $S_{rs} = \int \chi_r \chi_s dv$ used in the population analysis are listed in Table III. In the case of H_2O, S's for the overlap of O atom AOs with normalized H_2 GOs $a_1(H_2)$ or $b_2(H_2)$ are also included.

Leaving aside the inner-shell MOs, which are nearly but not quite $1s$, inspection of the coefficients shows at once that the lowest σ MO in CO (3σ), and the lowest a_1 MO in H_2O ($2a_1$), have large consistently positive overlaps and so must be very strongly bonding. The higher σ MOs in CO, and the higher a_1 MOs, show both positive and negative overlaps, indicating little net bonding. The 1π MO in CO and the $1b_2$ MO in H_2O are evidently strongly bonding. The result, shown by the LCAO-SCF calculations, that most of the bonding power of the σ electrons in CO, and of the a_1 electrons in H_2O, resides in the lowest-energy outer-shell MO of the species, is especially notable.

5. EXAMPLES AND APPLICATIONS: GROSS ATOMIC POPULATIONS AND CHARGES; AMOUNTS OF PROMOTION

In Tables IV and V, a survey is made of the atomic populations in the AOs and atoms of CO and H_2O; the AO and atomic charges are also given. These results have been computed, using Eqs. (6'), (7), and (8), from the coefficients and S's in Table I-III. Tables IV and V show many interesting details which largely speak for themselves. There are nevertheless several points about which comment may be helpful.

Referring to Table IV, it is notable that the individual MOs of CO are all strongly polar, although the molecule as a whole is almost nonpolar, i.e., $Q(O)$ and $Q(C)$ are small. It is also notable that the π MO, and the totality of the σ MOs, each separately show almost the same charge distributions as in two normal atoms:

$$\sum_{\sigma\ MOs} (i)\ N(i; O) = 3.108, \qquad \sum_{\sigma\ MOs} (i)\ N(i; C) = 2.892;$$

$$N_\pi(O) = 2.980, \qquad N_\pi(C) = 1.020,$$

as compared with

$$\sum_{\sigma\ AOs} (r)\ N(r; O) = 3.000, \qquad \sum_{\sigma\ AOs} (r)\ N(r; C) = 3.000;$$

$$N_\pi(O) = 3.000, \qquad N_\pi(C) = 1.000$$

for neutral O and C atoms both in $^3\Pi$ phases of their ground states; that is to say, for $2s^22p\sigma2p\pi^3$, $^3P\Pi$ combined with $2s^22p\sigma2p\pi$, $^3P\Pi$. The slight charge transfer from O to C in the 1π MO relative to this combination corresponds to (the presence of) a small amount of $2s^22p\sigma^22p\pi^2$, $^3P\Sigma^-$ combined with $2s^22p\pi^2$, $^3P\Sigma^-$. No other combination derived from two normal atoms exists which could be involved in the normal electron configuration of CO. It is very striking that just because of strong C^+O^- polarity in the 1π MO, together

Table III. Values of overlap integrals $S_{rs} = \int \chi_r \chi_s dv$.

χ_r \ χ_s	$2s_O$	$2p\sigma_O$	$2p\pi_O$	χ_r \ χ_s	$1s_O$	$2s_O$	$2p\chi_O$	$2p\gamma_O$	$1s_b(H)$
$2s_C$	0.4063	0.3147	0	$1s_a(H)$	0.0610	0.4946	0.2118	0.2760	0.3479
$2p\sigma_C$	0.4807	0.3018	0	$a_1(H_2)$	0.0736	0.5965	0.2554	0	
$2p\pi_C$	0	0	0.2409	$b_2(H_2)$	0	0	0	0.4935	

[19] See Sec. 6 of reference 6.

TABLE IV. Gross atomic populations and charges in CO (see Eqs. (6'), (7), (8)).

ϕ_i \ x_{r_k}	2s_O	2pσ_O	Partial populations $N(i; r_k)$ 2pπ_O	2s_C	2pσ_C	2pπ_C	$N(i; O)$	$N(i; C)$	$N(i)$
3σ	1.207	0.178		0.333	0.282		1.385	0.615	2.000
4σ	0.627	0.985		0.386	0.002		1.612	0.388	2.000
1π			2.980			1.020	2.980	1.020	4.000
5σ	0.026	0.085		0.776	1.113		0.111	1.889	2.000
$N(r_k)$	1.860	1.248	2.980	1.495	1.397	1.020	$N(O)=$ 6.088	$N(C)=$ 3.912	$N=$ 10.000
$Q(r_k)$ in e units	+0.140	−0.248	+0.020	+0.505	−0.397	−0.020	$Q(O)=$ −0.088	$Q(C)=$ +0.088	0.000

with lack of marked polarity in the totality of the σ MOs, an atomic population distribution very close to that of two normal atoms is reproduced. It is also notable that the CO molecule nevertheless (see discussion following Tables VI and VIII) achieves almost as strong π and σ bonding as in the isoelectronic molecule N_2. This close similarity in character of bonding, combined with lack of over-all polarity, seems to account well for the close similarity in physical properties between CO and N_2.

Like N_2, CO has one strongly bonding σ MO (3σ) and two more or less nearly nonbonding σ MOs (4σ and 5σ). However, whereas in N_2 the two nearly nonbonding σ MOs are of course nonpolar, in CO they are both very strongly polar, the deeper of the two (4σ) having strong C^+O^- polarity, the less deeply bound (5σ) having such strong C^-O^+ polarity that it approximates to a pure (but very strongly $2s-2p\sigma$ hybridized) carbon σ AO. This last fact and the fact that 5σ is the most easily ionized MO of CO (see Table I) make understandable the moderate ability of CO to act as an electron donor[20] (as e.g., in $2B_2H_6+CO\rightleftharpoons 2H_3BCO$, and perhaps in the initial stages of the reaction of CO with metals to form carbonyls), as contrasted with the much greater inertness of N_2.

Work of recent years[21] has shown that one cannot expect molecular dipole moments in general to be simply related to a sum of products $\Sigma Q r_e$ of atomic charges times interatomic distances. However, if one has accurate molecular wave functions, one can compute dipole moments. In this connection Table VI is of interest (the μ_{calc} values are from references 12 and 16, the Q values from Tables IV and V).

From Tables IV and V, an effective electron configuration for each atom in the molecule CO or H_2O can be written down, and from this the amount of $2s-2p\sigma$ promotion can be read off. For CO, reference may be made to the end of Sec. 3. For H_2O, the effective atomic electron configurations found are

$$1s_O^{2.00}2s_O^{1.85}2p_O^{4.50}; \quad 1s_{Ha}^{0.82}; \quad 1s_{Hb}^{0.82}.$$

It is especially notable that, in spite of the considerable total of electron transfer from the two H atoms onto the O atom, there is a deficit of 0.15e in the $2s_O$ AO as compared with a free oxygen atom in its ground state. This deficit, which represents promotion, is explained by the ensuing gains from $2s_O-2p_{zO}$ hybridization, and is, interestingly enough, approximately the same as the corresponding figure (0.14e) for the $2s_O$ AO in CO. This suggests that about this amount of promotion is likely

TABLE V. Gross atomic populations and charges in H_2O (see Eqs. (6'), (7), (8)).[a]

ϕ_i \ x_{r_k}	1s_O	2s_O	Partial populations $N(i; r_k)$ 2pz_O	2py_O	2px_O	$a_1(H_2)$	$b_2(H_2)$	$N(i; O)$	$N(i; H_2)$	$N(i)$
$1a_1$	2.0002	0.0005	0.0000			−0.0005		2.0007	−0.0005	2.000
$2a_1$	0.0008	1.638	0.049			0.309		1.688	0.309	1.997
$1b_2$				0.918			1.080	0.918	1.080	1.998
$3a_1$	−0.0001	0.209	1.534			0.257		1.743	0.257	2.000
$1b_1$					2.000			2.000		2.000
$N(r_k)$	2.0009	1.847	1.583	0.918	2.000	0.565	1.080	$N(O)=$ 8.349	$N(H_2)=$ 1.645	$N=$ 9.995
$Q(r_k)$ in e units	0.00	+0.15	−0.58	+0.08	0.00	+0.43	−0.08	$Q(O)=$ −0.35	$Q(H_2)=$ +0.35	0.00

[a] The slight deviations recorded of some of the $N(i)$'s from 2.000 are attributable to the fact that the coefficients in Table II (with a few exceptions) have been rounded off to three figures after the decimal point, as given in Ellison and Shull's first publication. The small *negative* partial populations listed and the excess of the values of $N(1a_1; O)$ and $N(1s_O)$ over 2.000, are, however, not due to rounding, but to the imperfections of the definitions of Eqs. (6'), (7).

[20] R. S. Mulliken, J. Am. Chem. Soc. **74**, 811 (1952), p. 822–823.
[21] C. A. Coulson, Proc. Roy. Soc. (London) **207A**, 63 (1951).

to be found characteristic of the oxygen atom in its stable covalent compounds. It appears very likely that rather reliable information on promotion in atoms in molecules can be obtained by SCF-LCAO calculations.[22]

6. EXAMPLES AND APPLICATIONS: OVERLAP POPULATIONS

In Tables VII and VIII are given details of overlap populations in CO and H_2O, computed from the coefficients and S's In Table I–III, using Eqs. (4). The break-downs are in terms of pairs of overlapping non-hybrid AOs. An alternative breakdown for each molecule based on a *smaller* number of pairs of overlapping $2s-2pz$ *hybrid* AOs (C and O atom AOs in CO, O atom AOs in H_2O) would be of considerable interest, but is omitted here; the reader may find it instructive to work these out. The last two columns of Table VII will be explained.

The bond structure of CO has already been discussed in connection with Tables I and IV. Each of these tables displays well some aspects of the complete picture, but a study of Table VII (overlap populations) adds further insight. In so far as overlap population is a good measure of covalent bonding, the individual $n(i)$'s in Table VII give measures of the bonding powers of the electrons in the various MOs ϕ_i, and their total, n, gives a measure of the total covalent strength. It is of interest that n for CO (1.018) is somewhat, but not greatly, less than n for N_2 (1.276).[5] It is further of interest that using the $n(i)$'s as measures, the total bonding power of the (six) electrons in the

TABLE VI. Dipole moments (in D).

	μ_{calc}	Qr_e	μ_{obs}
CO	1.00 (C+O−)	0.48 (C+O−)	0.12
H_2O	1.51 (H_2+O−)	0.98 (H_2+O−)	1.84

σ MOs ($\sum_\sigma$ MOs $n(i) = 0.364$) is about one third, and that of the four electrons in the 1π MO ($n(1\pi) = 0.654$) is almost two thirds of the total n. The corresponding figures for N_2 are 0.395 and 0.880.[5] These figures, for CO as for N_2, correspond rather well to the idea of the presence of a triple bond (one σ and two π bonds) in both these molecules, provided one admits,[10] contrary to some early ideas in quantum-mechanical valence theory, that π bonds can be as strong as σ bonds.

In diatomic spectroscopy, a long familiar empirical criterion of the bonding power of an electron in any MO has been the change Δr_e in the equilibrium interatomic distance r_e in a molecule upon removal of an electron from that MO. In the last two columns of Table VII, data on $\Delta r_e/r_e$ from the CO+ spectrum, using r_e as known (1.128 A) for CO, are compared with values of $-\Delta n/n$ using the calculated $n(i)$ values from the earlier columns of Table VII (note that since only *one* electron is removed on ionization, $-\Delta n(i)$ has been taken as one-half or one-fourth of $n(i)$ in the cases of σ and π MOs respectively). The correlation is good for the 1π (bonding) and the 5σ (slightly antibonding) MOs, but is poor for 4σ (observed, mildly bonding; computed,

TABLE VII. Computed overlap populations for CO (see Eqs. (4)).

ϕ_i χ_{r_k}, χ_{s_l}	Partial populations $n(i; r_k, s_l)$						Change on Ionzn.	
	$2s_O, 2s_C$	$2s_O, 2p\sigma_C$	$2p\sigma_O, 2s_C$	$2p\sigma_O, 2p\sigma_C$	$2p\pi_O, 2p\pi_C$	$n(i)$	calc $-\Delta n/n$	obsd $2\Delta r_e/r_e$
3σ	0.296	0.294	0.078	0.064		0.732		
4σ	−0.574	−0.232	0.376	0.124		−0.308	−0.151	+0.072
1π					0.654	0.654	+0.161	+0.206
5σ	0.186	−0.274	−0.146	0.174		−0.060	−0.029	−0.022
$n(r_k, s_l)$	−0.092	−0.212	0.308	0.362	0.654	$n =$ 1.018		

TABLE VIII. Computed overlap populations for H_2O (see Eqs. (4)).

ϕ_i χ_{r_k}, χ_{s_l}	Partial populations $n(i; r_k, s_l)$					
	$1s_O, a_1(H_2)$	$2s_O, a_1(H_2)$	$2p_{z_O}, a_1(H_2)$	$2p_{y_O}, b_2(H_2)$	$1s_a(H), 1s_b(H)$	$n(i)$
$1a_1$	−0.0012	0.000	0.000		0.000	−0.001
$2a_1$	−0.0018	0.419	0.028		0.024	+0.469
$1b_2$				0.658	−0.450	+0.208
$3a_1$	−0.0030	−0.432	0.332		0.084	−0.019
$1b_1$						0.000
$n(r_k, s_l)$	−0.0060	−0.013	0.360	0.658	−0.342	$n =$ 0.657

[22] Similar results as to amounts of promotion in first-row atoms have been obtained in reference 10 by use of the magic formula method, and (see survey in Sec. XII of reference 10) by other methods.

TABLE IX. Overlap population for H_2.

χ_r, χ_s / ϕ_i	$n = n(i; r,s)$ $1s_a(H), 1s_b(H)$	Change on Ionzn. calc $-\Delta n/n$	obs $2\Delta r_e/r_e$
$1\sigma_g$	0.858	+0.500	+0.429

antibonding). The writer thinks it likely that more refined and accurate computations would show better agreements and feels that moderate disagreements such as that noted are only what might be expected at the present stage of progress.

For comparison with Table VII, Table IX of corresponding data on the H_2 molecule is of interest.

Table VIII for H_2O indicates that the bonding is almost entirely confined to the deeply buried (see Table II) $2a_1$ MO and the $1b_2$ MO. It also indicates that the bonding in the $2a_1$ MO, in spite of an appreciable amount of $2s-2pz$ hybridization (see Table II) is almost exclusively between the $2s_O$ MO and the hydrogens.

The $1s_a(H)$, $1s_b(H)$ overlap populations are also of especial interest. In AO-VB theory, one would expect a considerable nonbonded repulsion between the H atoms. This would correspond in LCAO-MO theory to a net excess of antibonding (i.e., negative) H—H overlap population in the $1b_2$ MO over bonding (i.e., positive) H—H overlap population in the a_1 MOs. This expectation is realized, but the negative excess is surprisingly large $[n(1s_a,1s_b) = -0.342]$, due to a combination of a surprisingly large $H_2^+O^-$ polarity in the a_1 MOs (see Table V), combined with a surprising $H_2^-O^+$ polarity in the $1b_2$ MO. Ellison and Shull noted also that their computations lead to the prediction of a bond angle somewhat exceeding $120°$. All these effects are so surprising that it seems likely that the values of some of the integrals (in particular the three-center integrals) which were only estimated were insufficiently exact. Indeed, Ellison and Shull consider this to be among the possible explanations of the too-large predicted angles.

Another factor which must contribute somewhat to reducing the H-H nonbonded repulsions is $1s-2p\sigma$ hybridization in the H atom AOs. A rough consideration indicates that a stabilization of about 0.3 ev, but

more or less independent of bond angle, might be obtained in this way.

Attention should be called here to the fact that Linnett and Heath, Simanouti, and others have brought forward rather convincing evidence from infrared force constant data, to the effect that the theoretically expected nonbonded repulsions between H atoms in molecules of the type AH_n are unimportant, if not nonexistent.[23] Theoretically such a situation seems difficult to understand. If the evidence is valid, it will apparently be necessary to call on rather extensive configuration interaction to explain it.

An interesting feature of Table VIII is the occurrence of small negative overlap populations between $1s_O$ and the H atom AOs. These correspond to "forced hybridization" in LCAO-MO theory and to "nonbonded repulsions" between the $1s_O$ and the $1s_H$ electrons in AO-VB theory (see paper III).

7. FUTURE APPLICATIONS

To mention a few out of many possibilities, it will be intensely interesting to learn how the amount of gross charge Q on, and of $s-p$ promotion in, the central atom varies within such series as HF, H_2O, H_3N, H_4C; HF, HO, HN, HC, HB; CH, CH_2, CH_3, CH_4; CH_4, C_2H_6, C_2H_4, and C_2H_2. In contemplating the results for such series, the concept of promotion will probably emerge as more fundamental than that of hybridization or of valency. It will be very interesting to see how the amount of $s-p$ promotion in CH_4 and other "tetravalent" carbon compounds lags behind that required $(1.0e)$ for full formal tetravalence. There may even prove to be not much less promotion in the "bivalent" carbon atom of CH_2 than in "tetravalent" carbon atoms.

[23] D. F. Heath and J. W. Linnett, Trans. Faraday Soc. 44, 556 (1947) on H_2O; Heath, Linnett, and Wheatley, ibid. 46, 137 (1950), on H_2O, H_2S, H_2Se, NH_3, AsH_3, CH_4, etc.; T. Simanouti, J. Chem. Phys. 17, 245, 734 (1949); Heath and Linnett, J. Chem. Phys. 18, 147 (1950).