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Rabbit Ears Concepts of Water Lone Pairs:
A Reply to Comments of Hiberty, Danovich, and Shaik

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Abstract

We respond to recent comments (Hiberty et al., 2015) on our earlier article (Clauss et al., 2014) concerning "rabbit ears" depictions of lone pair orbitals in water and other species.

Introduction

Hiberty, Danovich, and Shaik (2015) (hereafter HDS) recently commented on our earlier contribution to this Journal, entitled "*Rabbit-ears hybrids, VSEPR sterics, and other orbital anachronisms*" (Clauss et al. 2014). HDS's comments focus on the fundamental question of whether "there exists a unique set of supposedly 'real', or 'best', orbitals for a given molecule". It is obvious that such a question lies at the heart of any orbital description of electronic structure, and, therefore, at the heart of chemical pedagogy. Is there a preferred representation of lone pairs that sets students on the right course and minimizes features that must be unlearned as their technical proficiency grows?

A reply to HDS's comments necessarily involves technical details that we had attempted to minimize in communicating with a non-specialist audience of chemical educators. However, the topic is of considerable interest to both specialist and non-specialist readers, and our lack of adequate detail may have led to misunderstanding that we now wish to clarify.

Areas of Substantial Agreement

We begin with the mathematical appendix of our paper, which examines a typical claim (Shaik and Hiberty, 2008) that the two highest occupied molecular orbitals (MOs) of water can be considered "equivalent" to the two sp^3-type lone pairs ("rabbit ears") that are often pictured in elementary chemistry textbooks. Such equivalence is based on 2x2 unitary transformation of the MO determinant to localized molecular orbital (LMO) form, and such LMOs were in turn considered by HDS to be representative of the natural bond orbitals (NBOs) (Weinhold and Landis, 2005, 2012; Weinhold, 2012) that were primarily used throughout our discussion.

We have no quibble with HDS's eq. (2) or their exemplary description of unitary equivalence in MO-LMO transformations. We note with approval that their revised description of this transformation now takes account of Bent's rule (Bent, 1961), so that the in-plane (σ-type) MO of the symmetry-compliant MO description is recognized as being of $sp^{0.87}$ type (46.5% p-character, vs. the 100% p-character of the out-of-plane π-type MO), and their 2x2 MO-LMO transform then yields two $sp^{2.75}$ LMOs with 112° bond angles ("close to sp^3 like"). Their comment therefore becomes consistent with other NBO-based descriptions of water hybrids and agrees with our recommendation to employ Bent's rule in place of VSEPR-type rationalizations for pedagogical discussions of molecular hybridization and shape, as illustrated in numerous examples of our paper.

What then are remaining points of misunderstanding in HDS's comments that might be clarified in the interest of possible full consensus? We concentrate here on their conclusions that (i) "*one must give up the belief that there exists a unique set of supposedly "real, or "best", orbitals*" [their italics] and (ii) "the directions of the lone pairs in the sp^3 representation match the directions of hydrogen bonds between the oxygen atom of H_2O and neighboring A-H molecules". These two conclusions are connected: In contrast to our examples supporting superiority of local-symmetry σ/π representation (as, e.g., in the furan case mentioned by HDS), the H-bond directionality of their Scheme 2 is offered as counterexample to suggest superiority of alternative sp^3 representation, emphasizing that "both orbital pictures are equivalent and both are perfectly valid, and their choice of usage can be done according to the problem at hand." We discuss each conclusion in turn in the following sections.

Is Validity of Unitary Transformations "General" in LMO and NBO Theory?

We concur that the numerical difference between LMOs (e.g., Boys, 1968) and NBOs "does not make much difference" for an isolated water molecule, but this is no longer the case for more complex species such as furan. We also concur that MOs and LMOs are unitarily equivalent in the sense of Fock's (1930) theorem, as emphasized by HDS. These authors acknowledge that such unitary transformations might similarly be used to argue for "equivalence" between core and valence MOs, but they maintain that this is a "strawman" argument, "since no chemist would think to create such core-valence hybrids". However one judges this argument, it is clear on all sides that unitary MO-LMO transformations are arbitrary and devoid of physical significance.

However, we wish to point out that HDS's remarks about the intrinsic arbitrariness of MO-LMO transformations do *not* apply to NBOs or their "natural hybrid orbital" (NHO) constituents. NHOs and NBOs are obtained by maximum-occupancy ("natural") algorithms that make no direct use of MO-type information and are not unitarily equivalent to MOs or LMOs, even in the single-determinant Hartree-Fock or Kohn-Sham limit. Indeed, if one wishes to consider alternative hybrid forms (e.g., sp^3 rabbit ears or other envisioned choices) to replace the optimal NHOs in NBO construction, the NBO program (Glendening *et al.*, 2013) will quantify the incremental "error" (sub-optimal Lewis occupancy) associated with each such choice [see the NBO Manual (http://nbo6.chem.wisc.edu/nbo6ab_man.pdf, p. B-12) for keyword input to "freeze" NHO orbital transformation to a pre-selected form]. Whether eigen-orbitals of the 1st-order reduced density operator (Löwdin, 1955) are considered "real" is open to philosophical discussion, but the fact that this operator provides quantitative criteria to determine which of several possible hybrid forms is "best" in describing the actual electron density is indisputable. In other words, there is a clear best description of lone pairs when using NBOs, but not when using MOs.

A reply might be that HDS's remarks were aimed at NLMOs (natural localized molecular orbitals, each uniquely related to a parent NBO as the "least delocalized" modification that achieves full double occupancy). NLMOs are indeed very similar to NBOs for an isolated water monomer, but the point is that the *differences* between NBOs and NLMOs are precisely the conjugative and hyperconjugative effects that were the subject of our work. Hence, any remarks pertaining to unitary equivalence of MOs and NLMOs (although certainly true) are irrelevant to the central issues under discussion.

Do Hydrogen Bonded Structures Suggest Rabbit-Ears Directionality of Lone Pairs?

HDS's claim that sp^3 lone pairs match (or exactly predict) the directionality of $H_2O\cdots HA$ hydrogen bonding seems to provide a potent argument for rabbit-ears depictions. However, one can easily test this claim with a simple model calculation on the $H_2O\cdots HF$ complex (B3LYP/6-311++G** level). For this purpose we employ monomers of fixed geometry and linearly aligned $O\cdots HF$ orientation, so that the optimized H-bond inclination with respect to the HOH plane can be uniquely determined for any chosen $R_{O\cdots H}$ distance, as shown in Figure 1.

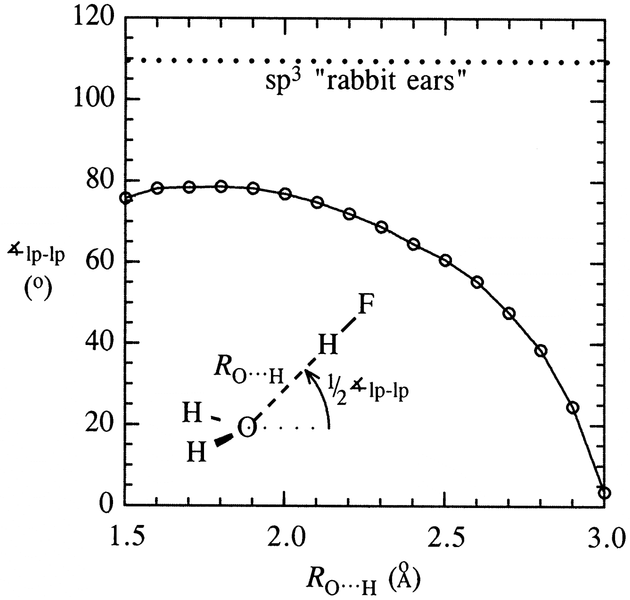

Figure 1. Apparent "lone pair-lone-pair angle" ($\angle_{\text{lp-lp}}$, degrees) as inferred from the optimized inclination angle ($\angle_{\text{incline}} = ½\angle_{\text{lp-lp}}$) of H-bonded $H_2O\cdots HF$ complex at various approach distances ($R_{O\cdots H}$, Å) from long-range to near-equilibrium separation (B3LYP/6-311++G** level; fixed monomer geometry). The dotted line marks the expected value (109.5°) for sp^3-hybridized "rabbit ears" lone pairs.

Fig. 1 shows that the favored H-bond approach angle does not track the tetrahedral direction of the envisioned sp^3-type single rabbit ear lobe (nor a bifurcated path equidistant between equivalent rabbit ear lobes). Instead, the optimal H-bond approach angle rises from its long-range ("dipole-dipole"-like) limit to pass gradually through intermediate inclination angles ranging up to about 40° near the equilibrium separation ($R_{O\cdots H} \approx 1.70$Å). However, none of the traversed $H_2O\cdots HF$ orientation angles corresponds to even the *smallest mathematically allowed* rabbit-ears separation angle (90°) of pure-p lone pairs, let alone that (109.5°) of tetrahedrally oriented sp^3 lone pairs, or the still larger angle (112°) of HDS's Scheme 2. Thus, one finds no real tendency for H-bonding geometry of the $H_2O\cdots HF$ complex to "match" or "exactly predict" the presumed direction of sp^3–like rabbit-ears lone pairs.

The actual geometry of the $H_2O\cdots HF$ complex will naturally be chosen to maximize total n_O-σ^*_{HF} donor-acceptor attractions (and minimize n_O-σ_{HF} donor-donor repulsions) with *both* oxygen lone pairs of the water monomer, hence orienting HF somewhere *between* the in-plane σ-type ($n_O^{(\sigma)}$) and out-of plane π-type ($n_O^{(\pi)}$) lone pair directions, consistent with the general n_B-σ^*_{HA} picture of A-H···B hydrogen bonding (Weinhold and Klein, 2014). The important contribution of in-plane $n_O^{(\sigma)}$ could also be verified by noting that significant net H-bond attraction persists when HF approaches H_2O at *zero* inclination angle, apparently separated as far as possible from either of the two rabbit-ears directions. The ready availability of attractive interactions with two inequivalent lone pairs over a wide angular range confers considerable angular flexibility and resultant entropic (and free energy) advantage to H-bonds involving oxygen (as contrasted, e.g., with the single lone pair of nitrogen). The angular flexibility of tandem $n_O^{(\sigma)}/n_O^{(\pi)}$ lone pairs in H_2O also allows easy accommodation to demands of solution or crystalline environment, leading to many known "classes" of water coordination in crystalline hydrates (including bizarre *planar* H-bond patterns in $K_2C_2O_4 \cdot H_2O$) that deviate sharply from the tetrahedral-like pattern of ice I (Chidambaram et al., 1964). The local-symmetry σ/π picture of water lone pairs therefore seems preferable also in its ability to explain such broader aspects of H-bond directionality.

Conclusions

We believe that clarification of technical aspects of MO-LMO unitary transformations and the uniqueness of NBO lone pairs reveals considerable agreement with HDS, and that remaining areas of disagreement (e.g., concerning H-bond directionality as an indicator of rabbit-ears character) serve to re-emphasize the major points of our original article. In particular, closer attention to accurate features of atomic hybrid composition and its relationship to electronegativity (Bent, 1961), atomic size, and other aspects of molecular shape, NMR shielding, and chemical reactivity (Alabugin et al., 2014) supports retention of the hybrid orbital concept (Tro, 2012; deKock and Strikwerda, 2012; Landis and Weinhold, 2012; Truhlar, 2012; Hiberty et al., 2012) and should be considered a better investment of pedagogical effort than that currently devoted to superficial rabbit ears and VSEPR-type rationalizations.

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