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The utility of Hamilton population analysis—a partitioning of the electronic energy of a molecule—is investigated within a one-electron molecular orbital framework of the extended Hückel type. The classical Mulliken overlap population description of the valence electron density in terms of one- and two-center ''atom'' and ''bond'' contributions, respectively, provides the starting point for the development of an atom-bond energy partitioning scheme. Within an extended Hückel framework simple analytic relations exist between Hamilton populations and Mulliken overlap populations, permitting a step-by-step comparative study of the techniques. The formalism developed for population analysis of two-orbital interactions is tested by performing Hamilton and overlap population analyses of chemical bonding in the isoelectronic series of main group fluorides BrF_5, $[TeF_5]^-$, $[SbF_5]^{2-}$ and the tetrahedral P_4 cluster. These molecules were specifically chosen to illustrate the circumstances under which Hamilton and overlap population descriptions of chemical bonding will differ and when they will qualitatively agree. Differences come to the fore when atoms of quite different electronegativity interact, or even in a homonuclear system with disparate atomic basis orbital energies. The significant atomic electronegativity differences in the fluorides result in substantive differences between Hamilton and overlap population descriptions of bonding in these compounds. In contrast the small $s-p$ energy separation in phosphorus results in qualitatively similar Hamilton and overlap population descriptions of P–P bonding in P_4. We argue that Hamilton population analysis, by explicitly including reference to the energies of the individual orbitals, affords a more reliable analysis of orbital interactions in molecules. © *2000 American Institute of Physics.* [S0021-9606(00)30929-1]

I. INTRODUCTION

Traditionally, Mulliken population analysis[1,2] has played a leading role in semiquantitative molecular orbital based analysis of chemical bonding. Population analysis is a way of moving from wave functions to the chemist's notions of charges and bond orders. It permits a partitioning of the *electrons* among orbitals and atoms, and the overlap population serves as a useful bonding index. In this article the utility of overlap population analysis is compared and contrasted with that of a relatively new bonding descriptor, the Hamilton population.[3,4]

As we discussed in a previous article,[4] Hamilton population analysis augments and extends the range of chemical bonding situations amenable to study by overlap population analysis. By effecting a partitioning of the total electronic *energy* (at least in a one-electron theory), Hamilton population analysis allows us to compare on a fair basis, for example, $s-s$ and $s-p$ interactions in the series of hydrogen halides HX (X=F,Cl,Br,I).[4]

Comparisons such as this are precarious if using overlap population analysis. Much experience has shown that the absolute values of the overlap populations are useful when utilized within analogous bonding situations involving the same orbitals on identical atoms, as, for instance, when comparing

the individual $s-s$, $s-p$, and $p-p$ components of C–O σ bonding in methanol versus dimethyl ether.

Consider, for instance, the $s-s$ and $s-p$ components of the sigma bond in H–F as calculated using overlap and Hamilton population partitionings within an extended Hückel framework.[5] The $s-s$ and $s-p$ overlap populations are 0.247 and 0.256, respectively. Should we therefore consider $s-s$ and $s-p$ interactions to be of equal importance in making up the H–F bond? The $2s$ and $2p$ orbitals on fluorine are hardly equivalent in their contributions to the total energy of a fluorine atom or a HF molecule. Indeed the respective $s-s$ and $s-p$ Hamilton populations of -12.91 and -7.19 eV for H–F are quite different. Thus the $s-s$ and $s-p$ interactions are not of equal ''strength'' when viewed from an energetic standpoint, even though the overlap population contribution of each is roughly the same.

In this paper we address the following question: ''Which population analysis technique is the best descriptor of chemical bonding?'' To answer this fundamental question we must first review the formulation of each analytical tool—initially within the general framework of a one-electron theory and later within a one-electron scheme of the extended Hückel type.

II. MULLIKEN OVERLAP POPULATION ANALYSIS

Mulliken overlap population analysis affects a partitioning of the electron density. The partitioning of the electron

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density into orbital and overlap populations provides a route to obtaining both qualitative measures of bonding between atoms—the overlap population and the electron densities associated with individual atoms.

The Mulliken charge on an atom k, q_k, is given by

$$q_k = N_k - \left\{ \sum_{\mu \in \mathscr{B}^{(k)}} \text{MOOP}_{\mu\mu} + \frac{1}{2} \sum_{\mu \in \mathscr{B}^{(k)}} \sum_{\nu \in \mathscr{B}^{(l)}} \text{MOOP}_{\mu\nu} \right\},$$

for $k \neq l$, $\qquad\qquad$ (1)

where $\mathscr{B}^{(i)}$ denotes the set of basis functions (atomic orbitals) associated with atom i and N_k is the number of valence electrons on atom k.

The quantities $\text{MOOP}_{\mu\mu}$ and $\text{MOOP}_{\mu\nu}$ may be called, respectively, the μth "on-site" and the $\mu\nu$th "off-site" overlap population. Such terms were not used previously by Mulliken and others, but they are intuitive and make a useful connection to what follows. In this context the term "on-site" refers to the occupancy of a particular atomic basis function, and "off-site" refers to the electron density associated with the interaction of two atomic basis functions on different centers.

Within the LCAO approximation, the wave function for the ith eigenstate of the molecule can be written as

$$\psi_i = \sum_{\mu} c_{\mu i} \phi_\mu, \qquad\qquad (2)$$

for an atom localized basis set $\{\phi_\mu\}$, $\mu = 1, 2, ..., N$. On defining the overlap between the basis functions ϕ_μ and ϕ_ν by the matrix element $S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$ the on- and off-site populations $\text{MOOP}_{\mu\mu}$ and $\text{MOOP}_{\mu\nu}$ are given by

$$\text{MOOP}_{\mu\mu} = \sum_{i}^{\text{MO's}} n_i |c_{\mu i}|^2, \qquad\qquad (3)$$

and

$$\text{MOOP}_{\mu\nu} = \sum_{i}^{\text{MO's}} n_i \{ c_{\mu i}^* c_{\nu i} S_{\mu\nu} + c_{\nu i}^* c_{\mu i} S_{\nu\mu} \}. \qquad (4)$$

III. HAMILTON POPULATION ANALYSIS

We now proceed to derive an on-/off-site partitioning of the electronic energy analogous to that just presented for the electron density.

On adopting a one-electron formalism within the LCAO approximation (2), the energy of the ith eigenstate is given by

$$E_i = \langle \psi_i | \hat{H} | \psi_i \rangle$$

$$= \sum_{\mu} \sum_{\nu} c_{\mu i}^* c_{\nu i} \langle \phi_\mu | \hat{H} | \phi_\nu \rangle$$

$$= \sum_{\mu} \sum_{\nu} c_{\mu i}^* c_{\nu i} H_{\mu\nu}, \qquad\qquad (5)$$

and the total energy is written

$$\mathbf{E}_{\text{tot}} = \sum_{i}^{\text{MO's}} n_i E_i, \qquad\qquad (6)$$

where n_i is the electron occupancy of the ith eigenstate. Substituting (5) into (6) gives

$$\mathbf{E}_{\text{tot}} = \sum_{i}^{\text{MO's}} \sum_{\mu} n_i |c_{\mu i}|^2 H_{\mu\mu}$$

$$+ \sum_{i}^{\text{MO's}} \sum_{\mu} \sum_{\nu} n_i \{ c_{\mu i}^* c_{\nu i} H_{\mu\nu} + c_{\nu i}^* c_{\mu i} H_{\nu\mu} \}. \qquad (7)$$

The first term of (7) consists solely of contributions from diagonal Hamiltonian matrix elements—elements that define the contributions to the total energy arising from electron occupancy of the valence basis functions. Thus, the first term of (7) is designated an "on-site" energy term, and the second term [which consists of energy contributions arising from the interaction of different basis functions ($H_{\mu\nu}, \mu \neq \nu$)] is designated the "off-site" energy term. The on-/off-site energy partitioning is the essence of Hamilton population analysis. Equations (8) and (9) define the μth on-site and $\mu\nu$th off-site Hamilton population, respectively,

$$\text{MOHP}_{\mu\mu} = \sum_{i}^{\text{MO's}} n_i |c_{\mu i}|^2 H_{\mu\mu}, \qquad\qquad (8)$$

$$\text{MOHP}_{\mu\nu} = \sum_{i}^{\text{MO's}} n_i \{ c_{\mu i}^* c_{\nu i} H_{\mu\nu} + c_{\nu i}^* c_{\mu i} H_{\nu\mu} \}. \qquad (9)$$

IV. ENERGY PARTITIONING WITHIN AN EXTENDED HÜCKEL FRAMEWORK

Within an extended Hückel framework,[5] the off-diagonal Hamiltonian matrix elements ($H_{\mu\nu}, \mu \neq \nu$) are parametrized in terms of the corresponding overlap matrix elements $(S_{\mu\nu})$[6] according to (10),

$$H_{\mu\nu} = \kappa \left(\frac{H_{\mu\mu} + H_{\nu\nu}}{2} \right) S_{\mu\nu}, \quad \text{such that} \quad \kappa = 1.75,$$

$$= \kappa_{\mu\nu} S_{\mu\nu}. \qquad\qquad (10)$$

At times a more complicated expression for $H_{\mu\nu}$ has been used;[7,8] this does not modify the argument in the sequel.

A comparison of the on- and off-site overlap and Hamilton populations defined by the pairs of equations (3), (8) and (4), (9), respectively, illustrates the close relation between Mulliken overlap population and Hamilton population analysis techniques within an extended Hückel framework. The relation is concisely summarized by Eqs. (11) and (12), respectively,

$$\text{MOHP}_{\mu\mu} = H_{\mu\mu} \text{MOOP}_{\mu\mu}, \qquad\qquad (11)$$

$$\text{MOHP}_{\mu\nu} = \kappa_{\mu\nu} \text{MOOP}_{\mu\nu}. \qquad\qquad (12)$$

If Hamilton population analysis partitions the *total energy* and Mulliken overlap population analysis partitions *electrons*, Eqs. (11) and (12), which relate on- and off-site

Hamilton and overlap populations, imply that we may think of *Hamilton population analysis as an energy-weighted overlap population analysis.*

It is important to note that when carrying out Hamilton population analysis, bonding orbital interactions result in negative HP's, in contrast to the corresponding positive overlap populations. The sign reversal can be directly traced to the ''energy weighting,'' $\kappa_{\mu\nu}$ (12). A positive overlap population transforms to a negative Hamilton population when multiplied by the sum of diagonal Hamiltonian matrix elements $(H_{\mu\mu}+H_{\nu\nu})$, both of which are negative numbers.

We now proceed with a discussion of the characteristics of overlap and Hamilton population analysis when applied to simple two-orbital systems.

V. POPULATION ANALYSIS IN TWO-ORBITAL SYSTEMS

In order to provide a clear comparison of overlap and Hamilton population analysis techniques, in this section we focus on the simplest chemical bonding situation possible, bonding in the hydrogen molecule. This simple two-orbital system can also be manipulated, within the bounds of the extended Hückel methodology, to model both homo- (scheme **1**)

and heteronuclear (scheme **2**)
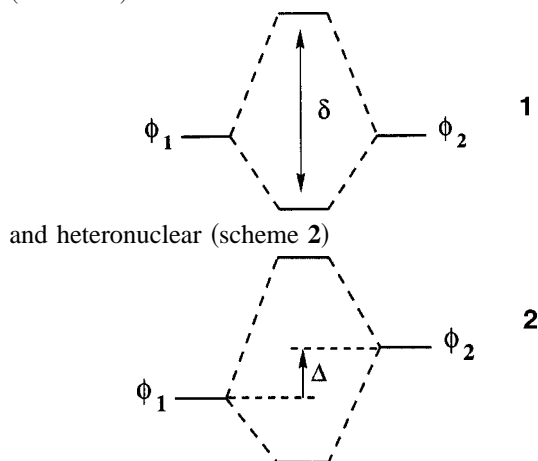
orbital interactions. This is accomplished in the numerical experiments we perform by varying the diagonal Hamiltonian matrix elements of the 1s orbitals (which define their energy); in effect, we simulate a ''pseudohydrogen,'' an atom whose orbital is spatially identical to that of hydrogen but of differing electronegativity.

In addition to varying the energy of the basis orbitals it is possible to alter the radial extent of the 1s orbitals by varying the Slater exponent. In the following work we fixed orbital exponents at the value traditionally used for hydrogen,[9] even as the electronegativity of an atom was varied, so as to focus attention on the behavior of overlap and Hamilton population analysis techniques as a function of basis orbital energy.

Consider the following numerical experiment. The H_1–H_2 overlap and Hamilton populations ($MOOP_{12}$ and $MOHP_{12}$, respectively) were calculated as the energy of the 1s orbital on hydrogen number 2, H_{22} increased from -18.6 to -9.6 eV in 1 eV increments. The energy of the 1s orbital for hydrogen number 1, H_{11}, was fixed at the elemental
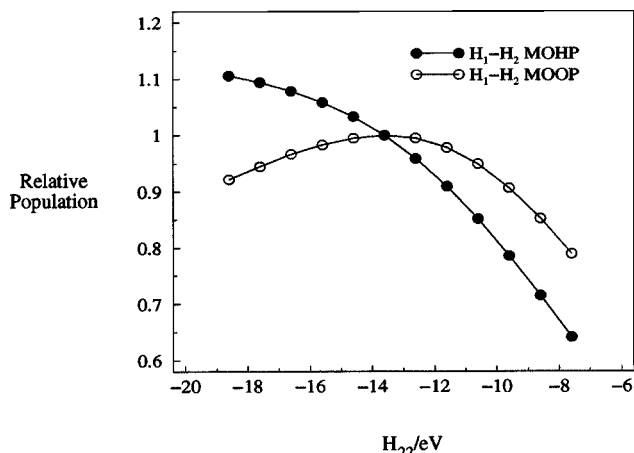

FIG. 1. H_1–H_2 overlap and Hamilton populations as a function of the diagonal Hamiltonian matrix element (basis orbital energy) for the 1s orbital on H_2, H_{22}. The diagonal Hamiltonian matrix element for the 1s orbital on H_1 is fixed at the elemental hydrogen value of -13.6 eV.

hydrogen value of -13.6 eV throughout. The results are summarized in Fig. 1, all overlap and Hamilton populations being plotted relative to their respective values for the homonuclear case defined by $H_{11}=H_{22}=-13.6$ eV.

On examination of Fig. 1 it is apparent that overlap and Hamilton populations behave in a fundamentally different way. The homonuclear case is a maximum in the overlap population curve, all departures from symmetry leading to a decrease in overlap population. On the other hand, the homonuclear case holds no more significance than any other point on the Hamilton population curve. The monotonic form of the Hamilton population curve shown in Fig. 1 can be traced to the linear relation between H_{22} and the ''energy-weighting,'' $\kappa_{\mu\nu}$ [see Eq. (10)] used to generate the MOHP from the corresponding MOOP according to Eq. (12). *From a Hamilton population viewpoint, and that of energy partitioning in general, bonding interactions involving energetically low lying basis functions are favored over those interactions between energetically higher lying basis functions.*

Within the LCAO concept we embrace the idea that to a good approximation the molecular electron density can be reproduced by a superposition of atomic electron densities. Thus, it is not surprising that on forming a molecular orbital the energy of the molecular orbital is representative of the energies of the constituent atomic ''basis'' orbitals. For a canonical illustration of this point consider the homonuclear case, for which on varying $H_{11}(=H_{22})$ the overlap population remains constant and the off-site Hamilton population, $MOHP_{12}$ varies linearly with respect to the diagonal Hamiltonian matrix element, as illustrated in Fig. 2.

Let us see if we can understand what is happening with the aid of perturbation theory. The wave functions for the homonuclear case (13) serve as the zeroth-order wave functions for the study of the perturbation from the homonuclear **1** to heteronuclear case **2**,

$$\psi_1=\frac{1}{\sqrt{2(1+S)}}\{\phi_1+\phi_2\} \quad \text{(bonding)},$$

$$(13)$$

$$\psi_2 = \frac{1}{\sqrt{2(1-S)}} \{\phi_1 - \phi_2\} \quad (antibonding),$$

where we have defined $S = \langle \phi_1 | \phi_2 \rangle$ to be the overlap matrix element between the basis functions ϕ_1 and ϕ_2. The overlap, S, between the H($1s$) orbitals is positive.

Formally, the wave function of the ith eigenstate in the heteronuclear case may be expressed as a series of corrections to the zeroth-order homonuclear wave function for the ith eigenstate, according to

$$\psi_i = \psi_i^0 + \psi_i^1 + \psi_i^2 + \psi_i^3 + \cdots . \tag{14}$$

In order to describe the form of the overlap population curve in Fig. 1, it is necessary to consider only the first-order correction to the zeroth-order wave functions, ψ_i^1.

Generally, the first-order correction to the ith wave function is written as

$$\psi_i^1 = \sum_{\mu \neq i} d_{\mu i} \psi_\mu^0, \quad \text{such that } d_{\mu i} = -\frac{\langle \psi_\mu^0 | \hat{H}' | \psi_i^0 \rangle}{(E_\mu^0 - E_i^0)}, \tag{15}$$

where E_i^0 denotes the ith eigenvalue of the zeroth-order (homonuclear) Hamiltonian and $\hat{H}'$ represents the perturbation to the zeroth-order Hamiltonian, $\hat{H}^0$.

The Hamiltonian for the perturbed system, $\hat{H}$ is written as

$$\hat{H} = \hat{H}^0 + \hat{H}' = \begin{pmatrix} H_{11} & H_{12} \\ H_{12} & H_{22} \end{pmatrix} + \begin{pmatrix} 0 & H_{12}' \\ H_{12}' & \Delta \end{pmatrix}. \tag{16}$$

Here H_{12}' denotes the correction to the off-diagonal Hamiltonian matrix element arising from the perturbation $H_{22} = H_{11} + \Delta$.

Thus, for the case of two-orbital interactions the first-order correction to the wave function is written as

$$\psi_1^1 = d_{21} \psi_2^0 = -\frac{\langle \psi_2^0 | \hat{H}' | \psi_1^0 \rangle}{(E_2^0 - E_1^0)} \cdot \psi_2^0. \tag{17}$$

Equation (17) can be simplified on noting that

$$\langle \psi_2^0 | \hat{H}' | \psi_1^0 \rangle = -\frac{\Delta}{2\sqrt{(1+S)(1-S)}}, \tag{18}$$

for a perturbation Δ defined by (16).

Thus, we approximate the perturbed bonding wave function by

$$\psi_1 \approx \psi_1^0 + \psi_1^1 \approx \frac{1}{\sqrt{N}} \left\{ (\phi_1 + \phi_2) + \left(\frac{\Delta}{\delta} \cdot \frac{1}{2(1-S)} \right)(\phi_1 - \phi_2) \right\}, \tag{19}$$

where δ is the energy difference between the bonding and antibonding homonuclear (zeroth-order) eigenvalues, $\delta = E_2^0 - E_1^0$ as illustrated in scheme **1**, and the normalizing factor, N, is defined by the relation

$$N = \frac{(1+\gamma^2) + (1-\gamma^2)S}{(1+S)}. \tag{20}$$

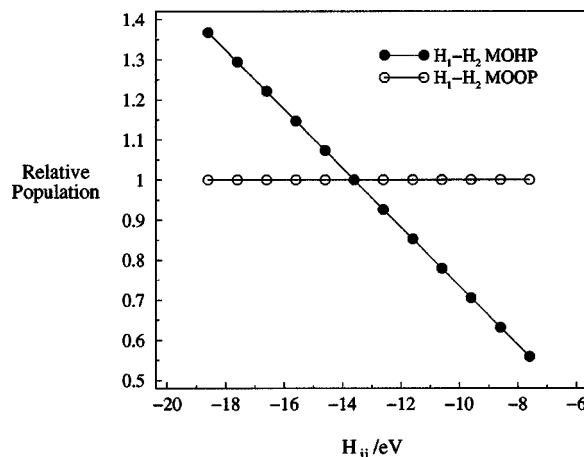On defining the positive quantity γ by

FIG. 2. H_1–H_2 overlap and Hamilton populations as a function of basis orbital energy for a degenerate two-orbital interaction.

$$\gamma = \frac{\Delta}{\delta} \cdot \frac{1}{2(1-S)}, \tag{21}$$

the bonding wave function for the heteronuclear case is approximated by the expression

$$\psi_1 \approx \frac{1}{\sqrt{N}} \{(1+\gamma)\phi_1 + (1-\gamma)\phi_2\}, \quad \text{such that } \gamma > 0. \tag{22}$$

The form of the overlap population curve shown in Fig. 1 can be understood from Eq. (22) if we now consider the definition of the Mulliken overlap population matrix element between orbitals 1 and 2, MOOP$_{12}$ (4). Substituting (22) in (4) gives

$$\text{MOOP}_{12} = \frac{4(1+\gamma)(1-\gamma)S}{N} = \frac{4(1-\gamma^2)S}{N}. \tag{23}$$

Thus, as the size of the perturbation Δ increases, the overlap population between basis functions 1 and 2 decreases as the square of Δ [as per the definition of γ given in Eq. (21)]. Thus, we can now account for the parabolic form of the overlap population curve shown in Fig. 1. Further, we are now in a position to understand the invariance of the overlap population for the homonuclear case ($\Delta = 0 \Rightarrow \gamma = 0$) with respect to the energy of the basis orbitals, as illustrated by Fig. 2.

Thus far, we have been able to reproduce, through the use of perturbation theory, the basic characteristics of overlap population analysis pertaining to simple two-orbital interactions. How are we to interpret these curves? Within an extended Hückel framework orbital interactions have been productively analyzed as a function of the overlap between the orbitals, as described by the Wolfsberg–Helmholtz approximation of Eq. (10). Further, the explicit absence of electrostatic contributions to the extended Hückel Hamiltonian (as well as some experience with ionic systems) leads us to conclude that it basically captures best the covalent bonding extreme.

Within such a covalent description, and using one-electron perturbation theory, we expect the strength of orbital interactions to increase with increasing orbital overlap and
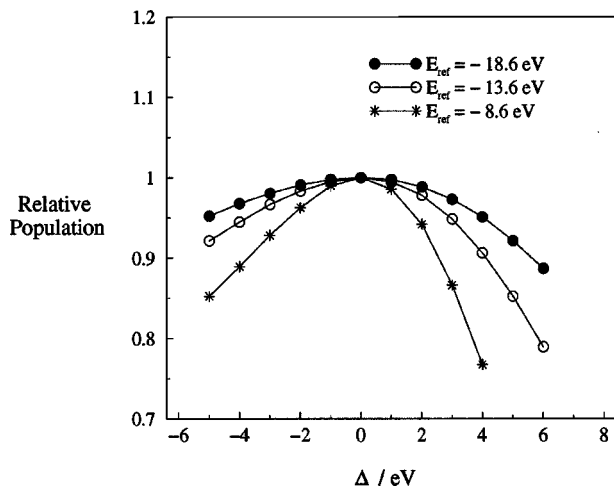
FIG. 3. $H_1–H_2$ overlap population as a function of the homo to heteronuclear perturbation Δ and the ''reference energy'' for each perturbation.

decrease on increasing the energy separation of the interacting orbitals.[2] Both of these ''criteria'' are realized in the expression for the off-site overlap population (23)—the energy separation of the interacting orbitals, Δ, varying linearly with γ, as given by Eq. (21).

Now consider Hamilton populations. Recall our earlier conclusion that Hamilton population analysis may be considered (within an extended Hückel framework) to be an energy-weighted overlap population analysis. We may then regard Hamilton populations as bonding descriptors that incorporate not only information on the overlap and ''energy match'' of the interacting orbitals but also information on the energetic contribution arising from the orbital interaction. The ''energy weighting'' we refer to is that given by the Wolfsberg–Helmholtz formula (10) and reflects, in its use of the diagonal Hamiltonian matrix elements for the basis orbitals, the basic tenet of the LCAO approximation—that the molecular electron density can, to a good approximation, be represented by a sum over atomic densities. Most importantly, the use of the energy weighting (10) extends the range of applicability of the overlap population to include a range of moderately ionic bonding situations.

We now proceed with an analysis of the variation in the off-site overlap population as a function of the energy of the ''fixed'' orbital, by a series of numerical experiments analogous to that summarized by Fig. 1. In doing so we are attempting to understand how the results of population analysis vary, not only as a function of the extent of the homo- to heteronuclear perturbation, but also as a function of the electronegativity of the atoms with which the basis orbitals are associated. In referring to electronegativity we are, within the context of out numerical experiments, varying the energy of the ''fixed'' basis function—a quantity we subsequently refer to as the ''reference energy'' for the experiment.

Consider the overlap population curves given in Fig. 3. The curves were generated in numerical experiments analogous to that summarized by Fig. 1—save for the value of the reference energy. From Fig. 3 we can see that as the reference energy increases, changes in overlap population for a given value of Δ increase. Thus, for the nondegenerate case

2, the overlap population, for any nonzero value of Δ, is not invariant with respect to the energy of the basis orbitals.

Consider the definition of the quantity γ as given by Eq. (22) and consider the overlap population (23) as a function of the reference energy for a fixed value of Δ (as defined by scheme 2). Since we are not altering the overlap between the basis orbitals, γ becomes a function of δ, the energy separation of the bonding and antibonding orbitals. Thus, to understand how overlap population varies with basis orbital energy (for a given value of Δ), it is necessary to define how δ varies with respect to the basis function energies.

Within an extended Hückel framework the eigenvalues for the heteronuclear case 2 are

$$E_1 = \frac{(H_{11}+H_{22})\cdot(1+\kappa S)}{2(1+S)} \quad \text{(bonding)},$$

$$E_2 = \frac{(H_{11}+H_{22})\cdot(1-\kappa S)}{2(1-S)} \quad \text{(antibonding)},$$

(24)

where $S = \langle \phi_1 | \phi_2 \rangle$ is the overlap matrix element between the basis orbitals and the constant κ has a value of 1.75.

From Eq. (24) δ, for the heteronuclear case, becomes

$$\delta = \frac{S(1-\kappa)}{(1-S^2)}(H_{11}+H_{22}).$$

(25)

Thus δ varies linearly as the sum of the basis orbital energies. Hence, as the reference energy increases the magnitude of δ decreases (for fixed Δ), and γ increases—producing the observed decrease in overlap population as defined by Eq. (23).

The increased sensitivity of overlap populations to the homo- to heteronuclear perturbation on increasing the reference energy is simply an illustration of the variational principle at work. On effecting a homo- to heteronuclear perturbation, the on-site overlap population of the energetically lower lying basis orbital increases at the expense of the off-site overlap population (23) in an effort to minimize the total electronic energy of the system. This is an effect that becomes increasingly important as the reference energy increases and the total electronic energy decreases.

We now proceed with an application of population analysis to main group compounds to illustrate the ramifications of the population analysis characteristics we have just highlighted for two-orbital interactions.

VI. APPLICATIONS OF POPULATION ANALYSIS TO MAIN GROUP COMPOUNDS

In this section we analyze the differences between Hamilton and overlap population descriptions of chemical bonding for several main group compounds. These have been selected to illustrate the range of bonding situations amenable to study by overlap and Hamilton population analysis. Initially we focus on the isoelectronic series of hypervalent square pyramidal fluorides BrF_5, $[TeF_5]^-$, $[SbF_5]^{2-}$ 3 and analyze the E–F (E=Br,Te,Sb) interactions in terms of the constituent $s-s$, $s-p$, and $p-p$ interactions. This is followed by an analysis of the P_4 molecule, which illustrates another bonding extreme.

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## A. The square pyramidal fluorides, EF_5, E=Br,Te,Sb

Despite being a point of intrinsic electronic interest, the hypervalency of these compounds is not our primary interest. The large range of basis orbital energies offered by this series of compounds (see Table I) affords us the opportunity to examine the behavior of overlap and Hamilton population analyses over the entire spectrum of interactions discussed in the preceeding section. The fluoride structures are illustrated schematically in scheme **3**,

$$F_a$$
$$F_b \diagdown \underset{F_b}{\overset{|}{E}} \diagup F_b \qquad E = Br,Sb,Te \qquad \mathbf{3}$$
$$F_b \qquad F_b$$
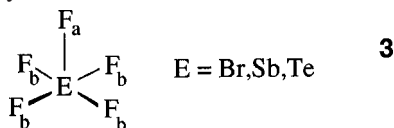
the subscripts a and b being used to denote axial and basal fluorine atoms.

The population analyses were performed using the YAe-HMOP extended Hückel package.[10] The extended Hückel parameters used in this study are summarized in Table I. The Amsterdam Density Functional (ADF) package[11] was used to generate molecular geometries for input to the extended Hückel calculations. The ADF calculations were performed using the Vosko–Wilk–Nusair parametrization of the LDA[12] with gradient corrections using the parametrizations of the Becke (exchange)[13] and Perdew (correlation).[14] A triple zeta basis set (ADF database IV) was used to model all atoms. The ADF optimized fluoride geometries were in reasonable agreement with previously reported geometries.[15]

For these, and all other main group compounds, the s and p basis orbitals on one atomic center will interact with both the s and p orbitals on neighboring centers. Thus there are four separate interactions that must be considered when forming homonuclear (scheme **4**)
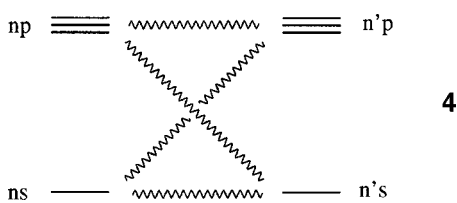
and heteronuclear (scheme **5**)
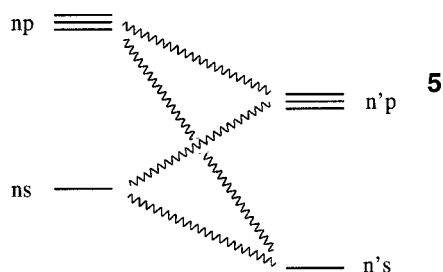
compounds.

Let us begin by analyzing the $s-s$, $s-p$, and $p-p$ contributions to bonding within the extended Hückel approximation for both the axial and basal E–F bonds (E=Br,Te,Sb). The E–F interactions here generally fall into the pattern of scheme **5**. The $s-s$, $s-p$, and $p-p$ contributions to axial and basal E–F (E=Br,Te,Sb) bonding are given in Table II for both Hamilton and overlap population analyses.

TABLE I. Extended Hückel parameters used in this study.

Atom	Orbital	H_{ii}/eV	ζ
H	$1s$	−13.600	1.300
F	$2s$	−40.000	2.425
	$2p$	−18.100	2.425
Br	$4s$	−22.100	2.588
	$4p$	−13.100	2.131
Te	$5s$	−20.800	2.510
	$5p$	−14.800	2.160
Sb	$5s$	−18.800	2.323
	$5p$	−11.700	1.999
P	$3s$	−18.600	1.750
	$3p$	−14.000	1.300
B	$2s$	−15.200	1.300
	$2p$	−8.500	1.300
C	$2s$	−21.400	1.625
	$2p$	−11.400	1.625

On examination of the extended Hückel parameters given in Table I, we note that the E–F interaction can be subdivided into two groups of basis orbital interactions. The $E(s)–F(p)$ and $E(p)–F(p)$ interactions involve basis orbitals with a modest energy separation and thus operate close to the regime around the overlap population maximum in Fig. 1. Thus, we expect the relative magnitudes of $E(s)–F(p)$ and $E(p)–F(p)$ overlap populations to qualitatively mirror the corresponding Hamilton populations.

In contrast, the $E(s)–F(s)$ and $E(p)–F(s)$ interactions operate in a regime toward the left-hand extreme of Fig. 1; we do not expect that these overlap populations will reflect the corresponding Hamilton populations.

This is indeed what we find on examination of the $s-s$, $s-p$, and $p-p$ components of E–F bonding in EF_5 (E=Br,Te,Sb). Consider, for instance, Br–F_{axial} bonding. From Table II we calculate that the $p-p$ component of the Br–F_{axial} overlap population is greater than the $s-s$ component by a factor of 5.1, in contrast to the more modest increase in Hamilton population by a factor of 2.5. This sizable discrepancy is due, primarily, to the energetically very low lying $F(2s)$ basis orbital, which transforms a relatively small $s-s$ overlap population into a significant Hamilton population via the Wolfsberg–Helmholtz ''energy weighting'' given in Eq. (10).

If we examine the $Br(s)–F(p)$ and $Br(p)–F(p)$ components of the Br–F_{axial} interaction, we note that for basis orbital interactions involving relatively modest energy separations the overlap and Hamilton population ratios for these components of the interaction are more similar at 1:3.8 and 1:3.0, respectively.

If we note that the $Br(s)–F(p)$ and $Br(p)–F(p)$ interactions involve basis orbitals separated by 4 and 5 eV, respectively—a small separation by extended Hückel standards[9]—we conclude that even for such interactions Hamilton and overlap population descriptions of orbital interactions can differ significantly.

B. The P_4 cluster

Now let us turn our attention to a somewhat different situation, P–P bonding in the tetrahedral P_4 cluster. Scheme

TABLE II. Decomposition of M–F bonding by Hamilton and Mulliken overlap population analysis for the isoelectronic square pyramidal fluorides BrF_5, $[TeF_5]^-$, and $[SbF_5]^{2-}$.

Interaction	Br–F$_{axial}$		Br–F$_{basal}$	
	HP/eV	OP	HP/eV	OP
Br(s)–F(s)	−2.00	0.035	2.38	−0.042
Br(s)–F(p)	−1.66	0.047	1.41	−0.040
Br(p)–F(s)	−4.17	0.080	−4.80	0.092
Br(p)–F(p)	−4.96	0.179	−3.50	0.127
Interaction	Te–F$_{axial}$		Te–F$_{basal}$	
	HP/eV	OP	HP/eV	OP
Te(s)–F(s)	−3.81	0.068	1.66	−0.030
Te(s)–F(p)	−2.36	0.069	0.53	−0.016
Te(p)–F(s)	−2.74	0.052	−5.58	0.106
Te(p)–F(p)	−4.09	0.141	−3.81	0.131
Interaction	Sb–F$_{axial}$		Sb–F$_{basal}$	
	HP/eV	OP	HP/eV	OP
Sb(s)–F(s)	−2.72	0.050	1.94	−0.035
Sb(s)–F(p)	−1.11	0.034	0.77	−0.024
Sb(p)–F(s)	−4.77	0.093	−4.70	0.092
Sb(p)–F(p)	−3.30	0.124	−2.33	0.087

TABLE III. Hamilton and Mulliken population analysis of P–P bonding in tetrahedral P_4.

Interaction	HP/eV	Relative HP	OP/e	Relative OP
$s-s$	−2.41	2.15	0.074	1.90
$s-p$	−1.12	1.00	0.039	1.00
$p-p$	−10.84	9.68	0.442	11.33

Hamilton population analysis as a versatile tool for detailed, albeit semiquantitative, analysis of chemical bonding. This belief is founded on the success of overlap population analysis—a formalism that, as we have seen, is incorporated within the Hamilton population concept.

Our evaluation of Hamilton population analysis continues and we suspect that the full utility of Hamilton population analysis as a transparent semiquantitative covalent bonding descriptor will only become apparent as the number of applications of this bonding descriptor mounts in the literature.

4 is relevant here, remembering that the energy separation between the $P(3s)$ and $P(3p)$ basis orbitals is ~4.6 eV—small when compared with s/p separations of ~21.9 eV in fluorine, ~9.0 eV in bromine, etc. Thus, $s-s$, $s-p$, and $p-p$ interactions all operate in the regime close to the maximum in the overlap population curve of Fig. 1. Hence, we expect Hamilton and overlap population analyses to yield qualitatively similar descriptions of P–P bonding in tetrahedral P_4.

Indeed, on examination of Table III, the results of Hamilton and overlap population partitioning of P–P bonding are qualitatively similar. The relative $s-s$, $s-p$, and $p-p$ contributions to P–P bonding as calculated by an overlap population analysis mirror those calculated by Hamilton population analysis.

VII. CONCLUSION

We have reasoned that Hamilton population analysis affords us the opportunity to study a significantly wider range of chemical bonding situations than those amenable to the study by Mulliken overlap population analysis.

We believe that the well-documented shortcomings of extended Hückel theory will not detract from the utility of

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