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Molecular Structural Formulas as One-Electron Density and Hamiltonian Operators: The VIF Method Extended

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The valency interaction formula (VIF) method is given a broader and more general interpretation in which these simple molecular structural formulas implicitly include all overlaps between valence atomic orbitals even for interactions not drawn in the VIF picture. This applies for VIF pictures as one-electron Hamiltonian operators as well as VIF pictures as one-electron density operators that constitute a new implementation of the VIF method simpler in its application and more accurate in its results than previous approaches. A procedure for estimating elements of the effective charge density-bond order matrix, $\bar{P}_{\mu\nu}$, from electron configurations in atoms is presented, and it is shown how these lead to loop and line constants in the VIF picture. From these structural formulas, one finds the number of singly, doubly, and unoccupied molecular orbitals, as well as the number of molecular orbitals with energy lower, equal, and higher than $-{}^1/_2E_h$, the negative of the hydrogen atom's ionization energy. The VIF results for water are in qualitative agreement with MP2/6311++G3df3pd, MO energy levels where the simple VIF for water presented in the earlier literature does not agree with computed energy levels. The method presented here gives the simplest accurate VIF pictures for hydrocarbons. It is shown how VIF can be used to predict thermal barriers to chemical reactions. Insertion of singlet carbene into H_2 is given as an example. VIF pictures as one-electron density operators describe the ground-state multiplicities of B_2, N_2, and O_2 molecules and as one-electron Hamiltonian operators give the correct electronegativity trend across period two. Previous implementations of VIF do not indicate singly occupied molecular orbitals directly from the pictorial VIF rules for these examples. The direct comparison between structural formulas that represent electron density and those that represent energy is supported by comparison of a simple electronegativity scale, $\chi_D = N/n^2$, with well-known electronegativity scales of Pauling, Mulliken, and Allen. This scale comes from the method used to calculate $\bar{P}_{\mu\mu}$ for sp^3 hybridized period-two elements and is comparable to electronegativity because it has the same form as $\langle 1/r \rangle$ for hydrogenic orbitals. It therefore provides a physical basis for the representation of one electron density and Hamiltonian operators by the same VIF picture.

I. Introduction

The electronic theory of molecules, both qualitative and quantitative, has long required notions of both electron density and energy. The utility of Lewis structures in judging stable molecular structures based on arrangement of electron pairs is an obvious example.[1] Pauling's electronegativity scale, used to predict bond polarity, is based on bond dissociation energies and the idea of resonance.[2] Molecular orbital methods describe both charge distribution and ionization energy of electrons.[3] The VSEPR model, used to predict stable molecular geometries, is supported by comparison with the Laplacian of electron density.[4] The success of density functional theory along with its increasing usage and development are all indications that molecular properties are based on energy and electron density and the fact that these two properties are linked.[5] The role played by the atomic representation of electron density in rationalizing chemical behavior is well recognized, and, according to the Hellmann−Feynman theorem, high-quality electron densities for molecules can be useful in calculating molecular properties quantitatively.[6] The definition of the relationship between qualitative methods in chemistry and those for quantum chemical computation has long been an area of interest to quantum chemists.[7] Valency interaction formulas (VIF) are a well-defined connection between the mathematical formalism of quantum-molecular theories and the qualitative notions valuable in chemical reasoning.[8]

The VIF method is a pictorial version of molecular orbital theory, and as such VIF pictures have been drawn as effective one-electron Hamiltonian operators in an atomic orbital (AO) or hybridized atomic orbital (HAO) representation. As an effective one-electron Hamiltonian operator, the VIF picture is then "diagonalized" using two pictorial rules to predict the number of molecular orbitals that are lower (bonding), the same (nonbonding), and higher (antibonding) in energy than a reference energy implicit in the original VIF picture. This information is recorded in the level pattern index, LPI(n_+, n_0, n_-). Analogous to other qualitative MO theories, electrons are then filled into the resulting MO level pattern according to the aufbau and exclusion principles and Hund's rule. This yields the electron count index, ECI(n_+, n_0, n_-), which enumerates the number of bonding (n_+), nonbonding (n_0), and antibonding (n_-) electrons that follow.

Sinanoğlu, Alia, and Hastings (SAH 94) have shown that the use of valence orbital ionization energies, VOIEs, to calculate the aforementioned reference energies results in VIF predictions that often agree with molecular orbital energies for second-

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period hydrides of the form AH_n.[9] It is sometimes not possible to choose a reference energy a priori that leads to agreement between results from VIF and computations on an arbitrary level of theory.[10] This is because the effect of coulomb and exchange energies is different for electrons in molecules and their separated atoms. These energies also differ according to the basis set and method of approximation used. This paper provides a more general interpretation of VIF pictures, which also allows the simplest accurate VIF pictures to be arrived at simply and without guesswork about the most appropriate reference energy.

It is shown here how VIF pictures as electron density operators lead to simple accurate pictures that work equally well whether one is considering energy or electron density and can be drawn easily without reference to tables of valence orbital ionization energies, VOIEs. This approach is applied easily and gives clear results where the original implementation of the VIF method does not. The methods presented are supported by comparison with well-known chemical properties and comparison of a physically intuitive electronegativity scale.

II. VIF Pictures with All Overlaps Implicit

VIF pictures whether depicting one-electron Hamiltonian operators or one-electron density operators, as will be presented in this paper, include overlaps between all atomic or hybridized atomic orbitals in the picture whether or not valency interaction lines are drawn. This is a different and broader interpretation than that given in the previous literature. The deletion of overlaps from molecular orbital calculations that correspond to VIF pictures as suggested by Sinanoğlu is unecessary. In 1984 Sinanoğlu[8] wrote that "the VIF models the molecule based on an effective one-electron Hamiltonian $h = \beta_{ij} A^{ij}$ where $\beta_{ij} = \langle e_i|h|e_j\rangle$ and $2A^{ij} = |e^i\rangle\langle e^j| + |e^j\rangle\langle e^i|$. A $|e_i\rangle$ is the abstract ket of the valence atomic orbital ϕ_i. In the mathematical formulation of the method, a line in the VIF represents A^{ij}." It is clear that Sinanoğlu also interpreted this to mean that the calculations that correspond to the approximations implicit in a simple VIF picture (EHTD) do not include the overlaps, S_{ij}, for interactions A^{ij} not shown in the picture (SAH 94). "Although the N-electron ground-state wave function is approximated in the standard SF-like VB, while the one-electron Hamiltonian h is approximated in the std (again SF-like) VIF, in both cases similar AO−AO'overlap deletions have been made and conclusions depend on hybridization in similar ways." The EHTD calculations presented in SAH 94 therefore exclude overlaps for interactions not drawn in the simple VIF pictures presented. Deletion of these overlaps is unnecessary because diagonalization or inversion of the full overlap matrix is a linear transformation, which preserves the signs of the eigenvalues of the one-electron Hamiltonian, invariants crucial to the VIF method. The current author rewrote the HAO program used for the 1994 paper so that calculation corresponding to a simple VIF picture includes all overlaps, even those for which valency interactions have not been drawn in the VIF picture. As expected, the signs of the eigenvalues are preserved with respect to the given reference energies and in accord with the predictions made using simple VIF pictures. Results for methane are shown in Table 1. These and all other calculations made with this revised HAO program indicate that VIF pictures correspond to calculations that include all overlaps, even those for which valency interaction lines are not drawn in the VIF picture. As shown by SAH 94, the VIF as a one-electron Hamiltonian operator is drawn according to a reference energy, α, and corresponds to $\bar{h} = \bar{h}_{\mu\nu}A^{\mu\nu}$ with $\bar{h}_{\mu\nu} = h_{\mu\nu} - \alpha S_{\mu\nu}$. This equation allows a more general interpretation that is not included in SAH 94 or any previous work by Sinanoğlu.

TABLE 1: Molecular Orbital Energies (eV) Compared to $\alpha = -13.75$ eV for CH_4 According to Extended Hückel Theory (EHT) and Compared to EHTD Calculations with Some Overlaps Deleted (EHTD SAH 94) and with All Overlaps Included (EHTD All $S_{\mu\nu}$)

EHT	EHTD (SAH 94)	EHTD all $S_{\mu\nu}$
47.16	27.00	24.69
18.48	27.00	24.69
18.48	27.00	24.69
18.48	13.11	16.20
−1.77	−3.87	−4.42
−1.77	−3.87	−4.42
−1.77	−3.87	−4.42
−10.81	−8.18	−7.51

All $A^{\mu\nu}$ and overlaps $S_{\mu\nu}$ can be considered to be implicit in the VIF picture so that $\bar{h}_{\mu\nu} = (h_{\mu\nu} - \alpha S_{\mu\nu}) \approx 0$ if $h_{\mu\nu} \approx \alpha S_{\mu\nu}$ and negligible elements $\bar{h}_{\mu\nu}$ or $\bar{P}_{\mu\nu}$ (to be presented later in this paper) can be set to zero with corresponding valency interactions not drawn in the VIF. $A^{\mu\nu}$ $(\mu \neq \nu)$ themselves are not set equal to zero or removed as Sinanoğlu suggests. This would be the same as setting ϕ_μ and/or ϕ_ν equal to zero and therefore require the removal of all possible pairs of valency points without valency interactions drawn between them. In addition, zero overlap ($S_{\mu\nu} = 0$) is not a good indicator that interactions should be absent in the VIF picture. For example, interactions between hybrid orbitals centered on the same atom are included in accurate VIF pictures while these orbitals comprise an orthonormal set so they have no overlaps between them. The interpretation given in the present article is consistent with the way that the actual basis AOs or HAOs overlap due to the symmetry of the molecule. Having the complete and invertible overlap matrix is crucial to Sinanoğlu's covariance theory, which is the basis of the VIF method. There is no disadvantage to defining the valency points as $A^{\mu\mu}$ while considering all $A^{\mu\nu}$ to be implicit. One then draws loops and valency interactions only for relevant values of $\xi = \bar{h}_{\mu\mu}/\beta_o$, $\kappa = \bar{h}_{\mu\nu}/\beta_o$ or likewise $\xi = \bar{P}_{\mu\mu}/\beta_o$, $\kappa = \bar{P}_{\mu\nu}/\beta_o$ presented in this paper. Relevant interactions are drawn according to intuitive notions of chemical bonding and tested using the pictorial VIF rules and by comparison to the molecule's known properties or computations. Furthermore, the interpretation given here is consistent with the way that the intended AO or HAO basis set actually transforms with application of the VIF rules. Valency points in a VIF picture represent $A^{\mu\mu}$ and all $A^{\mu\nu}$ $(\mu \neq \nu)$ are implicit. One-electron operators, $\bar{\omega} = \bar{\omega}_{\mu\nu}|e^\mu\rangle\langle e^\nu|$, are represented by a VIF picture if a method for determining elements $\bar{\omega}_{\mu\nu}$ can be determined. This paper presents a method for estimating elements of the charge density-bond order matrix, $\bar{P}_{\mu\nu}$, so that VIF pictures as one-electron density operators can be drawn and used for chemical deductions. The advantages to this method are demonstrated.

III. VIF Pictures as One-Electron Density Operators[11]

Electron density is a property that can be calculated from self-consistent field wavefunctions. For a single determinant ground-state wavefunction, Ψ_o, the electron density operator has the following form

$$\rho = |\Psi_o\rangle\langle\Psi_o| = P_{ii}|\psi_i\rangle\langle\psi_i| \; (\textit{summation convention}) \tag{1}$$

Lower case ψ_i is the ith molecular orbital, and P_{ii} is its corresponding element in the charge-density bond-order matrix, which is diagonal in the molecular orbital representation. P_{ii} is the molecular orbital electron occupancy and thus has possible values of 2, 1, or 0. Each of the molecular orbitals can be written as an expansion in terms of a set of atomic or hybridized atomic orbitals. Atomic orbital and hybridized atomic orbital basis sets for molecules are generally nonorthogonal, so the covariance theory of Sinanoğlu[12] and the unity trick that follows are applied to write the density operator in terms atomic, or hybridized atomic orbitals, where $|\phi_\mu\rangle$ is the abstract ket for atomic orbital ϕ_μ.

$$\rho = P_{ii}|\phi^\mu\rangle\langle\phi_\mu|\psi_i\rangle\langle\psi_i|\phi_\nu\rangle\langle\phi^\nu| = P_{ii}|\phi^\mu\rangle c_{\mu i}\, c_{i\nu}\langle\phi^\nu| = c_{\mu i}\, P_{ii}\, c_{i\nu}|\phi^\mu\rangle\langle\phi^\nu| \quad (2)$$

The molecular orbital coefficients, $c_{\mu i}$, transform the charge-density bond-order matrix with elements P_{ii} into the atomic orbital or hybridized atomic orbital representation with elements $P_{\mu\nu}$. Latin indices have been used for MOs and Greek for AOs or HAOs according to convention

$$\rho = P_{\mu\nu}|\phi^\mu\rangle\langle\phi^\nu| = P_{\mu\nu}A^{\mu\nu} \text{ where } A^{\mu\nu} = \frac{(|\phi^\mu\rangle\langle\phi^\nu| + |\phi^\nu\rangle\langle\phi^\mu|}{2} \quad (3)$$

To apply these equations in terms of VIF molecular structural formulas as one-electron density operators, one must first estimate the elements $P_{\mu\nu}$. Reasonable approximations can be made based on electron configurations in the separated atoms and the known or tentative three-dimensional geometry of the molecule. After the VIF picture is drawn, the two pictorial VIF rules are applied to determine the numbers of doubly, singly, and unoccupied molecular orbitals. One does not expect to retrieve values of 2, 1, and O for P_{ii} because the elements of $P_{\mu\nu}$ used are only estimates. The utility of this approach is based on Löwdin's definition of natural orbitals, θ_i, $\hat{\rho}\theta_i = n_i\theta_i$.[13] The density eigenfunctions, θ_i, are natural orbitals and the density eigenvalues, which have the Pauli restriction, $0 \leq n_i \leq 2$, lead to "the most rapidly convergent possible expansions of the electron density and other one-electron properties" as well as to natural bond orbitals (Weinhold, page 23). Sets of atomic orbitals (AO), hybridized atomic orbitals (HAO), natural atomic orbitals (NAO), natural bond orbitals (NBO), and molecular orbitals (MO) for a molecule are related to each other through linear transformations and are thus covariant representations. The linear transformation that makes diagonal a one-electron density operator will therefore preserve the signature matrix of the corresponding one-electron Hamiltonian and vice versa. The VIF rules when applied to either a VIF picture that represents a one-electron Hamiltonian or a one-electron density operator will thus preserve the salient qualitative feature of either. Sequential use of the VIF rules does not necessarily comprise the transformation $c_{i\mu}P_{\mu\nu}c_{\nu i} = P_{ii}$ but will preserve the LPI discussed above and the OOI defined in the next paragraph.

By choosing a reference electron density of one electron per orbital and then using the VIF picture and pictorial VIF rules, one determines the numbers of molecular orbitals that have electron occupancy greater than, equal to, or less than one electron, that is, the number of MO's with 2, 1, or 0 electrons, respectively. This information is then recorded in the orbital occupancy index, OOI(n_2,n_1,n_0).

The effective one-electron density operator represented by a VIF picture is found by subtracting the reference of one electron per orbital multiplied by the overlap between orbitals μ and ν from the $\mu\nu$th element of the charge-density bond-order matrix.

$$\bar{\rho} = \bar{P}_{\mu\nu}A^{\mu\nu} = \bar{P}_{\mu\nu}|\phi^\mu\rangle\langle\phi^\nu| = (P_{\mu\nu} - 1S_{\mu\nu})|\phi^\mu\rangle\langle\phi^\nu| \quad (4)$$

The elements of the effective charge-density bond-order matrix are therefore $\bar{P}_{\mu\nu} = (P_{\mu\nu} - 1S_{\mu\nu})$ where $S_{\mu\nu}$ is the $\mu\nu$th element of the overlap matrix. This is analogous to VIF pictures as effective one-electron Hamiltonian operators for which $\bar{h} = \bar{h}_{\mu\nu}A^{\mu\nu}$ and $\bar{h}_{\mu\nu} = (h_{\mu\nu} - \alpha\, S_{\mu\nu})$ and α is the reference energy. The VIF picture is drawn according to normalized values $\bar{P}_{\mu\nu}/\beta_o$ where β_o is chosen based on hybridization for intrahybrid interactions or bond order for interatomic interactions. The method is demonstrated for water, hydrocarbons, the insertion of singlet carbene into H_2, and second-row diatomic molecules later in this paper.

As already stated in this paper and different than earlier VIF implementations, components $A^{\mu\mu}$ and $A^{\mu\nu}$ exist for and between all orbitals in the basis set, $\{\phi^\mu\}$. Valency interaction formula pictures for $\bar{h}$ or $\bar{\rho}$ are greatly simplified if some elements $\bar{h}_{\mu\nu}$ or $\bar{P}_{\mu\nu}$ are at or close to zero and can be neglected while maintaining an accurate picture. One may anticipate this based on intuition about the molecule's geometry, use of symmetry and group theory methods, and also based on the chosen references for energy and/or electron density, respectively.

When the VIF reference for electron density is one electron per orbital and the reference energy, α_E, is the negative of the ionization energy of a hydrogen atom, $\alpha_E = -{}^1/_2E_h = -13.61$ eV, the effective electron density and one-electron Hamiltonian operators have the same VIF picture, the resulting numbers of doubly, singly, and unoccupied molecular orbitals are correct, and the VIF energy level pattern is in good agreement with those that result from computation. These choices give simple and accurate VIF pictures for molecules composed of hydrogen and second-period elements.

IV. Applications

VIF as an Effective One-Electron Density Operator for the Water Molecule. *Calculation of ξ and κ for a Water Molecule.* Elements $P_{\mu\nu}$ calculated according to electron configurations in oxygen and hydrogen atoms lead to accurate electron configuration in the water molecule's valence molecular orbitals, that is, a correct orbital occupancy index, OOI(n_2,n_1,n_0). To find appropriate $P_{\mu\nu}$ one must consider the atoms hybridization in the molecule, its number of valence electrons, and in some cases, bond orders in the molecule.

Water has a bent geometry with a bond angle of 104.5°, so a tetrahedral hybridization for the oxygen atom is a natural choice. The ground-state valence electron configuration of an oxygen atom is transformed using the sp^3 hybridization matrix, $\mathbf{T_{sp3}}^\dagger\ \mathbf{P_{AO}}\ \mathbf{T_{sp3}} = \mathbf{P_{sp3}}$. In the AO valence frame, oxygen has two 2s electrons and four 2p electrons. The average 2p electron occupancy for a ground-state oxygen atom is therefore ${}^4/_3$. The transformation of $\mathbf{P_{AO}}$ using a tetrahedral (sp^3) hybridization matrix ($\mathbf{T_{sp3}}$) is shown in eq 5. The elements of the resulting $\mathbf{P_{sp3}}$ for oxygen are easy to calculate by hand. Applying sp^n hybridization, the resulting diagonal elements are $\alpha_{sp^n} = (1)/(n + 1)(\alpha_s + n\alpha_p)$ and the resulting off-diagonal elements are $\beta_{sp^n} = (1)/(n + 1)(\alpha_s - \alpha_p)$ where n is the number of p orbitals used in the hybridization. Average orbital occupancies 2 and ${}^4/_3$ for α_s and α_p, respectively, are used. In this case, the diagonal elements of $\mathbf{P_{sp3}}$ are ${}^1/_4(\alpha_{2s} + 3\alpha_{2p}) = {}^3/_2$ and the off-diagonal elements are ${}^1/_4(\alpha_{2s} - \alpha_{2p}) = {}^1/_6$.

$$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ \frac{1}{2} & \frac{-1}{2\sqrt{3}} & \sqrt{\frac{2}{3}} & 0 \\ \frac{1}{2} & \frac{-1}{2\sqrt{3}} & -\sqrt{\frac{1}{6}} & \sqrt{\frac{1}{2}} \\ \frac{1}{2} & \frac{-1}{2\sqrt{3}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{2}} \end{pmatrix} \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & \frac{4}{3} & 0 & 0 \\ 0 & 0 & \frac{4}{3} & 0 \\ 0 & 0 & 0 & \frac{4}{3} \end{pmatrix} \times \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{\sqrt{3}}{2} & \frac{-1}{2\sqrt{3}} & \frac{-1}{2\sqrt{3}} & \frac{-1}{2\sqrt{3}} \\ 0 & \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} \\ 0 & 0 & \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}} \end{pmatrix} = \begin{pmatrix} \frac{3}{2} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} \\ \frac{1}{6} & \frac{3}{2} & \frac{1}{6} & \frac{1}{6} \\ \frac{1}{6} & \frac{1}{6} & \frac{3}{2} & \frac{1}{6} \\ \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{3}{2} \end{pmatrix} \quad (5)$$

The normalization factor β_o is chosen to be $^1/_6$ in order to normalize the intrahybrid line constants. See eq 6. Subtracting the reference electron density of one electron per orbital and then dividing by β_o to normalize the off-diagonal elements gives the following loop and line constants for oxygen, ξ_{Osp3} and κ_{Osp3}, respectively.

$$\xi_{\mathrm{Osp3}} = \frac{\left(\frac{3}{2} - 1{\cdot}1\right)}{\left(\frac{1}{6}\right)} = \left(\frac{1}{2}\right)\left(\frac{6}{1}\right) = 3,$$

$$\kappa_{\mathrm{Osp3}} = \frac{\left(\frac{1}{6} - 1{\cdot}0\right)}{\left(\frac{1}{6}\right)} = \left(\frac{1}{6}\right)\left(\frac{6}{1}\right) = 1 \quad (6)$$

The VIF loop constants for the sp^3 oxygen atom in water are thus $\xi_{\mathrm{Osp3}} = 3$ when the line constants are normalized, $\kappa_{\mathrm{Osp3}} = 1$. Notice that $S_{\mu\nu} = \delta_{\mu\nu}$ because sp^3 hybrid orbitals are an orthonormal set. Hydrogen atoms have one electron, so for them $\xi_{\mathrm{H1s}} = (1 - 1)/\beta_o = 0$. Their valency points have no loops in the VIF picture. We normalize the line strengths for the O−H bonds because these have a bond order of one and because it is convenient to do so. See Figure 1.

Considering the hybridized valency orbital basis set and the geometry of the water molecule, one notes that each hydrogen 1s orbital interacts not only with the oxygen sp^3 hybrid orbital pointing toward it but also with each of the two oxygen lone pair sp^3 orbitals and also with the oxygen sp^3 orbital pointed at the other hydrogen atom. There are therefore two kinds of interactions not shown in the VIF picture. In neglecting these, it has only been assumed that $P_{\mu\nu} \approx 1S_{\mu\nu}$ for these interactions so that $\bar{P}_{\mu\nu} = (P_{\mu\nu} - 1S_{\mu\nu}) \approx 0$. This is perfectly consistent with the symmetry of the molecule and does not impose physical constraints that are unrealistic. Components $A^{\mu\nu}$ and overlaps $S_{\mu\nu}$ are implicit whether or not their corresponding loops and lines have constants of zero.[14] This is a clear advantage of the interpretation given in this paper.

Application of the Two Pictorial VIF Rules. Reduction of the water VIF picture using the two pictorial VIF rules is also shown in Figure 1. The two pictorial VIF rules are the multiplication rule and the addition rule. They are restated here in terms of the more general interpretation given in this paper.

1. Multiplication Rule: A valency point ($A^{\mu\mu}$) may be multiplied by a nonzero constant. All constants (κ) of valency interactions attached to $A^{\mu\mu}$ are then multiplied by this nonzero constant. If $A^{\mu\mu}$ has a loop, then its constant, ξ, is multiplied by the square of the nonzero constant.

2. Addition Rule: A valency point ($A^{\mu\mu}$) may be "lifted" and superimposed on another valency point ($A^{\nu\nu}$). All valency interactions (*VI*) and loops attached to $A^{\mu\mu}$ are carried along. Constants, ξ and κ, of superimposed loops and *VI*, respectively, add. If $A^{\mu\mu}$ and $A^{\nu\nu}$ are connected by a *VI* of strength κ, then this *VI* curls up to form a loop with strength 2κ on $A^{\nu\nu}$. If $A^{\nu\nu}$ already had a loop, then the curled-up loop superimposes this original loop and the value 2κ is added to the original loop constant, ξ. $A^{\mu\mu}$, the *VI* attached to it, and loop if it has one, are not removed; they remain as if "chalk marks" left behind.

Reduction of the VIF for water is shown in Figure 1. First, the multiplication rule is used; a hydrogen valency point is multiplied by negative one. See Figure 1a. The valency interaction attached to this valency point had an original strength of one, which has now been multiplied by minus one, Figure 1b. In the next pictures (b−d), the multiplied interaction is used to cancel the adjoining oxygen intrahybrid valency interactions according to the addition rule. The straight arrows in Figure 1 show the sequence of steps used to reduce the VIF picture. Valency interaction formulas related by the two rules are structurally covariant as indicated by "sc" over the straight arrows in Figure 1. Sinanoğlu's theory of structural covariance can be used to classify sets of molecular structures with similar energy.[15] The theory of structural covariance will be used along with the ideas developed here in a future paper on hydrogen transfer reactions.[16] In the context of this example, "sc" means only that each picture is arrived at from the previous one by use of the VIF rules. For the example of the insertion singlet carbene into the hydrogen molecule, to be given later in this paper, the theory of structural covariance is used to compare relative energies of reactants transition structures, TS, and products.

No valency interactions remain in a fully reduced VIF picture. Application of the two rules to fully reduce a VIF picture is analogous to diagonalization of $P_{\mu\nu}$ to find natural orbital occupancies or of $h_{\mu\nu}$ to find the MO energy level pattern. Substituting $\xi_{\mathrm{Osp3}} = 3$ into the resulting loop expressions yields four valency points with loops that have positive constants, no valency points without loops, and two valency points with negative loops. This gives an orbital occupancy index of OOI-(4,0,2), meaning that there are four doubly occupied, no singly occupied, and two unoccupied molecular orbitals. See the boxed area in Figure 1. Some common VIF fragments, reduced, and their eigenvalues are shown in Table 2. Similar VIF fragments will occur in later examples in this paper and be treated in more detail using the VIF rules. A detailed account of how the VIF rules are used to reduce the VIF pictures within the box in Figure 1 is given in the appendix.

If the same VIF picture is taken to be an effective one-electron Hamiltonian operator, then the reference energy is the energy of a hydrogen 1s electron, $-^1/_2 E_h$. In this case, the loop constants from the fully reduced VIF picture are interpreted as valence molecular orbitals lower in energy than $-^1/_2 E_h$ if the loop constant is positive, molecular orbitals equal in energy to $-^1/_2 E_h$ for valency points without loops (i.e., with loop constants equal to zero), and higher in energy than $-^1/_2 E_h$ for loops with negative constants. This gives a level pattern index of LPI(4,0,2) with respect to a reference energy of $-^1/_2 E_h$. The valence molecular orbitals from water's geometry optimized using MP2/

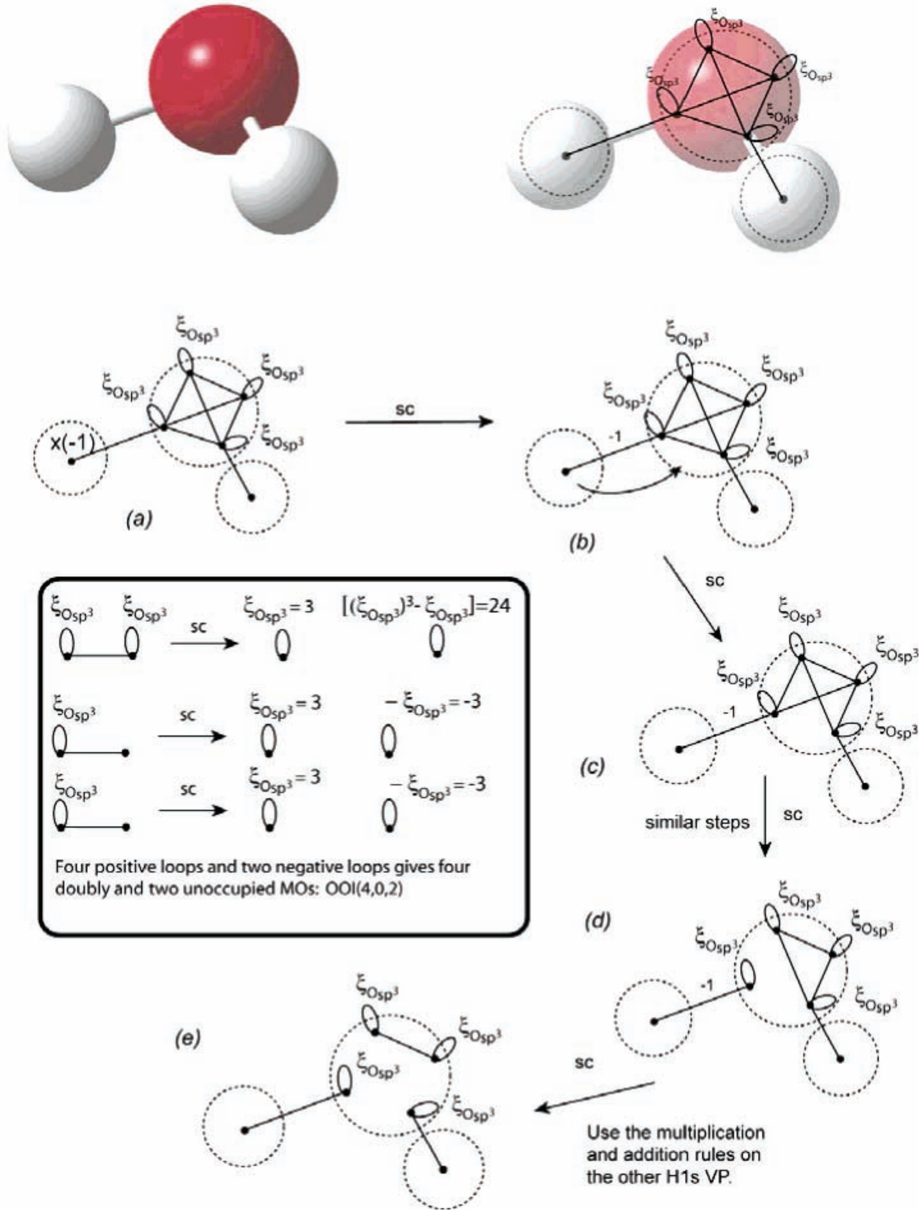


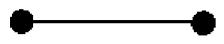
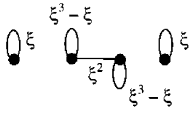
Figure 1. Top: A VIF picture is drawn according to water's three-dimensional geometry. (a) The multiplication rule is applied to the hydrogen 1s valency point on the left-hand side of the structure. (b−e) The addition rule is applied to cancel the oxygen intrahybrid valency interactions. (e) OH-bonding and lone-pair interactions are shown in the partially reduced VIF picture. Boxed area: The VIF fragments from part e are fully reduced. Four loops with positive constants and two loops with negative constants result, consistent with waters four doubly and two unoccupied valence molecular orbitals.

6-311++G 3df3dp are shown in Table 3. The Gaussian 03[17] package was used to make this calculation. Notice that four of the MO energies are lower than $-^1/_2E_h$ and two are higher in agreement with the LPI. There is also a large gap in energy between the HOMO and LUMO ($[0.043\ E_h - (-0.510\ E_h)] = 0.553\ E_h$). The LPI with respect to $-^1/_2E_h$ has made a clear distinction between energies of the frontier orbitals. The simplest accurate VIF pictures for water has no loops and was presented in SAH 94. Valence molecular orbital energies calculated using EHT and the EHTD calculations made according to this simple VIF picture do not agree. See Table 4. The method presented here gives results that are in better agreement with computation than those presented in SAH 94 and do not require reference to tables of VOIEs as the method presented in SAH 94 would require in order to find accurate loop constants for oxygen.

In summary, the current method provides an accurate depiction of water that agrees with computations while the method used in SAH 94 is not in agreement. In addition, the same VIF picture that as a one-electron density operator distinguishes between doubly, singly, and unoccupied MOs clearly distinguishes the energy gap between the HOMO and LUMO when considered as a one-electron Hamiltonian operator. This is important because the HOMO and LUMO have proven to be good guides to chemical reactivity.

VIF One-Electron Density Operators and Hydrocarbons. VIF pictures drawn as effective one-electron density operators are the simplest accurate pictures for hydrocarbons because no electronegativity loops are required regardless of the hybridization of the carbon center. This is because carbon in hydrocarbons will contribute one valence electron per each of its valence atomic orbitals regardless of their hybridization. Table 5 shows VIF pictures for singlet and triplet carbene, methyl radical, ethane, ethene, and ethyne. Singlet carbene with an MP2/6-311G3df3pd calculated bond angle of 102° has sp^3 hybridized carbon while triplet carbene with a bond angle of 138° according to the same level of approximation has sp^2 hybridized carbon.

TABLE 2: Common VIF Fragments (Column One) Can Be Fully Reduced to the VIF Pictures in Column Two[a]

Common VIF fragments reduced and their eigenvalues		
VIF fragment	**Reduced using the VIF rules**	**Eigenvalues**
		1, -1
		$\frac{1}{2}\left(\xi-\sqrt{4+\xi^2}\right), \frac{1}{2}\left(\xi+\sqrt{4+\xi^2}\right)$
		$\xi+1,\ \xi-1$
		$\frac{1}{2}\left(-1-\sqrt{5}+2\xi\right), \frac{1}{2}\left(1-\sqrt{5}+2\xi\right),$ $\frac{1}{2}\left(-1+\sqrt{5}+2\xi\right), \frac{1}{2}\left(1+\sqrt{5}+2\xi\right)$

[a] The pictures in column one also correspond to matrices with eigenvalues shown in column three. Notice that the number of positive, negative, and zero loop constants in column two are the same as the number of positive, negative, and zero egenvalues in column three.

TABLE 3: Valence Molecular Orbital Energies for Water Based a MP2/6-311++G 3df3dp Geometry Optimizarion Carried out Using the Gaussian03 Package

valence MO energies (E_h) for water MP2/6-311++G 3df 3dp
0.072
0.043
−0.510
−0.581
−0.716
−1.353

TABLE 4: EHTD Molecular Orbital Energies (eV) Calculated Using the HAO MO Program Compared to Full EHT Energies[a]

EHT	EHTD
26.89	21.13
17.07	16.37
2.52	2.52
1.85	−1.07
−0.21	−2.82
−15.93	−14.98

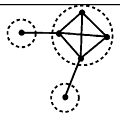
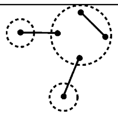
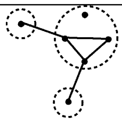
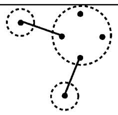
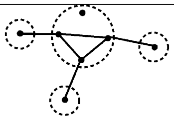
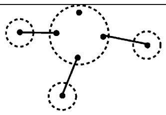
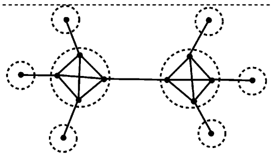
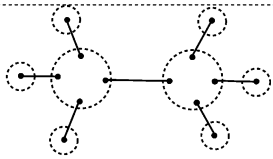
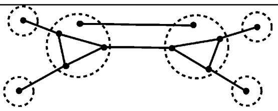
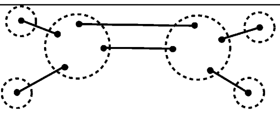
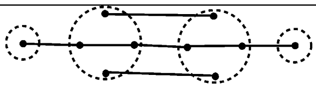
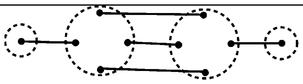
[a] Subtracted from each are the appropriate $\alpha_{\text{ave}} = -17.3$ eV reference energy. These numbers are taken from SAH 94 table 8.

Accurate orbital occupancies are obtained according to the pictorial VIF rules for each example. In previous VIF approaches, carbon atoms in a VIF picture would have electronegativity loops depending on the hybridization used. One would then need to decide whether these loops should be neglected and eventually find that the simplest accurate pictures do not require them. It is easier to verify the accuracy of a VIF picture based on molecular orbital occupancy and spin multiplicity instead of according to molecular orbital energies, which vary according to the method of approximation used. Comparing VIFs for singlet and triplet carbene, one sees that orbital occupancies change with the HCH bond angle indicating that the method is sensitive to the changes in frontier orbitals that occur according to changes in molecular geometry.

VIF Study of the Insertion of Singlet Carbene into H_2. Because the orbital occupancy and level pattern indices obtained from a VIF picture are sensitive to molecular geometry VIFs for reactants, transition structures, and products can be used to predict reaction selection rules. This has been applied to understand thermal barriers to [1,3]-hydrogen transfer reactions[18] Table 6 shows VIFs for reactants, transition structures, and products for insertion of singlet carbene into H_2. Transition structures for the least motion, symmetry-forbidden, and symmetry-allowed transition structures are shown.[19] The VIF pictures represent both one-electron density and Hamiltonian operators. These pictures indicate that reactants, the symmetry-allowed transition structure, and methane have four doubly occupied MOs, no singly occupied MOs, and four unoccupied MOs. In each of these cases there are four bonding, no nonbonding, and four antibonding MOs with respect to the reference energy of $-{}^{1}/_{2}E_h$. The VIF for the symmetry-forbidden transition structure predicts two nonbonding singly occupied MOs. Because this reaction takes place on a singlet potential energy surface, there is no exchange stabilization expected as for triplet carbene. VIF correctly predicts that the highest occupied molecular orbital is destabilized in the symmetry-forbidden transition structure and so has correctly predicted the thermal barrier to this reaction path. The TS for the forbidden path reduced using the VIF rules has the same picture as that for the methyl radical and a detached hydrogen atom and so by the theory of structural covariance, should be closer in energy to the methyl radical plus a hydrogen atom. The same conclusion is drawn whether one interprets the VIFS as one-electron density or Hamiltonian operators. The two together give a more complete picture: there is a nonbonding electron in the 1s orbital of a detached hydrogen atom.

VIF Pictures as Effective One-Electron Density Operators for B_2, N_2, and O_2. Simple and accurate VIF pictures as electron density operators can be drawn for diatomic molecules with both atoms given sp hybridization. Figure 2 shows a VIF for a generic diatomic molecule. To determine the molecular orbital

TABLE 5: VIF as One-Electron Density Operators for Some Simple Hydrocarbons

molecule	VIF	reduced VIF	OOI
singlet carbene			3,0,3
triplet carbene			2,2,2
methyl radical			3,1,3
ethane			7,0,7
ethene			6,0,6
ethyne			5,0,5

electron occupancies that these pictures correspond to, one calculates the loop constants for the sp σ system, ξ_{sp}, and for the π system, ξ_{2p} while normalizing valency interactions when possible and then reduces the resulting pictures using the VIF rules. One may also refer to the VIF fragments and expressions in Table 2 to find expressions for loop constants in the reduced picture. The number of doubly, singly, and unoccupied MOs are thus found and recorded in the OOI.

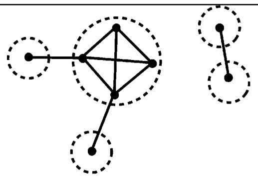
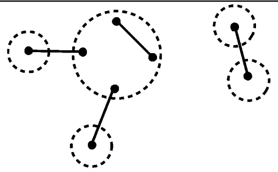
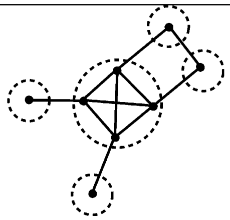
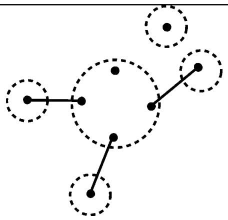
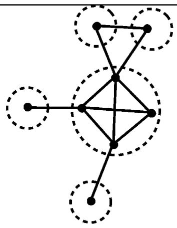
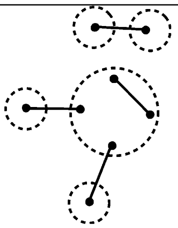
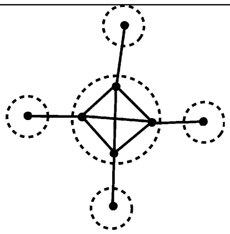
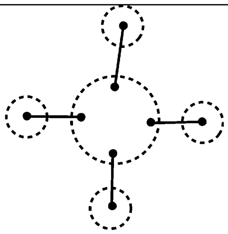
VIF-Electron Density for B_2. Each boron atom has three valence electrons; two of these will contribute to the σ system and one to the π system. For boron, $\alpha_{sp} = {}^1/_2(2 + 1\cdot 0) = 1$ and $\beta_{sp} = {}^1/_2(2 - 1\cdot 0) = 1$. The VIF loop constants for the σ system are therefore $\xi_{sp} = (1-1)/(1) = 0$ and the line constants are $\kappa_{sp} = 1$. Each boron atom has one electron averaged over its remaining two p orbitals so $\xi_p = {}^1/_2$. Each of diboron's π bonds has one electron and a bond order of ${}^1/_2$. β_p is therefore chosen to be ${}^1/_2$. Loops for the π system are $\xi_p = ({}^1/_2 - 1)/({}^1/_2) = -1$. The VIF picture as a one-electron density operator for B_2 is reduced in Figure 3. The results show that there are two doubly and two unoccupied molecular orbitals in the σ system while there are two singly and two unoccupied molecular orbitals in the π system giving OOI(2,2,4) altogether. The two unpaired electrons indicate that diboron has a triplet ground state, as expected. Because the spin multiplicity of B2 is well-known, the accuracy of the results are verified easily. The way that this relates to the VIF energy picture is seen by comparison to the examples of O_2 and N_2, which follow.

VIF-Electron Density for N_2. Each nitrogen atom has five valence electrons; three of these will contribute to the σ system and two to the π system. For nitrogen, $\alpha_{sp} = {}^1/_2(2 + 1\cdot 1) = {}^3/_2$ and $\beta_{sp} = {}^1/_2(2 - 1\cdot 1) = {}^1/_2$. The VIF loop constants for the σ system are therefore $\xi_{sp} = ({}^3/_2 - 1)/({}^1/_2) = 1$ and the line constants are normalized, $\kappa_{sp} = 1$. Each nitrogen atom has two electrons averaged over its remaining two p orbitals so $\xi_p = 1$. Each of dinitrogen's π bonds has two electrons and a bond order of 1. $\beta_p = 1$ is therefore a reasonable choice. Loops for the π system are $\xi_p = (1-1)/(1) = 0$. The VIF picture as a one-electron density operator is reduced in Figure 4. The results show that there are three doubly and one unoccupied molecular orbital in the σ system while there are two doubly and two unoccupied molecular orbitals in the π system giving OOI(5,0,3) altogether. All of N_2's electrons are paired, indicating a singlet ground state.

VIF-Electron Density for O_2. Each oxygen atom has six valence electrons; three of these will contribute to the σ system and three to the π system. For oxygen, $\alpha_{sp} = {}^1/_2(2 + 1\cdot 1) = {}^3/_2$ and $\beta_{sp} = {}^1/_2(2 - 1\cdot 1) = {}^1/_2$. The VIF loop constants are therefore $\xi_p = ({}^3/_2 - 1)/({}^1/_2) = 1$ and the line constants are normalized, $\kappa_{sp} = 1$. Each oxygen atom has three electrons averaged over its remaining two p orbitals so $\alpha_p = {}^3/_2$. Each of dioxygen's π bonds has a bond order of ${}^1/_2$ so β_p is chosen to be ${}^1/_2$. Loops for the π system are $\xi_p = ({}^3/_2 - 1)/({}^1/_2) = 1$. The VIF picture as a one-electron density operator is reduced in Figure 5. The results show that there are three doubly and one unoccupied molecular orbital in the σ system while there are two doubly and two singly occupied molecular orbitals in the π system giving OOI(5,2,1) altogether. Two of O_2's electrons are unpaired, indicating the triplet ground state for dioxygen.

Comparison with VIF-Energy Pictures for B_2, N_2, and O_2. Each VIF picture, as a one-electron density operator, has a reference of one electron per orbital. The same pictures have an energy reference of $-{}^1/_2E_h$. From this rough approximation, one surmises that the π-bonding molecular orbitals in B_2 have energy of about $-{}^1/_2E_h$ while its π-antibonding orbitals are higher in energy than this. Dinitrogen's π-bonding molecular orbitals are lower in energy than $-{}^1/_2E_h$ and its π-antibonding

TABLE 6: VIFs for Reactants, Transition Structures, and Products for the Insertion of Singlet Carbene into the Hydrogen Molecule[a]

species	VIF	reduced VIF	OOI/LPI
reactants: $CH_2 + H_2$			4,0,4
symmetry forbidden TS			3,2,3
symmetry allowed TS			4,0,4
Product: CH_4			4,0,4

[a] VIFs represent both one-electron density and hamiltonian operators.

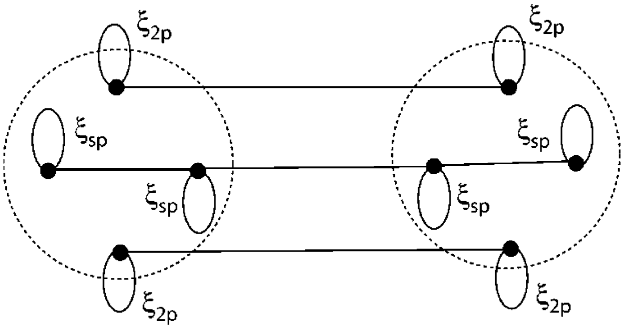


Figure 2. Generic VIF picture for a diatomic molecule with sp hybridization for each atom. Valency interactions have been normalized so that $\kappa = 1$, its default value.

molecular orbitals are higher in energy than $-{}^{1}/_{2}E_\mathrm{h}$. Dioxygen's π-antibonding orbitals would have energies of about $-{}^{1}/_{2}E_\mathrm{h}$ while its bonding π-bonding molecular orbitals would be lower in energy than this. These VIF pictures as effective one-electron Hamiltonian operators outline the periodic trend in electronegativity across period two. Table 7 and Figure 6 summarize these results. Previous implementations of VIF purely in terms of energy do not yield these results directly from the application of the VIF rules because loop constants chosen according to VIOE values do not lead to isolated valency points indicating singly occupied molecular orbitals. One can check the accuracy of the pictures according to whether they predict correct spin multiplicities and then also make qualitative arguments about energies of frontier orbitals. This is done without having to choose a reference energy that would be suitable both for isolated atoms and for molecules that contain them but in much different electronic environments. This is a clear advantage. The accuracy of the approach given here is due to the relationship between electron density and energy, a relationship frequently expressed in electronegativity scales.

V. Electron Density, Energy, and Electronegativity

Utilization of relationships between electron density and energy in theories of atoms and molecules has a long history. The Thomas−Fermi theory relates energy and electron density by treating electrons as a minimum energy electron gas. This method is valid if the potential, $V(r)$, does not change significantly within the de Broglie wavelength of the electron.[20] Iczkowski and Margrave define electronegativity as $\chi = -(\mathrm{d}E/\mathrm{d}N)_{q\,=\,0}$ evaluated for a neutral atom but based on ionization energies and electron affinities for that atom.[21] Their method is based on an expansion of energy in the number of electrons, N, and is a generalization of Mulliken's electronegativity, $\chi_\mathrm{M} = {}^{1}/_{2}(EI + EA)$. Parr et al. define an electronic chemical potential and electronegativity according to $\mu = (\partial E/\partial N)_v = -\chi$ and show that according to this definition the Thomas−Fermi model leads to $\mu = -\chi = 0$ for neutral atoms.[22]

In this paper, it is suggested that VIF structural formulas that represent one-electron density operators also represent one-

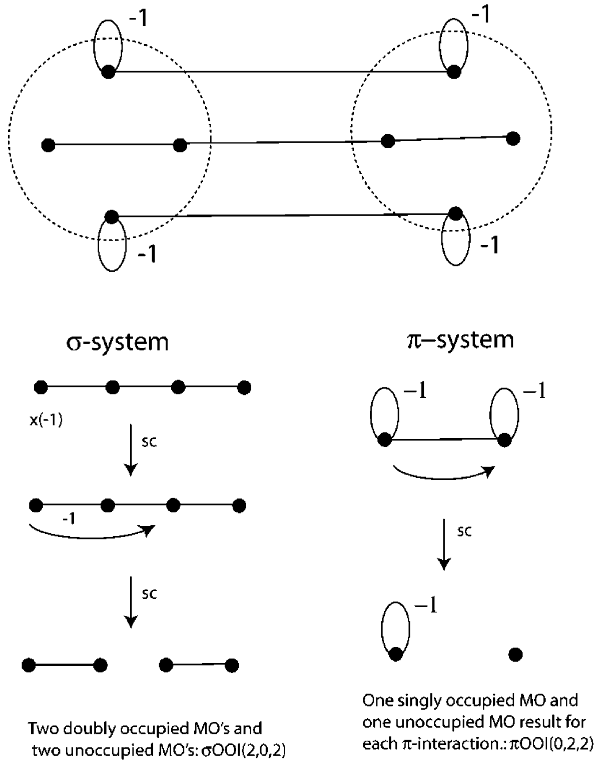


Figure 3. VIF picture as an electron density operator for B_2. σ and π systems are reduced separately giving σOOI(2,0,2) and πOOI(0,2,2) and a total OOI(2,2,4).

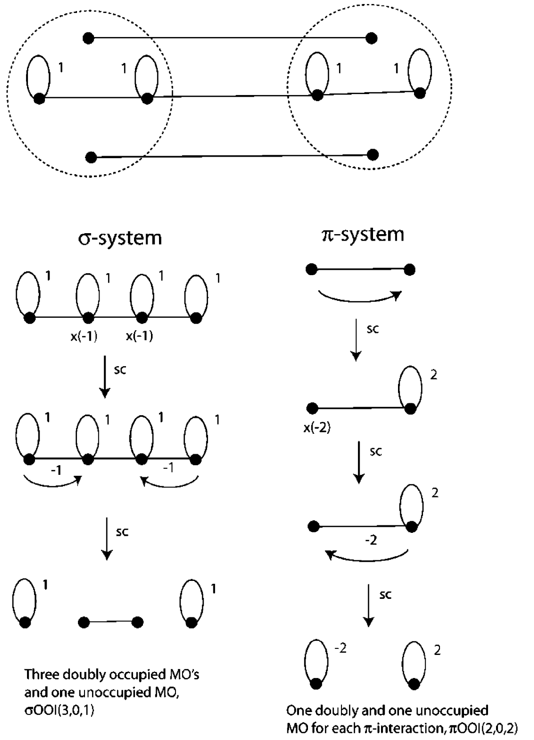


Figure 4. VIF as an electron density operator for N_2. σOOI(3,0,1) and πOOI(2,0,2) result, so the total OOI(5,0,2) indicates dinitroten's singlet ground state as expected.

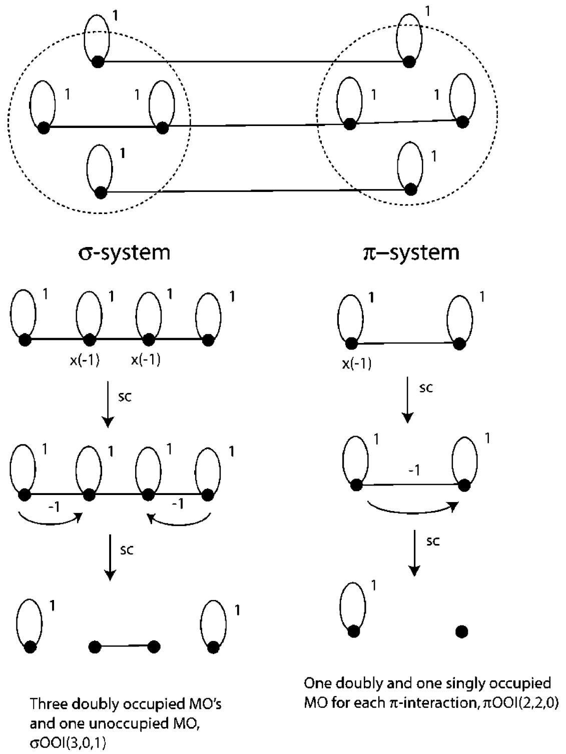


Figure 5. VIF as an electron density operator for O_2. σOOI(3,0,1) and πOOI(2,2,0) result, giving total OOI(5,2,1) as expected for dioxygen's triplet ground state.

TABLE 7: Summary of Orbital Occupancy and Level Pattern Indices

molecule	orbital occupancy index	level pattern index
B_2	OOI(2,2,4)	LPI(2,2,4)
N_2	OOI(5,0,3)	LPI(5,0,3)
O_2	OOI(5,2,1)	LPI(5,2,1)

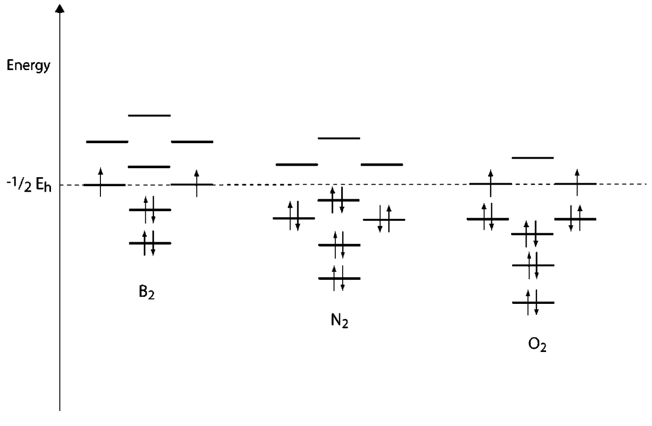


Figure 6. Energy level diagrams for B_2, N_2, and O_2 derived using VIF as one-electron density and Hamiltonian operators. OOI and LPI are consistent and the correct electronegativity trend across period two is shown.

electron Hamiltonian operators. Calculation of $P_{\mu\mu}$ values for period-two sp^3 hybridized centers gives a simple electronegativity scale with χ proportional to the number of valence electrons. It is shown that this scale is in agreement with other electronegativity scales for hydrogen and second-period elements. It also agrees with an electronegativity scale based on VOIE because they are used to draw VIF pictures as effective one-electron Hamiltonian operators. This is evidence that the values of $P_{\mu\nu}$ calculated according to electron configurations and used to draw simple VIF pictures as effective one-electron density operators are roughly proportional to qualitatively accurate $\bar{h}_{\mu\nu}$ used to draw a VIF picture as an effective one-electron Hamiltonian operator.

The approach here is extremely simple. An atom's ability to hold on to electrons while in a molecule, that is, its electrone-

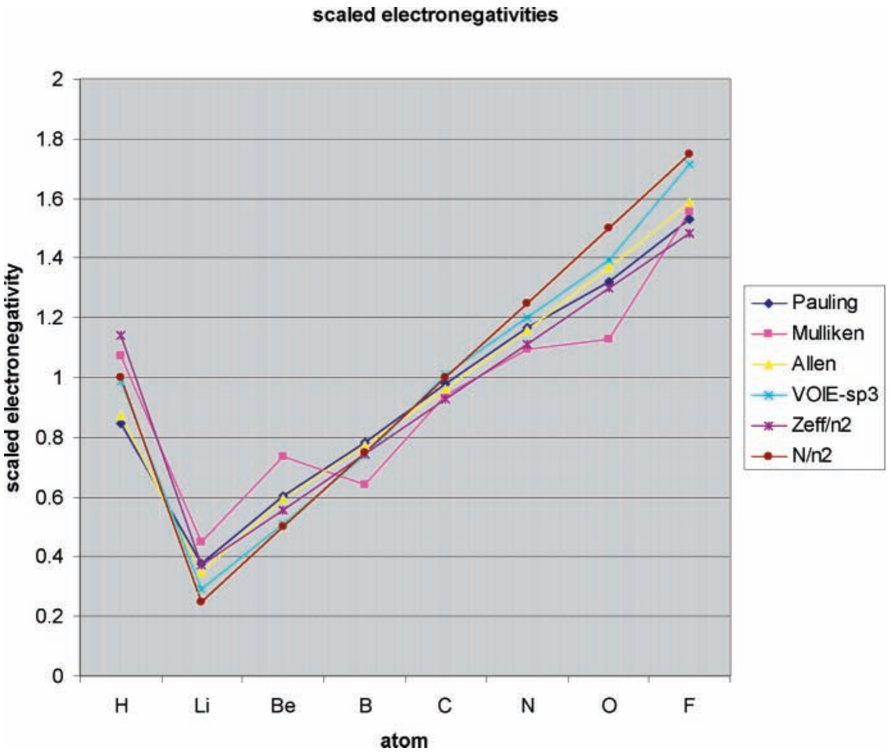


Figure 7. $\chi_D = N/n^2$, Z_{Eff}/n^2, and electronegativities scaled. Scaling factors were calculated as the average value of χ_D/χ_A for the atoms shown.

gativity, χ, is proportional to the number of valence electrons it has as a neutral atom and inversely proportional to its number of valence orbitals, n^2, where n is the principle quantum number. We will refer to this electronegativity as χ_D where the subscript stands for density.

$$\chi_D = \frac{\#\ of\ valence\ e^-}{n^2} \qquad (7)$$

Just as the energy of an sp^3 hybrid orbital is the average energy of the valence orbitals for a period-two element, diagonal elements of $\mathbf{P}_{sp3}$ as they are calculated here are average valence orbital electron occupancies, $P_{sp^3} = \alpha_{sp^3} = (1)/(3 + 1)(\alpha_s + 3\alpha_p)$. χ_D is the average valence orbital electron occupancy. The form of χ_D is similar to $\langle 1/r \rangle = Z/a_o n^2$, the expectation value of the reciprocal radius for a hydrogenic orbital and reminiscent of Gordy's electronegativity scale $\chi_D = Z_{eff}/r_{covalent}$.[23] For neutral atoms, the atomic number is equal to the number of electrons. From this expectation value, we could set Z equal to the number of valence electrons to give a very rough nuclear shielding approximation in which the nucleus and core electrons are treated as the cation that would result from removing the valence electrons. In this rough approximation, the valence electrons do not shield each other at all. The qualitative accuracy of this approach is underlined by the fact that if Z is replaced by Z_{eff} calculated using Slater's rules then there is an excellent agreement with Pauling's, as well as Allen's, electronegativities once these are scaled. See Figure 7. Scaling factors were calculated as the average value of χ_D/χ_A for each electronegativity scale.

Table 8 shows the scaled electronegativities plotted in Figure 7 and also shows scaled $\chi_E = (1)/(3 + 1)(\alpha_s + 3\alpha_p)$ based on sp^3 hybridization where α_s an α_p are VOIEs as would be used in a VIF picture as an effective one-electron Hamiltonian operator for a tetrahedral center. See SAH 94. The electronegativities plotted in Figure 7 show qualitative agreement. Perhaps Allen's scale, based on configuration energy, $(a\alpha_s + b\alpha_p)/(a + b)$ where α_s and α_p are VOIE and a and b are numbers of electrons in these orbitals, respectively, has the widest range of applicability.[24] Note that Allen's χ_{spec} is **Tr (Ph)** $= P^{\mu\nu}h_{\nu\mu} = P_{\mu\nu}h_{\nu\mu}$ divided by the number of valence electrons. The electronegativity scale $\chi = N/n^2$ does not agree as well with other electronegativity scales for periods three and higher. Its applicability to heavier elements will be studied on a case-by-case basis.

TABLE 8: $\chi_D = N/n^2$ and $\chi_E = (^1/_4)(\alpha_s + 3\alpha_p)$ = VOIE-sp^3 Electronegativities Compared to Scaled Pauling, Mulliken, and Allen Electronegativities[a]

scale factors =		1.141	−0.073	0.384	0.150	0.064
atom	N/n^2	Z_{eff}/n^2	VOIE-sp^3	Pauling	Mulliken	Allen
H	1.000	1.141	0.989	0.846	1.074	0.870
Li	0.250	0.371	0.289	0.377	0.450	0.345
Be	0.500	0.556	0.509	0.603	0.733	0.596
B	0.750	0.742	0.740	0.784	0.642	0.776
C	1.000	0.927	1.010	0.980	0.938	0.962
N	1.250	1.112	1.203	1.168	1.092	1.159
O	1.500	1.298	1.394	1.322	1.128	1.366
F	1.750	1.483	1.714	1.530	1.558	1.586

[a] Scaling factors were calculated as the average value of χ_D/χ_A for the atoms shown and are given in the first row.

In considering that χ, with units of energy per electron, is roughly proportional to the number of valence electrons in a neutral atom divided by n^2, support is found for the idea that structural formulas based on electron density can be good indicators of a molecules qualitative energetic stability. Specifically, this is supporting evidence that VIF pictures as effective electron density operators and as effective one-electron Hamiltonian operators are the same picture.

VI. Summary and Conclusions

A more general interpretation for VIF molecular structural formulas has been given in which simple VIFs include all possible overlaps between valence atomic orbitals. This applies whether the VIF picture represents a one-electron Hamiltonian or density operator. It has been shown how VIF molecular structural formulas can represent effective one-electron density operators. VIF pictures drawn with a reference electron density of one electron per orbital correspond to the reference energy of $-{}^{1}/{}_{2}E_h$ if the same pictures are also taken to represent effective one-electron Hamiltonian operators. The method that has been presented here allows the simplest accurate VIF pictures for water, hydrocarbons, and period-two diatomic molecules to be drawn. This is an advantage over earlier implementations of VIF, which require selection of reference energy. VIF reference energies are frequently of dubious validity due to differences in coulomb and exchange energies in isolated atoms compared to those in molecules. In the present method, accuracy is verified easily through comparison with known orbital occupancies or spin multiplicities. Because qualitative information regarding energies of frontier orbitals is also implicit, the same pictures can be used to make predictions about chemical reactivity. VIF pictures for reactants, transition structures, and products in the insertion of singlet carbene into molecular hydrogen correctly distinguish between symmetry-allowed and -forbidden reaction pathways. Electron occupancies found using VIF pictures as one-electron density operators for B_2, N_2, and O_2 are consistent with the ground-state electron configurations for these molecules and at the same time show the correct trend in electronegativity across the second period.

Use of the same structural formula to represent electron density and energy is supported by a simple electronegativity scale $\chi_D = N/n^2$, which compares well with a scale based on VOIE and to popular electronegativity scales formulated by Pauling, Mulliken, and Allen. This electronegativity scale has the same form as the expectation value of the reciprocal radius for a hydrogenic atom and thus has a clear interpretation related to both energy and electron density.

VII. Future Work

The results presented here provide a basis for drawing simple and accurate structural formulas that represent both one-electron density and Hamiltonian operators without reference to external data such as tables of VOIEs. This paper is intended to be the first in a series of four. The next paper will show how VIF pictures as one-electron density and Hamiltonian operators give accurate qualitative descriptions of a variety of simple organic molecules with common functional groups. Following this will be a paper that applies these methods to hydrogen transfer reactions. This paper will show how VIF methods apply well to transition structures with unconventional bonding and how the density and energy interpretations give a consistent picture of bond breaking and bond formation. The final paper in the series will have diborane as its focus. It will be shown that because a VIF picture relates to both electron density and energy, one can use the picture to deduce bond placement between atoms (bond order) according to machine-computed MO energy levels.

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Appendix

This appendix describes the application of the VIF rules in more detail using words and pictures. Figure A1 shows the reduction of an OH bond VIF fragment from the boxed area in Figure 1. Starting at the upper left of Figure A1, the multiplication rule is applied. The valency point for the hydrogen 1s orbital is multiplied by $-\xi_{Osp3}$, the negative of the loop constant for the oxygen sp^3 valency point. This is done so that in the next step, with the application of the addition rule, the valency interaction between these two valency points can be cancelled. The valency interaction now has $\kappa = -\xi_{Osp3}$. See the bottom center of Figure A1.

The addition rule is now applied as indicated by the curved arrow. The oxygen sp^3 valency point is "lifted" and superimposed on the hydrogen 1s valency point. Its loop is stretched over the valency interaction and the loop and line constants add: $\xi_{Osp3} + (-\xi_{Osp3}) = 0$. The valency interaction has been cancelled, so is not drawn in the fully reduced picture (top right of Figure A1). During the application of the addition rule, the oxygen sp^3 valency point and its loop remain like a chalk mark left behind. The valency interaction between the two valency points curled up to form a loop with a constant of $-2\ \xi_{Osp3}$. The oxygen sp^3 valency point also brought with it its own loop superimposed on the loop formed by the curled-up valency interaction. The valency point that originally corresponded to the hydrogen 1s orbital now has a loop with a constant equal to $-2\xi_{Osp3} + \xi_{Osp3} = -\xi_{Osp3}$. After this complete reduction, both valency points and their loops now correspond to molecular orbitals rather than atomic or hybridized atomic orbitals. The value of ξ_{Osp3} is substituted and it is found that one molecular orbital has a loop constant of positive three and the other has a loop constant of negative three. In terms of electron density, positive loop constants correspond to doubly occupied MOs and negative loop constants to empty MOs. In terms of energy, positive loop constants correspond to molecular orbital energies lower than $-{}^{1}/{}_{2}E_h$ and negative loop constants are for molecular orbitals with energy higher than $-{}^{1}/{}_{2}E_h$.

Reduction of the VIF fragment that results from the oxygen lone-pair valency points is similar. See Figure A2. Starting at the upper left of Figure A2, the multiplication rule is applied. The valency point for the oxygen sp^3 orbital on the right is multiplied by $-\xi_{Osp3}$. This is done so that in the next step, with the application of the addition rule, the valency interaction between these two valency points can be cancelled. The valency interaction connecting the two valency points, with its original line constant equal to one, now has a line constant equal to $-\xi_{Osp3}$. The loop attached to the valency point that was

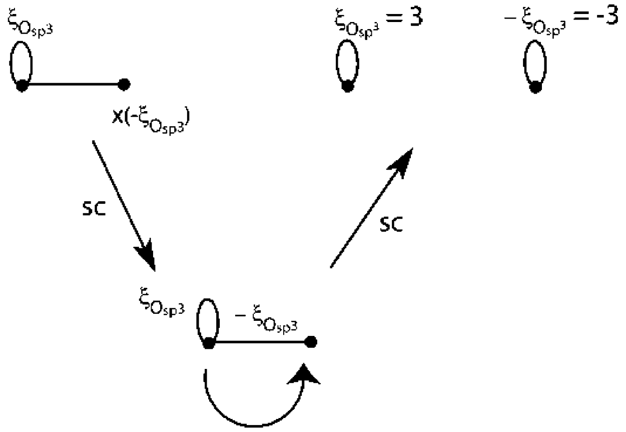

Figure A1. Reduction of an OH bond VIF fragment from Figure 1.

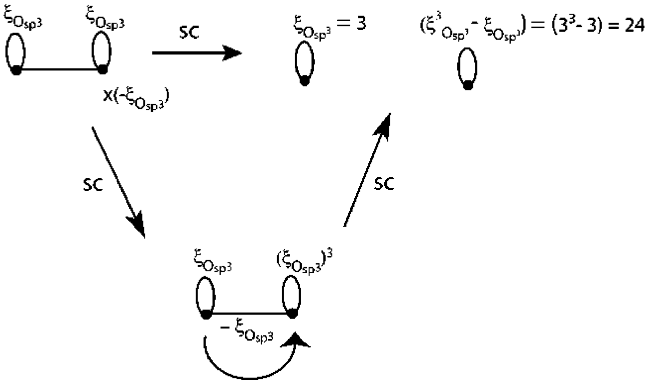

Figure A2. Reduction of the oxygen lone-pair VIF fragment from Figure 1.

multiplied now has a loop constant equal to $(\xi_{\mathrm{Osp3}})^3$ because it was multiplied by $(\xi_{\mathrm{Osp3}})^2$ and originally had a loop constant of ξ_{Osp3}. See the bottom center of Figure A2.

The addition rule is now applied as indicated by the curved arrow. The oxygen sp^3 valency point on the left is "lifted" and superimposed on the one on the right. Its loop is stretched over the valency interaction between the points so that the loop and line constants add: $\xi_{\mathrm{Osp3}} + (-\xi_{\mathrm{Osp3}}) = 0$. The valency interaction has been cancelled, so it is not drawn in the fully reduced picture (top right of Figure A2). During the application of the addition rule, the oxygen sp^3 valency point on the left and its loop remain. The valency interaction has curled into the loop already present and adds $-2\xi_{\mathrm{Osp3}}$ to its constant. The oxygen sp^3 valency point on the left also brought with it its own loop superimposed on the loop already on the right valency point, its constant adding to the others and resulting in a total loop constant of $(\xi_{\mathrm{Osp3}})^3 - 2\xi_{\mathrm{Osp3}} + \xi_{\mathrm{Osp3}} = (\xi_{\mathrm{Osp3}})^3 - \xi_{\mathrm{Osp3}}$. After full reduction using the rules, each valency point corresponds to a molecular orbital and 3 is substituted for ξ_{Osp3}. The resulting loop constants are 24 and 3, respectively, both positive. The corresponding molecular orbitals are therefore doubly occupied and have an energy lower than $-{}^1/_2E_{\mathrm{h}}$.

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