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Rabbit Ears Hybrids, VSEPR Sterics, and Other Orbital Absurdities

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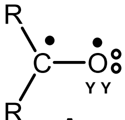
Introduction

The first contact of many students of organic chemistry in the early 1960s with molecular orbital (MO) theory was through Streitwieser's influential 1961 book.[1] It mainly covered Hückel-type calculations in which non-carbon atoms are only treated by changes of α and β parameters. Other complicating factors –– such as the existence or spatial positioning of H atoms, lone pairs, or the skeletal sigma-bonding framework –– were ignored entirely. "Lone pair" is not even an entry in the book's index.

Howard Zimmerman recognized the importance of distinguishing between the hybridized and unhybridized lone pairs at the carbonyl oxygen for understanding ketone photochemistry.[2] He employed "circle-dot-*y*" notation for carbonyl groups, in which the s-rich lone pair (collinear with the CO axis) is shown as small circles, the out-of-plane π_{CO} electrons as a pair of dots, and the unhybridized in-plane p-type lone pair as a pair of *y*'s, as shown in **A.**



A

As pointed out by Jorgensen and Salem in their 1973 book that informed a generation of organic chemists about more realistic details of electronic orbitals:[3]

> *If we are seeking favorable intramolecular interactions between lone-pairs and other orbitals, it is absolutely necessary to consider those lone pair orbitals which have the proper local symmetry.*

Although the importance of distinguishing between lone pairs of different symmetry was clearly stated over forty years ago, the distinction appears to have been widely ignored by subsequent organic and general chemistry textbook authors. Instead, the widespread teaching of valence shell electron-pair repulsion (VSEPR) theory has fostered an unfortunate tendency to envision lone pair MOs of improper local symmetry. VSEPR was introduced in 1957 by Gillespie and Nyholm[4] as a simplified way to envision heteroatom lone pairs in molecular skeletal structure (see the historical context provided in an early pedagogical review by Gillespie[5]). According to VSEPR theory, two equivalent "rabbit ears" lone pairs are directed above and below the skeletal bonding plane at approximately tetrahedral angles for disubstituted group-16 (chalcogen) atoms, and three equivalent "tripod" lone pairs are similarly directed around monosubstituted group-17 (halogen) atoms. As we emphasize below, such "equivalent" (equal-energy, tetrahedrally hybridized and oriented) depictions of lone pairs cannot be consistent with the local σ-π electronic symmetry of the skeletal bonding framework.

Deliberate teaching of incorrect conceptions of lone pairs (and their purported "steric demands") that must be unlearned as students progress to deeper understanding of structure and bonding cannot be efficient or desirable.[6] Although it is widely conceded that MO theory is required for proper understanding of molecular structure and bonding, VSEPR-type textbook illustrations of lone pairs often appear in close proximity to introductory MO concepts with which they are logically and mathematically incompatible. It has been steadfastly maintained by Gillespie and others that equal-energy lone pairs are "mathematically equivalent" to the proper s-rich and pure-p lone pairs (e.g., of H_2O or HF), but this is certainly untrue except at such low levels of theory as not to warrant serious current consideration (for mathematical aspects of this purported equivalency, see Appendix). Although problems with VSEPR rationalizations have been pointed out repeatedly in *J. Chem. Ed.* and elsewhere,[7] many textbook authors and teachers remain firmly committed to teaching rabbit-ears/VSEPR structural and steric concepts which this contribution argues are unjustifiable.

To clarify the relationship between localized Lewis structure (lone pair/bond pair) and delocalized MO descriptions of molecular electronic structure, we make frequent use of natural bond orbitals (NBOs)[8] or the closely related natural localized molecular orbitals (NLMOs).[9,10] NBOs are a unique,[*] intrinsic, and complete set of orthonormal orbitals that optimally express the localized Lewis-like aspect of the wavefunction and are readily obtained for arbitrary wavefunctions as well as density functional and perturbative treatments of MO or correlated type. The leading "Lewis-type" NBOs/NLMOs have one-to-one mapping onto the localized structural elements of the Lewis dot diagram, but also serve as ideal basis functions to re-express MOs in the language of structural chemists. The many pedagogical advantages of localized NBO vs. delocalized MO description, with illustrative examples of the former, are presented in a recent monograph.[11]

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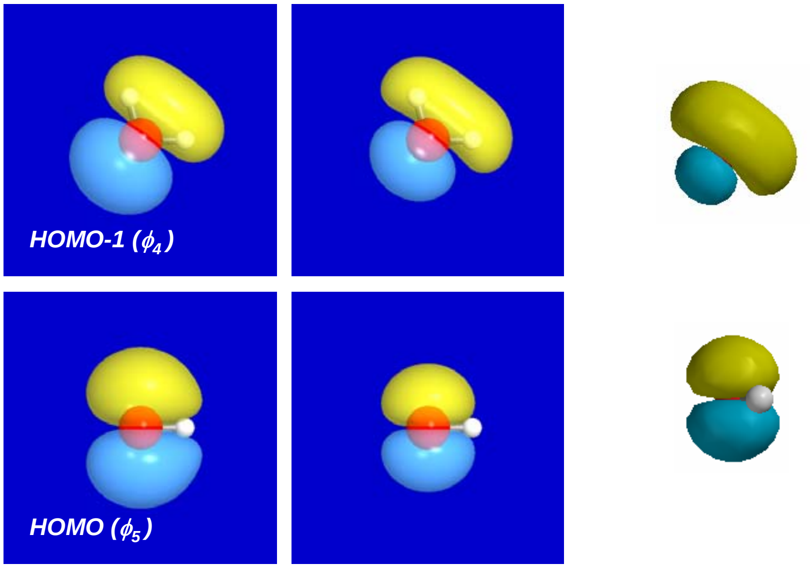
[*] As noted below, MOs may be chosen rather arbitrarily, equivalent up to unitary transformations that have *no* effect on total energy or other observable properties, whereas NBOs are *uniquely* determined by the form of the *N*-electron wavefunction. MOs provide no criterion for which unitarily-equivalent set is considered "best," because all satisfy the full double-occupancy condition. In contrast, the Lewis-type NBOs generally have *distinct* occupancies (<2, because *some* occupancy must appear in non-Lewis NBOs to describe resonance-type delocalization effects) so the NBO maximum-occupancy criterion clearly distinguishes which orbitals are best, and by how much.

Are the Lone Pairs of Water "Equivalent"?

The idea that VSEPR-type lone pairs are "mathematically equivalent" to proper s-rich and pure-p lone pairs of water rests on superficial understanding of Fock's theorem[12] concerning the unitary equivalence of doubly-occupied localized vs. canonical MOs (LMOs vs. CMOs) in single-determinant Hartree-Fock (HF) or density functional (DFT) approximations. However, at any reasonable level of MO theory, the lone pair MOs of water (whether of canonical or optimally localized NLMO form) are quite *distinct* and *in*equivalent, both in form and energy. Whether one can find *some* unitary mixture of lone-pair MOs that gives resulting equal-energy orbitals is essentially irrelevant. Indeed, one could equally well find an equal-energy mixture of core and valence-type MOs, but this provides no real justification for claiming that core and valence orbitals are somehow "equivalent."

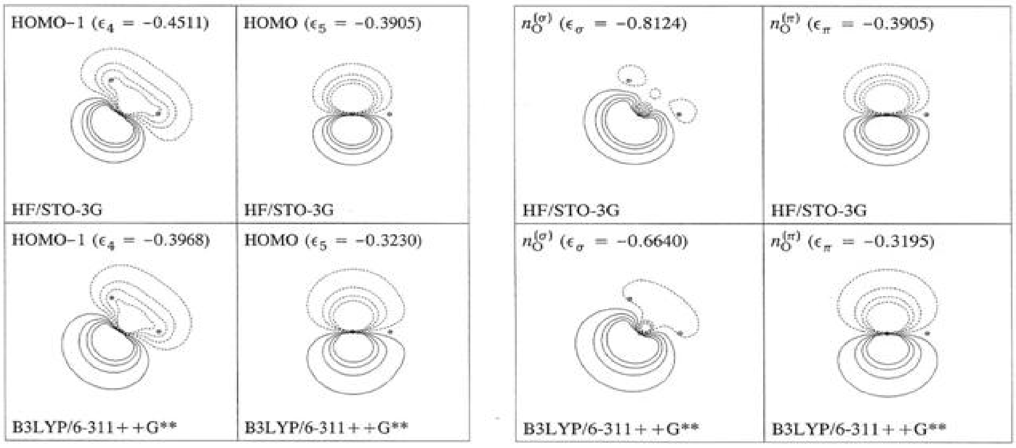
Figure 1 displays 3-d surface plots of lone-pair-type MOs for H_2O at diverse DFT, HF, and semi-empirical levels, illustrating their essential visual similarity to MO images of Jorgensen and Salem and *dis*similarity to VSEPR-style cartoon images. The selected DFT and HF levels (reasonably high-level B3LYP/6-311++G** vs. low-level HF/STO-3G, in the arcane notation of quantum chemists) span a wide range of accuracy for treating details of chemical interactions, but *all* concur on such qualitatively important features as the inequivalent shapes and energetics of lone pairs.



(a) B3LYP/6-311++G**　(b) HF/STO-3G　(c) PM3

Figure 1. Highest occupied (lone pair-like) MOs of water at various (a) DFT, (b) HF, and (c) semi-empirical MO levels (as labeled), showing distinct σ-type (ϕ_4) and π-type (ϕ_5) orientation and shape at all levels.

Figure 2 shows additional radial and angular details of lone pairs in 2-d contour plots, comparing lone pair-type MOs (Fig. 2a) with the uniquely determined s-rich ($n_O^{(\sigma)}$) and pure-p ($n_O^{(\pi)}$) lone-pair NBOs (Fig. 2b) at each level. The essential differences in lone pair hybridization are seen most clearly in the NBO plots, whereas MOs tend to form confusing mixtures of 1-center lone pair orbitals with symmetry-adapted combinations from other centers [cf. Eqs. (1a,b) and Table 1 below].



(a) Molecular Orbitals (MOs) **(b) Natural Bond Orbitals (NBOs)**

Figure 2. 2-d contour plots comparing (a) MOs and (b) NBOs for lone pairs of water at HF/STO-3G and B3LYP/6-311++G** levels, showing strong *in*equivalencies of hybridization, energy and shape. The chosen contour plane lies within (for σ-type orbitals) or perpendicular to (for π-type orbitals) the plane of nuclei marked by crosshairs.

Mathematically and group theoretically, one can easily see (Ref. 11, p. 52ff) that atomic s-p symmetries can only be broken by chemical bonding interactions, and these cannot involve p-orbitals outside the line (for diatomics) or plane (for triatomics) of chemical bonding. Thus, for H_2O the pure p_z (out-of-plane) lone pair must always remain distinct from the s-rich hybridized lone pair in the xy-plane of skeletal bonding. The CMOs, NBOs, or NLMOs of H_2O must therefore exhibit the strict σ/π separation (as irreducible representations of C_{2v} symmetry) that distinguishes the unhybridized π-type $n_O^{(\pi)}$ (pure p_z) lone pair from the hybridized σ-type $n_O^{(\sigma)}$ (~sp^2) lone pair in the molecular plane. Even if the in-plane $n_O^{(\sigma)}$ were to unaccountably lose all s-character in gross violation of Bent's rule[13] (see below), the orientations and energies of $n_O^{(\sigma)}$, $n_O^{(\pi)}$ must still differ qualitatively from those of VSEPR-style rabbit ears.

As Fock's theorem suggests, slightly different CMO mixings (i.e., different diagonalizations of sub-blocks for each irreducible representation[14]) may be manifested by different "flavors" of MO theory, such as the low-level HF/STO-3G (minimal basis HF) and higher-level B3LYP/6-311++G** (extended-basis DFT) levels displayed in Fig. 1. This confuses the issue slightly, because the delocalized HOMO−1 ϕ_4 will contain somewhat different unitary mixtures of the $n_O^{(\sigma)}$ lone-pair NBO with the in-phase combination of σ_{OH}, $\sigma_{OH'}$ bond NBOs. For the MOs of Fig. 2, these mixtures are shown in Eqs. (1a,b),

(1a) $\phi_4 = 0.79 n_O^{(\sigma)} + 0.43(\sigma_{OH} + \sigma_{OH'}) + \ldots$ (HF/STO-3G)

(1b) $\phi_4 = 0.86 n_O^{(\sigma)} + 0.36(\sigma_{OH} + \sigma_{OH'}) + \ldots$ (B3LYP/6-311++G**)

corresponding to 62% vs. 74% lone-pair character for HF/STO-3G vs. B3LYP/6-311++G**, respectively. However, as shown in Fig. 2, the energies and shapes of underlying $n_O^{(\sigma)}$, $n_O^{(\pi)}$ NBOs are quite distinct at each level and highly transferable from one level to another. These numerical examples make it clear, consistent with the group-theoretical arguments of the preceding paragraph, that $n_O^{(\sigma)}$, $n_O^{(\pi)}$ lone pairs cannot exhibit VSEPR-type "equivalency" at *any* theoretical level of useful chemical accuracy.*[*]

Does the Local Symmetry of Inequivalent Lone Pairs Persist in Larger Molecules?

Although the inequivalency of $n_O^{(\sigma)}$, $n_O^{(\pi)}$ lone pairs is dictated by strict triatomic C_{2v} symmetry in water, one might question whether similar σ/π separation ("effective" local symmetry) is manifested in larger molecules. Many examples might be cited to demonstrate that this is generally so. Here we briefly mention three representative organic compounds containing disubstituted oxygen whose structural/reactive properties support the (computationally unambiguous) picture of inequivalent $n_O^{(\sigma)}$, $n_O^{(\pi)}$ oxygen lone pairs and rule out conflicting VSEPR/rabbit-ears conceptions.

Figure 3 compares 3d visual images of the oxygen lone pair NBOs of water with those of methanol, formic acid, and furan, all at B3LYP/6-311++G** level. The visual orbital images appear virtually indistinguishable, confirming the high transferability of $n_O^{(\sigma)}$, $n_O^{(\pi)}$ local-symmetry NBOs into larger species.

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[*] Note that multi-configurational "Generalized Valence Bond" (GVB) wavefunctions, even if initially formulated with rabbit-ear orbitals, are also found to converge to final lone-pair NBOs of clearly inequivalent form, similar to those of other methods discussed above.

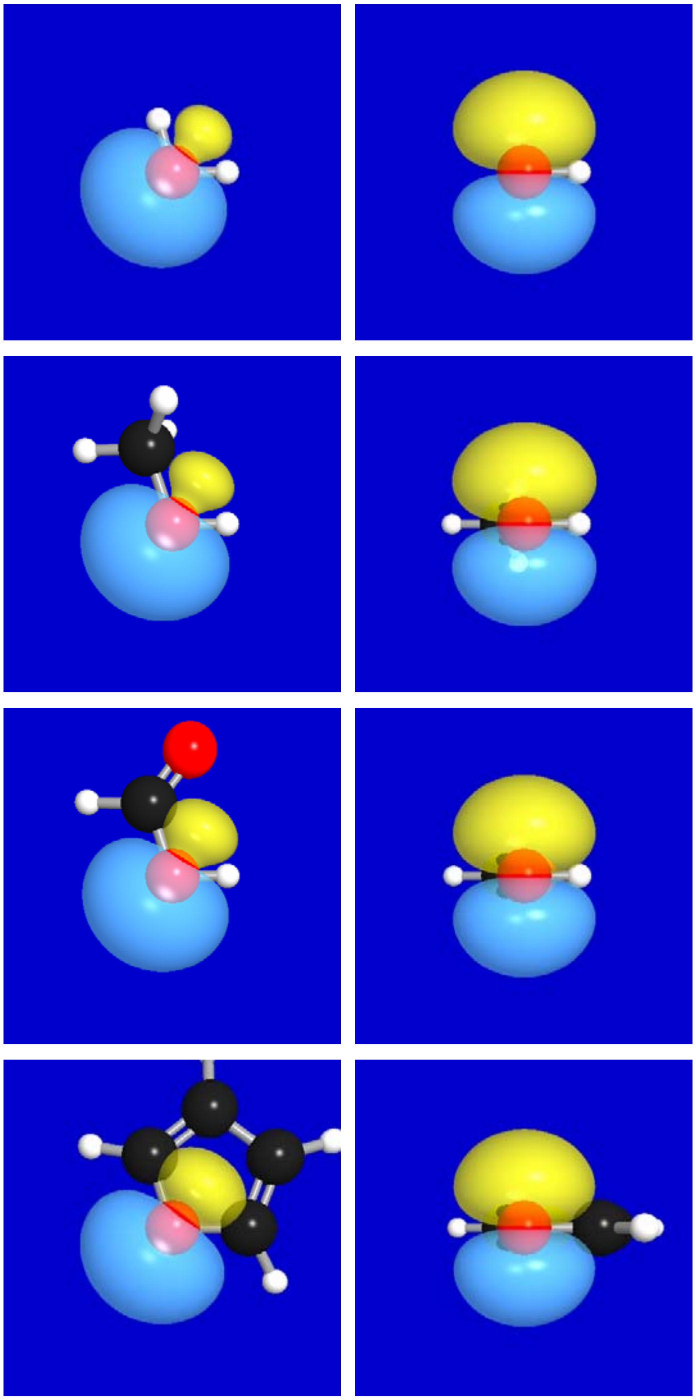
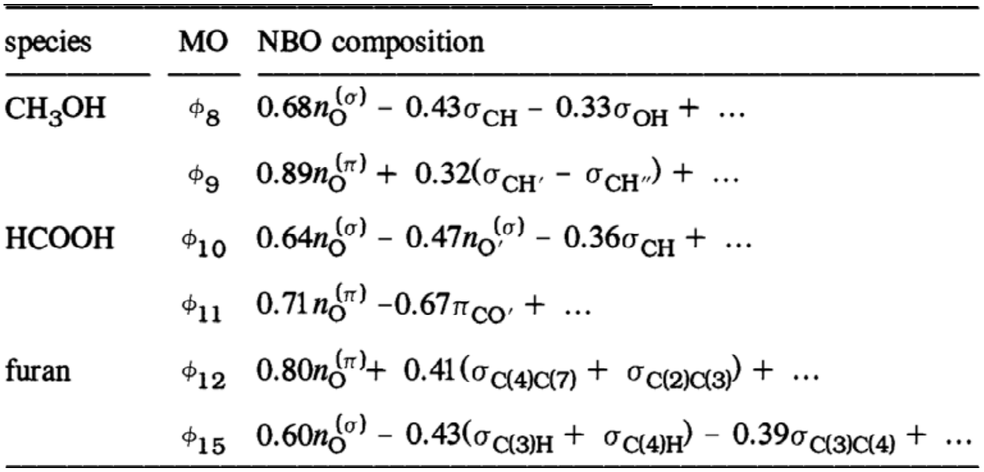


Figure 3. 3-d surface plots of $n_O^{(\sigma)}$ (left), $n_O^{(\pi)}$ (right) lone pairs for (a) water, (b) methanol, (c) formic acid, and (d) furan (B3LYP/6-311++G** level), viewed as pre-NBOs (pre-orthogonal visualization NBOs, using Bader's surface contour[15]) for optimal comparisons in the respective molecular planes.

The corresponding MO comparisons are only slightly more complex. As shown in Table 1, the high-lying MOs exhibit somewhat different mixings of intrinsic lone pair and bond NBOs in each species, but despite such confusing mixing (of no physical consequence), the MOs of highest lone-pair parentage all exhibit $n_O^{(\sigma)}$, $n_O^{(\pi)}$ -type inequivalencies similar to those of Figs. 1 and 2. Thus, computational results at any reasonable level of accuracy (including semi-empirical approximations) strongly support the effective conservation of local $n_O^{(\sigma)}$, $n_O^{(\pi)}$ (C_{2v}-like) character in larger molecules.



species	MO	NBO composition
CH_3OH	ϕ_8	$0.68 n_O^{(\sigma)} - 0.43\sigma_{CH} - 0.33\sigma_{OH} + \ldots$
	ϕ_9	$0.89 n_O^{(\pi)} + 0.32(\sigma_{CH'} - \sigma_{CH''}) + \ldots$
HCOOH	ϕ_{10}	$0.64 n_O^{(\sigma)} - 0.47 n_{O'}^{(\sigma)} - 0.36\sigma_{CH} + \ldots$
	ϕ_{11}	$0.71 n_O^{(\pi)} - 0.67\pi_{CO'} + \ldots$
furan	ϕ_{12}	$0.80 n_O^{(\pi)} + 0.41(\sigma_{C(4)C(7)} + \sigma_{C(2)C(3)}) + \ldots$
	ϕ_{15}	$0.60 n_O^{(\sigma)} - 0.43(\sigma_{C(3)H} + \sigma_{C(4)H}) - 0.39\sigma_{C(3)C(4)} + \ldots$

Table 1. NBO composition of "most lone pair-like" MOs (from CMO keyword option) in methanol, formic acid, and furan [cf. text Eq. (1b) for water], showing leading mixings with parent $n_O^{(\sigma)}$, $n_O^{(\pi)}$ NBOs. [O′ denotes the ketone oxygen in formic acid, and C(2), C(9) denote the carbon atoms directly bonded to O in the chosen furan numbering.]

What Does Experimental Evidence Tell Us About Lone Pairs?

Aside from the clear computational picture, the characteristics of lone pairs can also be inferred from experimental evidence concerning their observed effects on molecular properties. Many contradictions are encountered in attempts to apply VSEPR-style reasoning to rationalize experimental properties of known compounds containing disubstituted oxygen or sulfur. One well-known "textbook example" is provided by the dipole analysis of hydroxylamine conformers by Jones, Katrizky, and coworkers.[16] These workers measured the dipole moment of trimethylhydroxylamine to be 0.88 Debye and attempted to analyze its rotameric conformations about the NO bond by the VSEPR-inspired rabbit-ear lone pair analysis as shown in Figure 4. Using simple bond-dipole additivity relationships based on other known compounds (because this was still at a time when organic chemists could not routinely perform the required electronic structure calculations!), these workers estimated the dipole moments for conformers **B**, **C**, and **D**, as shown in the figure. Because the observed dipole moment was less than that estimated for the staggered structures **C** and **D**, they concluded that eclipsed structure **B** must be present. Because **C** has "large" lone pairs crowded together, its contribution was neglected, and the molecule was concluded to be approximately a 3:1 mixture of **D**:**B**.

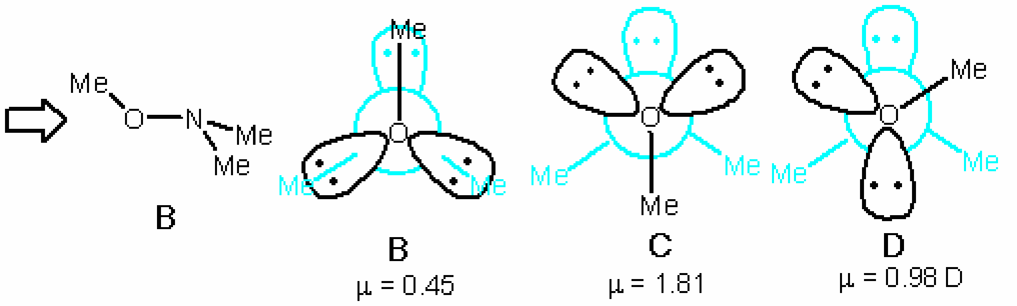


Figure 4. VSEPR-type rabbit-ears cartoons for trimethylhydroxylamine conformers in Newman projections (with arrow showing view direction, and rear NMe_2 group in light blue).

However, this conclusion is fundamentally incorrect,[17] and the error can be traced to the rabbit-ear lone pair representation that was used. Similar analysis using the proper $n_O^{(\sigma)}$ and $n_O^{(\pi)}$ lone pairs is shown in Figure 5. **B** and **C** are energy minima, but **B** is no longer "eclipsed," and **D** (selected as the most important contributor by rabbit-ears analysis) is not even an energy minimum! (Even semi-empirical calculations get this right, because they use proper lone pairs.) As shown in Figure 1 of Riddell's review of hydroxylamine geometries,[18] **D** lies on the side of a hill on the energy surface for ON rotation, so it cannot be contributing to the observed dipole moment because no significant amount is present. The s-rich lone pairs are shown close to oxygen in Fig. 5, because they are so compact and low in energy as to have no significant interaction ("overlap") with adjacent methoxy substituents, and therefore make no significant contribution to the torsional energy surface.

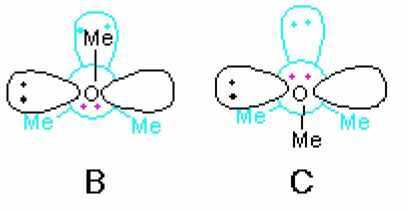


Figure 5. Similar to Fig. 4, for proper p-rich (black lobes) and s-rich (magenta dots) lone pairs at oxygen.

Still more striking experimental contradictions to VSEPR-inspired rabbit ears conceptions are provided by sulfur compounds, including the ubiquitous CSSC disulfide structural motifs of proteins and peptides. Early structural understanding of such species came from electron diffraction measurements on HSSH,[19] MeSSMe,[20] ClSSCl,[21] and FSSF,[22] but because organic and biochemists were unfamiliar with such techniques, the significance of the work was too long overlooked. Here again the use of rabbit-ears lone pairs leads to misunderstanding. As shown in Figure 6, the VSEPR-inspired view of disulfide linkages (with each sulfur bearing "bulky" rabbit-ears lone pairs at tetrahedral angles) would lead to the expectation of XSSX dihedral angle $\theta = 180^{o}$, to minimize "steric clashes" between lone pairs. Alternatively, if anomeric n_S-σ^*_{SH} interactions are judged most important, the tetrahedral rabbit-ears orientation predicts a preferred $\theta \cong 60^{o}$ conformation. However, neither expectation is correct! The preferred θ is found to be near 90^{o} for all the above examples (as the inequivalent $n_S^{(\sigma)}$, $n_S^{(\pi)}$ model suggests), and the correct result is calculated even by simple semi-empirical methods that incorporate the necessary lone pair inequivalencies pointed out by Jorgensen and Salem.[3]

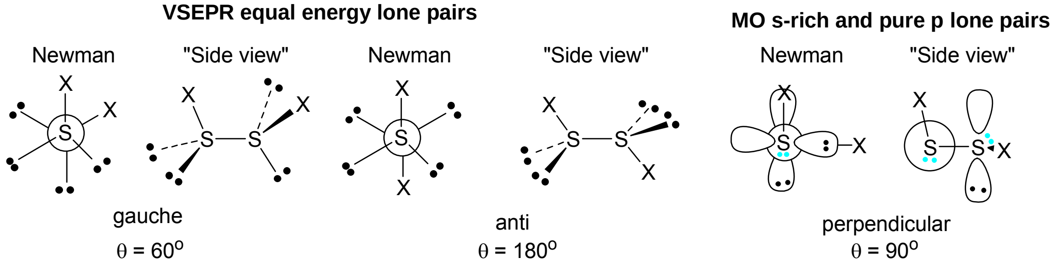


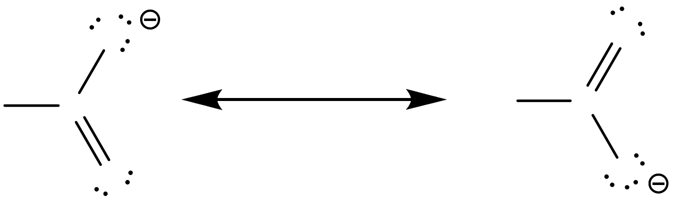
Figure 6. Expected conformers of XSSX compounds in VSEPR (left) vs. MO (right) lone-pair formulations.

The disulfide species are also instructive with regard to the seemingly unending debates about steric vs. hyperconjugative (stereoelectronic) effects in torsional phenomena.[23] It has been common[24] to rationalize the $\theta \cong 90^{o}$ conformational preference of disulfides in terms of a "4e-repulsive" interaction between vicinal $n_S^{(\pi)}$ lone pairs. However, stuctural data strongly suggest that the 90^{o} preference arises because the high-energy pure-p $n_S^{(\pi)}$ lone pair is thereby able to align most favorably with vicinal σ^*_{SH} acceptor orbitals for maximal $n_S^{(\pi)}$-σ^*_{SH} hyperconjugative stabilization ("2e-attraction" between donor and acceptor orbitals[25]). If the 2e-attraction model is correct, one ought to see characteristic SS bond length variations reflecting $n_S^{(\sigma)}$-σ^*_{SX} attraction, and therefore sensitive to X *electronegativity* (rather than "steric bulk") variations. This is indeed found to be the case, with experimental SS bond lengths of 2.056 Å for HSSH,[19] 2.029 Å for MeSSMe,[20] 1.943 Å for ClSSCl,[21] and 1.890 Å for FSSF.[22] Similar resolutions of steric vs. hyperconjugative controversies are found for hydrazines,[26] peroxides,[27] and numerous other species.[28]

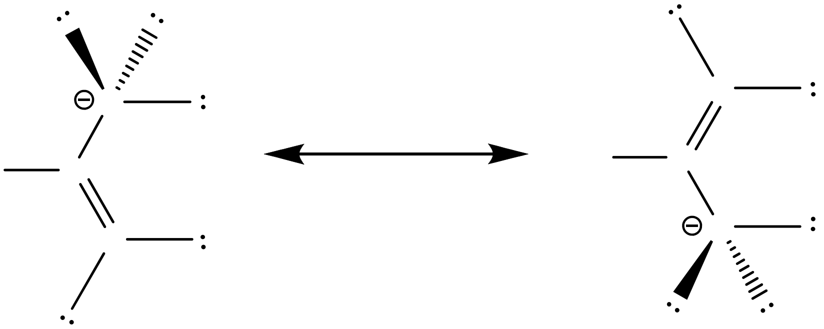
Other Pedagogical Dilemmas of Using VSEPR-derived Lone Pairs

As known from studies of stereochemical and anomeric phenomena,[29] lone pairs commonly act as powerful electronic donors (Lewis bases) in conjugative and hyperconjugative donor-acceptor interactions. Many details of structure and reactivity are therefore *sensitive* to lone pair shape, energy, and orientation, enabling one to clearly distinguish equivalent (rabbit ears) from inequivalent ($n_O^{(\sigma)}/n_O^{(\pi)}$) lone pairs. This has important implications in how we teach about lone pairs in general chemistry and introductory organic chemistry. The currently common practice of using VSEPR to predict and explain electronic structure, particularly the spatial orientation of lone pair electrons, results in a need to start "unteaching" incorrect perceptions or having to use convoluted, invalid rationalizations almost immediately to help students work around their incorrect perceptions about lone pairs.

In introductory organic chemistry, contradictions with VSEPR arise early when students are introduced to the concept of resonance involving oxygen or nitrogen atoms conjugated to π systems. The contradictions at that point often go unnoticed by students and are glossed over by instructors who prefer not to start unteaching VSEPR immediately after it was covered. As a result, students are taught to draw resonance structures without considering the types of orbitals involved. If they do consider the types of orbitals, it becomes apparent that they are forming π-bonds using sp^3 orbitals. For example, when students learn about the acidity of carboxylic acids and the importance of resonance stabilization of carboxylate anions, they are taught to recognize resonance of the type shown in (2a) for the formate anion as being particularly stabilizing.



Using the VSEPR model, if students consider the orbitals involved in these resonance forms, then the lone pairs would have local symmetry as shown in (2b) which would prevent any of the lone pairs on the anionic oxygen from forming a π-bond to the carbon atom.



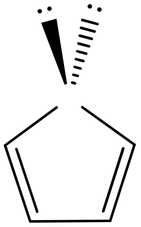
Many instructors avoid addressing this contradiction, while others refer to the anionic oxygen “rehybridizing” to sp^2 allowing it to enter into resonance. Invoking such rehybridization arguments when there was no valid basis for considering the oxygen to be sp^3 hybridized to begin with is clearly a pedagogically unsound practice.

O

(2b) H C

Whether such contradictions arise when the concept of resonance is first introduced, they invariably arise some weeks later when the structure and reactivity of conjugated and aromatic compounds are discussed in greater detail. For example, when discussing aromaticity, furan (C_4H_4O) is commonly cited as a heterocyclic compound that exhibits the classical chemical characteristics of aromaticity.[30] However, students trained to use VSEPR consider the oxygen lone pairs in furan to be in equivalent sp^3 orbitals projecting above and below the plane of the ring as shown in (3), which leads them to the logical conclusion that furan should not be aromatic because neither lone pair can be part of the π system of the ring. (If instead the rabbit ears lone pairs are both counted as belonging to the π system, the usual $4n+2$ rule for aromaticity is again violated.) The observed aromaticity of furan directly contradicts VSEPR-type equivalency of oxygen lone pairs and supports the MO and NBO picture (Fig. 3d) of inequivalent $n_O^{(\sigma)}/n_O^{(\pi)}$ hybridization.

O



Numerous related organic chemistry examples could be cited where VSEPR-inspired thinking leads to contradictions and incorrect conclusions. Indeed, most conjugated systems containing heteroatoms tend to be viewed incorrectly by students trained to use VSEPR, resulting in a range of incorrect perceptions about the structure, stability, and reactivity of these systems. By the time students have completed one semester of introductory organic chemistry, they have encountered so many of these examples that their use of VSEPR to predict and explain electronic structure hurts their understanding more often than it helps.

Still other pedagogical dilemmas are presented by the VSEPR-inspired concept that lone pairs are sterically repulsive compared to bond pairs. Gillespie[5a] recommended teaching that the tetrahedral hydride bond angles of methane were reduced to observed values in ammonia (107.3°) and water (104.5°) because:

> [lone pairs] *overlap with neighboring orbitals more extensively and therefore will repel electrons in these neighboring orbitals more strongly than an electron pair in a bonding orbital* [with the result that] *lone pair electrons will tend to move apart and squash bonding electron pairs together*

Such language leads to the widespread perception that lone pairs are somehow "effectively bigger" than bonding electron pairs. However, we may well ask what evidence (other than mnemonic success of the VSEPR model itself) supports the claim that lone pairs are effectively "bigger," "more repulsive," or "sterically demanding" compared to bond pairs, or the assumption that moving lone pair electrons apart (i.e., in the orthogonal xz-plane) should "squash" the σ_{OH} hydride bonds to reduced angle in the molecular xy-plane of water?

On the experimental side, organic chemists often assess the relative size of substituents by determining the equilibrium constant and free energy difference between the axial and equatorial conformers of a six-membered ring containing the substituent.[31] For any substituent larger than a hydride bond, the conformation that places the bulky substituent in the equatorial position is expected to be lower in energy, due to the unfavorable non-bonded 1,3 diaxial interactions with CH bonds that occur when the substituent is in the axial position. As shown in Figure 7, this method can be applied to piperidine ($C_5H_{10}NH$) to assess the effective size of the nitrogen lone pair relative to the σ_{NH} hydride bond. Fig. 7 displays the experimental free energy difference (+0.36 kcal/mol)[32] which demonstrates that the n_N lone pair of piperidine definitely prefers the *axial* position, and thus appears *smaller* than the σ_{NH} hydride bond by this experimental criterion.[33]

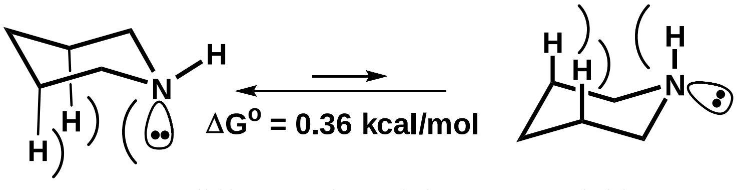


Figure 7. Free energy difference for axial vs. equatorial isomers of piperidine, indicating that the lone pair is effectively *smaller* than the hydride bond pair at nitrogen.

How Can One Satisfactorily Explain X-O-Y Bond Angles Without VSEPR?

As recognized by Pauling, Slater, Coulson, and others,[34] the basic origins of near-tetrahedral bond angles in main-group bonding lie in the *hybridization* concept. The subtle variations from tetrahedrality are similarly due to the subtle variations of hybridization (and therefore bond angle) with *electronegativity*, as expressed most succinctly in Bent's rule,[13] viz.:

Central main-group atoms tend to direct bonding hybrids of higher p-character toward atoms of higher electronegativity

With this powerful mnemonic in hand, the student can easily employ elementary concepts of Lewis structure, periodic electronegativity trends, and bond hybrid vs. angle relationships to make VSEPR-style predictions of molecular structure with confidence and accuracy.

The fundamental relationship between main-group hybrids [e.g., hybrids $sp^{\lambda i}$, $sp^{\lambda j}$ (with hybridization parameters λ_i, λ_j) to atoms *i*, *j*] and bond angle θ_{ij} is given by *Coulson's orthogonality theorem*[35]

(4) $\cos(\theta_{ij}) = -(\lambda_i\lambda_j)^{-1/2}$

which should be known by every freshman chemist. Each hybrid parameter λ is merely a convenient way of expressing the percentage p-character of the hybrid, viz.,

(5) $\lambda = (\%\text{-p})/(\%\text{-s})$

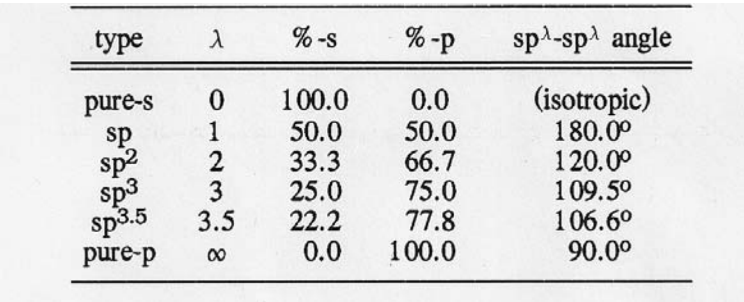
which might vary as shown in Table 2 from 0-100% (or any value in between). Because only three p orbitals and one s orbital comprise the atomic valence shell, the four valence hybrid λ_i's must satisfy the conservation law

(6a) $1/(1 + \lambda_1) + 1/(1 + \lambda_2) + 1/(1 + \lambda_3) + 1/(1 + \lambda_4) = 1$ (conserve s-character)

or equivalently

(6b) $\lambda_1/(1 + \lambda_1) + \lambda_2/(1 + \lambda_2) + \lambda_3/(1 + \lambda_3) + \lambda_4/(1 + \lambda_4) = 3$ (conserve p-character)

Each conservation law (6a,b) makes clear that increasing the electronegativity of any ligand (thereby increasing λ_i, according to Bent's rule) must necessarily *reduce* the p-character in other hybrids, and thereby alter the bond angles according to Eq. (4). This is simply how hybridization (orbital mixing) works, with no “squashing” required. The simple hybrid/angle equations (4)-(6) allow one to trump VSEPR theory by predicting not only the *direction* but also the approximate *magnitude* of angular change.



type	λ	%-s	%-p	sp^{λ}-sp^{λ} angle
pure-s	0	100.0	0.0	(isotropic)
sp	1	50.0	50.0	180.0°
sp^2	2	33.3	66.7	120.0°
sp^3	3	25.0	75.0	109.5°
$sp^{3.5}$	3.5	22.2	77.8	106.6°
pure-p	∞	0.0	100.0	90.0°

Table 2. Hybridization parameter ($0 \leq \lambda \leq \infty$), percentage s/p-character, and associated bond angle for representative sp^{λ} hybrids [cf. Eqs. (4)-(6)].

Consider, for example, replacement of methane (CH_4) by substituted CH_3X. According to Bent's rule, the equivalent sp^3 hybrids of methane (each with 75% p-character) must then be replaced by *in*equivalent hybrids (with $\lambda_H \neq \lambda_X$, to reflect the inequivalent bonding demands of H and X ligands) subject to the conservation constraint (6b),

(7a) $3\lambda_H/(1 + \lambda_H) + \lambda_X/(1 + \lambda_X) = 3$

which can be solved to give

(7b) $\lambda_H = 2 + 3/\lambda_X$

The altered λ_X, λ_H values can then be substituted in Eq. (4) to obtain estimated θ_{HX} and θ_{HH}, bond angles. For example, if X is highly electronegative (e.g., X = F), its hybrid acquires *more* than 75% p-character [e.g., $\lambda_F = 3.65$ (78.5% p-character), $\lambda_H = 2.79$ (73.6% p-character) in CH_3F (B3LYP/6-311++G** level, idealized tetrahedral geometry)], and Eq. (4) then gives

(8a) $\theta_{HF} = \arccos[-1/(\lambda_F\lambda_H)^{1/2}] = 108.3$

(8b) $\theta_{HH} = \arccos[-1/\lambda_H] = 111.0$

in sensible qualitative agreement with fully optimized values (108.6°, 110.3°, respectively). Approximations of λ_X from electronegativity values (as well as limitations of the resulting numerical estimates) are discussed elsewhere,[36] but one requires only the elementary relationship (4) between bond angle θ_{ij} and hybrid descriptors λ_i, λ_j to see how Bent's rule predicts the direction of angular changes from familiar electronegativity differences.

Replacement of a bond pair by a lone pair is also straightforward if we think of the lone pair as bonding to a "ghost" atom X (least electronegative of all!). In H_2O, for example, we expect the in-plane lone pair to exhibit *reduced* p-character, with correspondingly higher p-character in hydride bonds [e.g., $\lambda_{n(\sigma)} = 0.97$ (49.3% p-character) vs. $\lambda_H = 3.05$ (75.3% p-character)]. The predicted hybridization shifts thereby lead to bond-angle changes corresponding to "increased angular volume" around lone pairs, as suggested (for the wrong reasons) by VSEPR theory.

Indeed, with only slight changes of terminology, we can easily re-phrase the familiar VSEPR examples in more accurate and incisive hybrid language. For example, we should describe lone pairs as "s-rich" or "angularly rounded" (rather than "fat" or "more repulsive"). Of course, the temptation to envision rabbit-ear lone pairs should never arise in the reformulated presentation, because the out-of-plane $n_O^{(\pi)}$ lone pair (pure-p, with $\lambda_{n(\pi)} = \infty$) is always excluded from the Bent's rule competition for in-plane p-character.

Why does Bent's rule work? Electrons of a free carbon atom will naturally prefer to remain in a low-energy s-orbital rather than high-energy p-orbital. Chemical C-X bonding can force s-p mixing (hybridization) to lower the overall energy, but the optimal s/p-composition of the C hybrid will naturally depend of how "close" the electron pair remains to the carbon atom. If X is relatively electro*positive*, so that the C-X bond is highly polarized *toward* C, the optimal C hybrid incorporates *increasing s-character* (and increasingly broad angular "roundness") to minimize the energy. However, if X is electronegative, so that C-X polarization takes the electron pair *away from* C, the optimal C hybrid incorporates *increasing p-character* (and increasingly narrow angular directionality). Bent's rule can also be appropriately re-formulated for transition metal species (see Ref. 11, p. 421ff), where it continues to provide excellent guidance to molecular structure predictions for mononuclear and polynuclear metallic species. In contrast, VSEPR theory exhibits numerous spectacular failures in this domain (see Ref. 11, pp. 389-390, 400, 402, 428, 433, 449, 454, 574).

The hybridization changes implied by Bent's rule can also be recognized in "Walsh diagrams" that exhibit MO or NBO orbital energy as a function of bond angle or other variable of interest. Figure 8 displays the NBO-based Walsh diagrams for bond (σ_{OH}) and lone pair ($n_O^{(\sigma)}$, $n_O^{(\pi)}$) orbitals as p-character reallocates during HOH bond-bending. As shown in Fig. 7, the energy of the in-plane $n_O^{(\sigma)}$ lone pair steadily decreases at smaller HOH bond angles, reflecting its diminished p-character as required by the increased p-character (and higher orbital energy) for the two σ_{OH} bonds. In contrast, the out-of-plane $n_O^{(\pi)}$ is scarcely affected by angular deformations, testifying to its profound inequivalence to $n_O^{(\sigma)}$ with respect to the competition for p-character. Although other factors (including nuclear-nuclear repulsion and Coulomb/exchange variations) contribute to ΔE_{tot}, the dominant orbital-energy dependence is clearly exhibited by the ε($n_O^{(\sigma)}$) and ε(σ_{OH}) NBO variations in Fig. 8, as anticipated by Bent's rule.

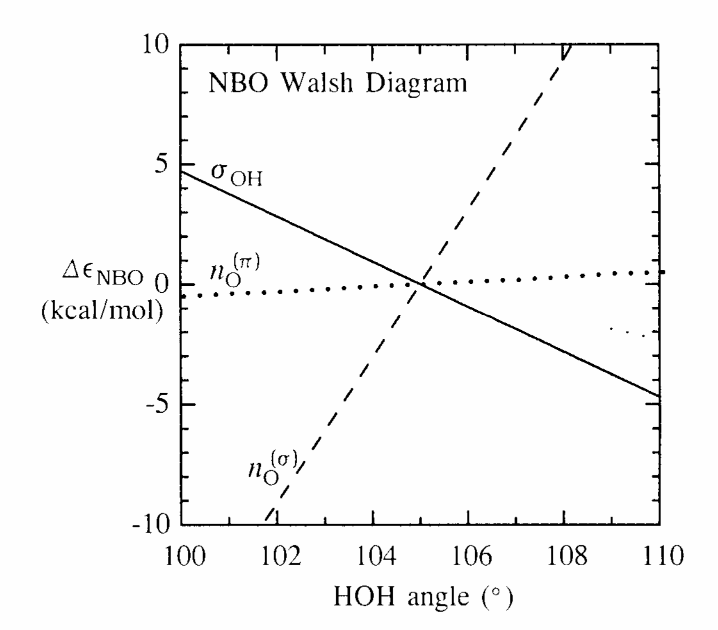


Figure 8. NBO-based Walsh diagram (B3LYP/6-311++G** level), showing NBO orbital energies for σ_{OH} bond (solid line), $n_O^{(\sigma)}$ lone pair (dashed line), and $n_O^{(\pi)}$ lone pair (heavy dotted line) as function of HOH bond angle, reflecting competing in-plane demands for p-character in accordance with Bent's rule.

How Can One Quantify "Steric Repulsion" of Lone Pairs?

Physicist Victor F. Weisskopf first proposed a visually and mathematically effective formulation of steric repulsion as "kinetic energy pressure."[37] Steric space-filling or "hardness" properties are generally understood to originate in the Pauli exclusion principle (wavefunction antisymmetry for exchange of identical electrons or other fermions), which limits the maximum occupancy of any spatial orbital to *two* electrons of opposite spin. Equivalently, this principle prevents electron pairs from crowding into the same spatial region, because their orbitals cannot maintain mutual *orthogonality* without incurring additional oscillatory "ripple patterns" (nodal features) that increase the 2nd-derivative "curvature," and thus the kinetic energy of the orbital. Attempted compression of filled orbitals must therefore result in increasingly severe ripple-like nodal features in the outer overlap region, analogous to the inner nodal features that maintain orthogonality to core electrons of the same symmetry, with the resulting kinetic energy increase acting as "pressure" to resist further compression.

Why orbitals must remain mutually orthogonal, and why the curvature of orbital ripple patterns determines kinetic energy, goes back to deep quantum mechanical principles of Hermitian eigenvalue problems. However, the idea that increased number of nodes corresponds to unfavorable increase in orbital energy should be familiar to all students. Chemistry students learn the value of using the visual overlap of nodeless free-atom orbitals (such as the pre-orthogonal “pre-NBOs”) to estimate orbital interaction strength, but one should recognize that this is a convenient mnemonic fiction, and that physical solutions of Schrödinger-type eigenvalue equations, as well as the associated perturbation theory equations, are *always* mutually orthogonal, consistent with Weisskopf's formulation of the steric concept.

Weisskopf's picture forms the basis of *natural steric analysis*,[38] a standard option (STERIC keyword[39]) of the NBO program[40] that quantifies total “steric exchange energy” (E_{NSX}) as well as its pairwise contributions from distinct electron pairs. The R-dependent variations of E_{NSX} provide an excellent approximation for the rare-gas interaction potentials that are considered the prototype of steric exchange effects, and $\Delta E_{NSX}(R)$ variations also satisfy numerous consistency checks with empirical van der Waals radii and other physical criteria of steric size.[41] We can therefore employ NBO steric analysis to directly assess the steric-exchange effects with respect to HOH bond-angle variations, as plotted in Figure 9. The figure shows that increasing the HOH angle always causes the overall E_{NSX} steric repulsions to *decrease*, contrary to the lone pair “squashing” that would be expected in VSEPR theory. Various levels of HF or DFT theory differ slightly in overall slope and individual orbital contributions, but *no* reasonable theoretical level provides support for “VSEPR sterics” as presented in current chemistry textbooks.

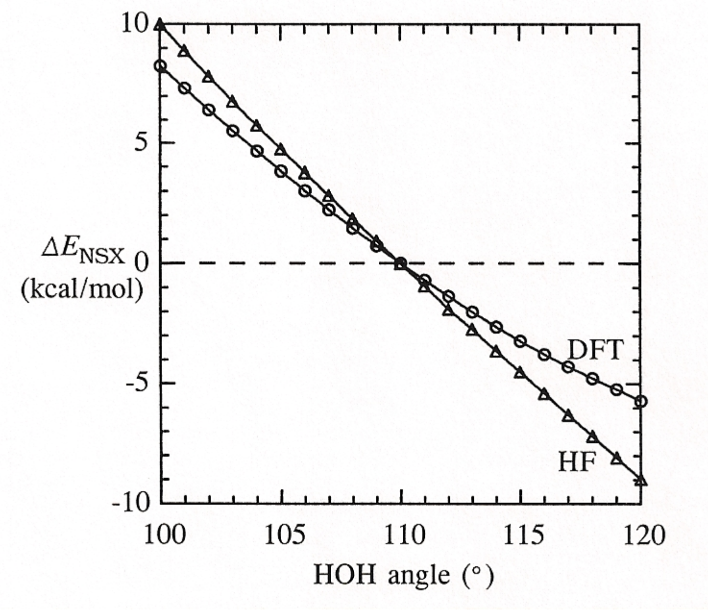


Figure 9. Natural steric-exchange energy variations (ΔE_{NSX}) with H_2O bond angle (referenced to 110°), showing the uniform decrease of steric repulsion toward smaller HOH angles, contrary to expectations of VSEPR theory. Similar trends are found for HF/STO-3G (triangles) and B3LYP/6-311++G** (circles) levels of theory.

An even simpler way to assess relative lone-pair vs. bond-pair "steric size" is by plotting realistic $n_O^{(\sigma)}$, σ_{OH} orbital shapes. (Recall that the orthogonal $n_O^{(\pi)}$ lone pair makes no contribution to sterics in the molecular plane.) Bader and coworkers[15] proposed the outermost contour value 0.0316 a.u. as closely approximating the effective van der Waals boundary inferred from crystallographic data. With this contour value (the default in the NBOView orbital plotter[42]), Figure 10 compares the apparent orbital sizes in 1-d orbital amplitude (left) and 2-d contour (right) plots. As shown in these plots, one can visually judge that $n_O^{(\sigma)}$ appears everywhere "sterically hidden" or "inside" σ_{OH} within a broad cone of approach angles along the forward direction. Neglecting a short-range feature on the $n_O^{(\sigma)}$ backside (seldom the approach direction of chemical interest!), the $n_O^{(\sigma)}$ orbital appears sterically visible only in a narrow (near-transverse) angular sector near the nucleus, where its "more rounded" shape is in accordance with Bent's rule. Such simple visual comparison may have greater pedagogical impact than the ΔE_{NSX} evaluations of Fig. 9 in establishing that VSEPR-inspired steric concepts have no theoretical basis in the framework of modern computational methodology.

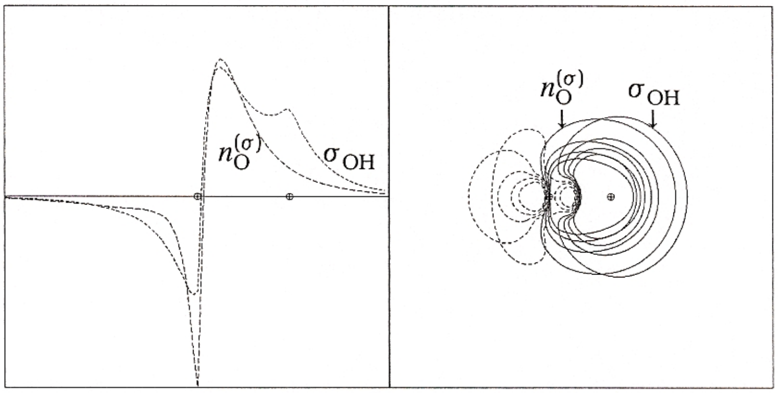


Figure 10. Apparent "steric size" of lone pair ($n_O^{(\sigma)}$) vs. bond pair (σ_{OH}) NBOs of H_2O (B3LYP/6-311++G** level), compared in terms of 1-d orbital amplitude profiles (left) or 2-d contours (right), with outermost contour corresponding to Bader's van der Waals surface (Ref. 15).

Conclusion

The foregoing examples serve to illustrate how *qualitative* chemical misrepresentations are inspired by VSEPR concepts, and why the teaching of such concepts ought to be abandoned. Fairly simple changes in emphasis and language allow one to retain the popular molecular structural predictions of the "VSEPR module," but to integrate (and extend!) these predictions in the framework of more accurate teaching of hybridization and Bent's rule concepts. The latter form the basis for modern valency and bonding principles that extend successfully to main-group and transition-group species far beyond the scope of freshman chemistry. These principles are also completely consistent with (indeed, derived from and inspired by) the best available computational evidence from modern wavefunction methods. Pedagogical eradication of VSEPR/rabbit-ear trappings is thus a win-win situation, both for the freshman-chemistry course as well as the advanced courses that bring students to the frontiers of modern chemical research.

In the present work we have also illustrated the use of NBO-based tools that allow modern ab initio computational technology (widely accessible to students in web-based or laptop implementations) to be easily "translated" into the classroom language of Lewis-structural and resonance concepts. Such tools, if made a routine component of basic chemical training (e.g., in a "computer experiment" module of the freshman chemistry or organic laboratory), offer the prospect of qualitative improvements in the pedagogical accuracy and efficiency of the chemistry curriculum, enabling students to pursue more advanced bonding questions of their own choosing and interest. In line with similar suggestions elsewhere,[43] we believe that upgrading student familiarity with the theory and practice of modern computational chemistry concepts (and downgrading dependence on superficial VSEPR-type rationalizations) offers the surest path to urgently needed pedagogical reforms in general chemistry teaching.

APPENDIX

A version of the unitary invariance argument for inequivalent and equivalent lone pairs is presented in a recent monograph[44] (pp. 107-109) which may be taken as representative. In this argument, equivalent rabbit-ear hybrids h_r, $h_{r'}$ are expressed (in unnormalized form) by proportionality relations of the form

$$\text{(A-1a)} \quad h_r \propto n + \lambda p$$

$$\text{(A-1b)} \quad h_{r'} \propto n - \lambda p$$

where $p = p_y$ (perpendicular to the molecular plane), n is an in-plane sp^n-type hybrid, and λ is a mixing parameter (left unspecified in their discussion). Visually (cf. Scheme 5.3 of Ref. 44), such mixtures suggest a superficial resemblance to sp^3 hybrids. However, only $\lambda = 1$ is allowed by Fock's theorem, because the transformation is otherwise non-unitary and h_r, $h_{r'}$ become nonorthogonal. The envisioned orthonormal rabbit-ears hybrids must therefore be expressed explicitly as

$$\text{(A-2a)} \quad h_r = 2^{-1/2}(n + p)$$

$$\text{(A-2b)} \quad h_{r'} = 2^{-1/2}(n - p)$$

with associated orbital energies

$$\text{(A-3a)} \quad \varepsilon_r = (\varepsilon_n + \varepsilon_p + 2F_{np})/2$$

$$\text{(A-3b)} \quad \varepsilon_{r'} = (\varepsilon_n + \varepsilon_p - 2F_{np})/2$$

These orbitals are indeed equivalent ($\varepsilon_r = \varepsilon_{r'}$) because off-diagonal $F_{n,p} = \langle n|F|p\rangle$ between MOs are vanishing.

However, the transformed orbitals h_r, $h_{r'}$ are generally not "sp^3 hybrids" and must exhibit rather strange energetic interactions. If we assume, e.g., that n is an sp^2 hybrid along the z axis

$$\text{(A-4)} \quad n = 3^{-1/2}(s + 2^{1/2}p_z)$$

then h_r, $h_{r'}$ become explicitly

$$\text{(A-5a)} \quad h_r = 6^{-1/2}[s + 3^{1/2}p_y + 2^{1/2}p_z]$$

(A-5b) $h_{r'} = 6^{-1/2}[s - 3^{1/2}p_y + 2^{1/2}p_z]$

neither of which (83% p-character) is of idealized sp^3 form. Moreover, these orbitals have the surprising Fock matrix interaction element

(A-6) $F_{r,r'} = \langle h_r|F|h_{r'}\rangle = 1/2\ \langle n{+}p|F|n{-}p\rangle = (\varepsilon_n - \varepsilon_p)/2$

even though $\langle h_r|h_{r'}\rangle = 0$! For water (B3LYP/6-311++G** level), this interaction evaluates to an alarmingly large value

(A-7) $F_{r,r'} = -108$ kcal/mol

which could not be considered "ignorable" except in the context of a crude Hückel-like model (with the assumption $F_{r,r'} = k\langle h_r|h_{r'}\rangle = 0$, perforce vanishing). In this limit, the lone pairs must also be implicitly assumed to be degenerate ($\varepsilon_n = \varepsilon_p$) for consistency. Thus, the supposed "equivalence" of (n,p) vs. (h_r,$h_{r'}$) lone pairs rests on approximations that are unacceptable by current standards of accuracy.

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