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Is There a Need to Discuss Atomic Orbital Overlap When Teaching Hydrogen–Halide Bond Strength and Acidity Trends in Organic Chemistry?

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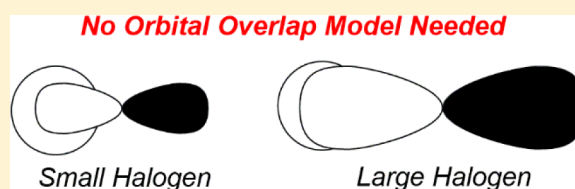
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S Supporting Information

ABSTRACT: Undergraduate organic chemistry textbooks and Internet websites use a variety of approaches for presenting and explaining the impact of halogen atom size on trends in bond strengths and/or acidity of hydrogen halides. In particular, several textbooks and Internet websites explain these trends by invoking decreasing orbital overlap between the hydrogen 1s atomic orbital and successively larger group 17 halogen atomic orbitals. A similar orbital overlap rationalization is often extended to the trends in alkyl halide bond strengths. We examined this orbital overlap explanation using quantum mechanical calculations. Calculations reveal that orbital overlap increases rather than decreases with successively larger group 17 halogen atomic orbitals. This suggests that an orbital overlap explanation is physically incorrect and unneeded. Alternative to orbital overlap, we briefly discuss physically correct models for rationalizing halogen bond strength and acidity based on quantum mechanical valence bond theory and molecular orbital theory.

KEYWORDS: Organic Chemistry, Computational Chemistry, MO Theory, Valence Bond Theory, Covalent Bonding, Second-Year Undergraduate, Upper-Division Undergraduate, Graduate Education/Research, Misconceptions/Discrepant Events



■ INTRODUCTION AND MOTIVATION FOR CALCULATIONS

An early and important topic taught in undergraduate organic chemistry is the chemical properties of hydrogen halides ($\text{H}-\text{X}$, where $\text{X} = \text{F}, \text{Cl}, \text{Br}$, and I). The most important chemical properties of hydrogen halides are bond strengths and acidities because these properties play a critical role in the reactivity and selectivity of substitution, elimination, and free-radical reactions. This subject can sometimes be difficult for students because unlike the first row of the periodic table hydrogen halides have the unique correlation where the weakest and least polar bond is the most Bronsted acidic as a result of halogen atom size.

Inspection of commonly used undergraduate organic chemistry textbooks and Internet Web sites indicates that there are several approaches for presenting and explaining the impact of halogen atom size on the trends in bond strengths and acidity of hydrogen halides and the bond strengths of alkyl halides. Some textbooks and Internet Web sites only present trends with little or no discussion. Some textbooks and Internet Web sites correlate Bronsted acidity and decreasing bond strength or correlate these trends with bond length.^{1–4} Alternatively, several textbooks^{5–8} and Internet Web sites⁹ explain this atomic size effect by decreasing orbital overlap between the hydrogen 1s atomic orbital and successively larger halogen atomic orbitals. A similar argument is often made for

alkyl halides with bonding between a carbon fragment orbital and halogen atomic orbitals.¹⁰

While decreasing orbital overlap as the halogen atom size becomes larger is an appealing interpretation, we wondered whether this explanation is physically correct and could be corroborated with quantum mechanical calculations. Here we report quantitative molecular orbital analyses, based on Kohn–Sham density functional calculations, that reveal trends in halogen bond strengths and Bronsted acidity and alkyl halide bond strengths cannot be rationalized by decreasing orbital overlap between the hydrogen 1s atomic orbital or carbon atomic orbitals and successively larger halogen atomic orbitals. As an alternative to presenting an orbital overlap explanation to students, we briefly discuss three physically correct models for rationalizing halogen bond strength and acidity based on quantum mechanical valence bond theory and molecular orbital theory.

■ CALCULATION OF ORBITAL OVERLAP

Orbital overlap (S_{AB}) is the total coextensive interference of orbitals (Ψ_A and Ψ_B) defined by the spatial integral shown in eq 1. In valence bond theory and molecular orbital theory, orbital overlap provides the underlying quantum mechanical mechanism and description of covalent bond formation.

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$$S_{AB} = \int \Psi_A^* \Psi_B dV \quad (1)$$

As discussed in the introduction section, several undergraduate organic chemistry textbooks rationalize the trends in covalent bond strengths of hydrogen halides (and alkyl halides) as well as Bronsted acidity of hydrogen halides based on decreasing orbital overlap between the hydrogen 1s atomic orbital (or carbon atomic orbitals) and successively larger halogen atomic orbitals.^{5–9} To examine this explanation, we have carried out BP86/TZ2P molecular orbital density functional theory calculations using the Amsterdam Density Functional (ADF)¹¹ program to directly evaluate the orbital overlap between the halogen atoms and hydrogen or alkyl group fragment orbitals that lead to bond formation. Our calculated trend in orbital overlap does not depend on the density functional or basis set size (see Supporting Information).

The second column in Table 1 reports the calculated orbital overlap values between radical fragments for H–F, H–Cl, and

Table 1. Calculated BP86/TZ2P Orbital Overlap for H–X and C–X Bonds (X = F, Cl, Br)

molecule	bonding orbital overlap	molecule	bonding orbital overlap	molecule	bonding orbital overlap
HF	0.36 (0.42) ^a	CH ₃ F	0.27	(CH ₃) ₃ CF	0.23
HCl	0.47 (0.52) ^a	CH ₃ Cl	0.34	(CH ₃) ₃ CCl	0.30
HBr	0.48 (0.53) ^a	CH ₃ Br	0.35	(CH ₃) ₃ CBr	0.30

^aOrbital overlap calculated for electronically constrained ionic (H⁺/X[–]) fragments.

H–Br at their equilibrium geometries. In contrast to the expectation based on undergraduate organic textbooks and many Internet Web sites, the trend in orbital overlap is H–Br \approx H–Cl > H–F. The orbital overlap value for H–Br is calculated to be 0.48, and this is only slightly larger than that for H–Cl with a value of 0.47. Both H–Br and H–Cl have significantly larger orbital overlap than H–F, which has a calculated overlap value of 0.36. Overall, the calculated orbital overlap values reveal that the weaker H–Br and H–Cl covalent bonds have larger total orbital overlap between bonding radical fragments than the stronger H–F bond. This is consistent with the idea that a larger atomic orbital provides more total coextensive space for σ orbital overlap than a smaller atomic orbital.^{12,13} The calculated orbital overlap values are also consistent with the idea that the H–Br bond is more covalent than the H–F bond.

Figure 1 plots the H and X radical fragment orbital overlap values as a function of H–X bond length. The maximum orbital overlap for H–F, H–Cl, and H–Br occurs at a H–X bond length that is ~ 0.2 – 0.4 Å shorter than the calculated equilibrium bond length. This is because the equilibrium bond distance is not determined by the bonding orbital interactions alone. Instead, it results from a balance between the stabilizing orbital interactions and repulsive forces such as nuclear–nuclear repulsion and closed-shell electron–electron repulsion, which push the two fragments somewhat further away from each other. Importantly, the H–Br and H–Cl orbital overlap values are larger than the H–F orbital overlap values at all interatomic distances, and the maximum possible orbital overlap for H–Br and H–Cl is larger than the maximum possible orbital overlap for H–F. Thus, the more extended

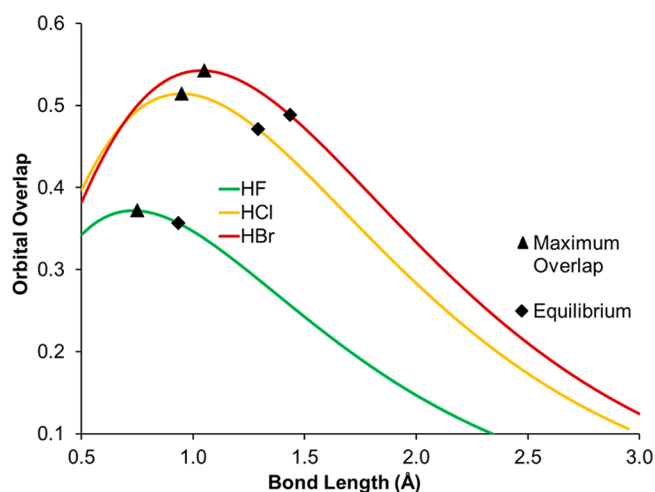
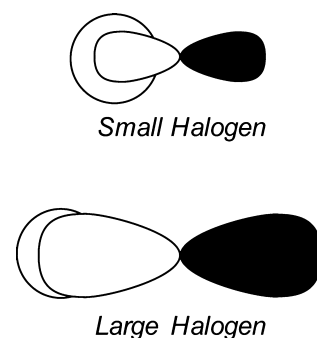


Figure 1. Plot of H–X orbital overlap versus bond length.

valence p_σ orbital lobe of heavier halogen atoms more effectively overlaps with the relatively diffuse hydrogen 1s atomic orbital (see illustration in Scheme 1).

Scheme 1. Schematic Illustration of Overlap between Hydrogen 1s and Halogen p_σ Atomic Orbitals in Hydrogen Halides



We have also examined whether the orbital overlap trend for alkyl halides is similar to that calculated for hydrogen halides. Columns 4 and 6 in Table 1 report the calculated orbital overlap values for the equilibrium bond lengths of methyl and *tert*-butyl halides. The orbital overlap values for methyl and *tert*-butyl halides are ~ 0.1 smaller than the corresponding hydrogen halide orbital overlap values. Due to the longer C–X bond lengths in *tert*-butyl halides the overlap is on average 0.04 less than the overlap calculated for methyl halide bonds. Most important is that similar to the trend in orbital overlap values calculated for the hydrogen halides, methyl fluoride and *tert*-butyl fluoride C–F bonds have the smallest orbital overlap, while the C–Cl and C–Br bonds of alkyl chlorides and alkyl bromides have larger orbital overlap.

The calculated trends in orbital overlap values for hydrogen halides and alkyl halides indicates that explanations for relative bond strengths based on decreasing orbital overlap with successively larger group 17 halogen atomic orbitals is physically incorrect. The calculated orbital overlap values presented in Table 1 also suggest that the higher acidity of H–Br and H–Cl compared with H–F also cannot be rationalized based on diminished orbital overlap. Because acidity is related to the relative ease of heterolysis of hydrogen–halide bonds, we also evaluated the total orbital overlap

between H^+ and X^- ionic fragments at the equilibrium bond lengths. While the calculated orbital overlap values between the ionic fragments are slightly larger than the overlap values between radical fragments (Table 1, column 2), the trend in orbital overlap ($H^+Br^- \approx H^+Cl^- > H^+F^-$) is the same. This ionic fragment orbital overlap, in addition to the covalent fragment orbital overlap, indicates that proton affinity values and acidity cannot be explained by decreasing orbital overlap.

■ PHYSICALLY CORRECT MODELS

Alternative to an orbital overlap explanation for trends in hydrogen halide bond strengths and acidity, there are several physically correct models that can be presented to students. The following sections provide brief details of three models. Instructors can present one or more of these models at various levels of depth that is tailored to the particular student audience.

Model 1: Relative Orbital Contribution

The relative percent contributions of fragment orbitals to the σ bonding molecular orbital in hydrogen halides and alkyl halides is dependent on the orbital mixing coefficients and is a different concept than orbital overlap. One useful methodology to quantitatively evaluate relative contributions of fragment orbitals to a molecular orbital is based on gross Mulliken populations. This procedure is advantageous over examining molecular orbital mixing coefficients since the gross population values are normalized. In addition, unlike the related scheme for computing atomic charges, relative fragment orbital contributions based on population analysis are generally basis set insensitive.¹⁴

The contributions of the hydrogen atom 1s orbital and the halogen atom valence s and p orbitals to the valence σ bonding molecular orbital for H-F, H-Cl, and H-Br were calculated using the fragment orbital gross Mulliken population technique implemented in ADF.¹¹ The results of this analysis are presented in Table 2.

Table 2. BP86/TZ2P Percent Fragment Orbital Contribution to the H-X σ Bonding Molecular Orbital^a

molecule (HX)	% contribution H	% contribution X (p_σ)	% contribution X (s)
HF	11	77	7
HCl	24	63	10
HBr	29	59	9

^aThe total percent contribution does not sum to 100% because orbital contributions less than 5% were not included.

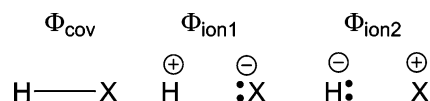
The trend in contribution of the halogen p_σ orbital follows the order of $H-F > H-Cl > H-Br$, and the trend in hydrogen atom 1s orbital follows the opposite order of $H-Br > H-Cl > H-F$. These orbital contributions demonstrate that while fluorine has the smallest total orbital overlap with hydrogen it has the greatest relative contribution to the H-F σ bonding molecular orbital. In contrast, bromine that has the largest orbital overlap with hydrogen and has the least relative contribution to the H-Br σ bonding molecular orbital. We have also verified that a similar trend exists for the orbital mixing coefficients. This trend suggests that rather than orbital overlap determining the relative contribution of the halogen atom orbitals to the H-X σ bonding molecular orbital, atomic

electronegativity and polarity of the bond are the determining factors.

Model 2: Valence Bond Model

In early work, Pauling outlined the impact of halogen size on the polarity and strength of H-X bonds from a valence bond perspective.¹⁵ In valence bond theory, the wave function for a bond is constructed from a set of valence bond resonance structures with localized two electron bonding.¹⁶ For H-X bonds, the valence bond wave function (Ψ_{VB}) is constructed from one covalent (a Heitler-London type function) and two ionic resonance structures shown in Scheme 2 ($\Psi_{VB} \approx c_1\Phi_{cov} + c_2\Phi_{ion1} + c_3\Phi_{ion2}$).

Scheme 2. Hydrogen Halide Covalent and Ionic Resonance Structures



Within this valence bond context, the relative strength of H-X bonds can be attributed to the relative amount of ionic character in the bond, which corresponds to the relative size and electronegativity of the halogen atoms. The larger the contribution of the ionic resonance structure the stronger the covalent bond, which is due to covalent-ionic resonance.¹⁷ For example, in H-F the ionic resonance structure Φ_{ion1} is stabilized and is close in energy to the covalent resonance structure, Φ_{cov} , and this leads to significant covalent-ionic resonance energy stabilization.^{15,17} In contrast, in H-Br and H-Cl, the ionic resonance structures are much higher in energy relative to their covalent resonance structures due to less electrostatic stabilization. This results in less ionic character and less covalent-ionic resonance energy stabilization.¹⁵

The Pauling model for H-X bonds discussed above has been supported by low-level approximate numerical calculations.¹⁵ To confirm these results and bolster the validity of this model, we have carried out quantum mechanical valence bond calculations using the XMVB¹⁸ program interfaced with GAMESS¹⁹ to provide estimates of the resonance structure contributions for hydrogen halides. Table 3 reports our SCF/6-

Table 3. SCF/6-31G Valence Bond Weighting of Resonance Structures for Hydrogen Halides

molecule	Φ_{cov}	Φ_{ion1}	Φ_{ion2}
HF	0.57 (0.50) ^a	0.42 (0.43) ^a	0.01 (0.07) ^a
HCl	0.67 (0.56) ^a	0.27 (0.31) ^a	0.06 (0.13) ^a
HBr	0.71 (0.60) ^a	0.20 (0.25) ^a	0.09 (0.15) ^a

^aLowdin valence bond weighting.¹⁶

31G valence bond results for H-F, H-Cl, and H-Br. In accord with Pauling, the weighting of Φ_{ion1} decreases from 0.42 to 0.27 to 0.20 and the weighting of Φ_{cov} increases from 0.57 to 0.67 to 0.71 for H-F, H-Cl, and H-Br, respectively. These calculations confirm that a physically correct model that can be presented to students is that more polar hydrogen halide bonds have greater ionic resonance contribution that results in a stronger hydrogen halide bond.

Model 3: Molecular Orbital Interaction Model

Simple molecular orbital interaction diagrams are often presented in undergraduate organic classes. This type of

powerful diagram can also be used to explain the trends in H–X bond strengths. We have used quantitative Kohn–Sham molecular orbital analysis as implemented in ADF with the BP86/TZ2P level of theory to provide an estimate of the radical fragment orbital energies and the resulting molecular orbital energy stabilization. These orbital energies comprise all components of the bond energy, including electrostatic interactions, exchange repulsion, and charge transfer interactions. The molecular orbital interaction diagram shown in Figure 2 depicts how the bond strengths for hydrogen halides can be understood by the interaction between H and X radical fragment orbitals.

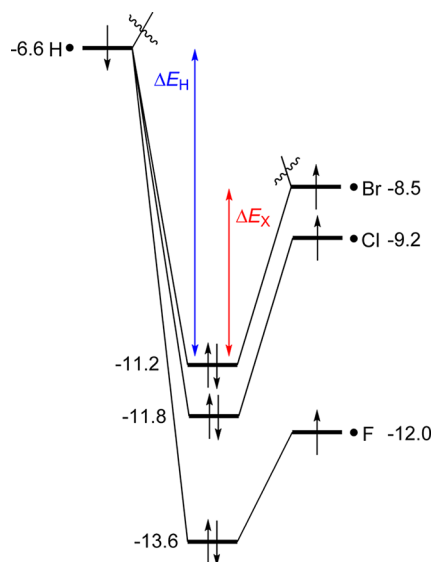


Figure 2. BP86/TZ2P molecular orbital interaction diagram for H–X bond strengths. Orbital energies reported in eV. Antibonding orbital energies are not shown.

In Figure 2, the halogen radicals have different fragment orbital energies that correlate with differences in electronegativity. Upon interaction, both the hydrogen and halogen radical electrons are stabilized, which is depicted as ΔE_H and ΔE_X .²⁰ However, the most important energetic stabilization is from the hydrogen radical electron stabilization. This stabilization correlates well with the energy of the halogen fragment orbital, which provides the largest contribution to the bonding molecular orbital and thus effectively accepts charge from hydrogen. Consequently, the H–X bond becomes $H^{\delta+}-X^{\delta-}$ polarized. For example, in the H–F bond, there is significant hydrogen radical electron stabilization resulting from the hydrogen radical interaction and electron delocalization onto a highly electronegative fluorine atom. In contrast, in the H–Br bond, the hydrogen radical is not highly stabilized since delocalization of the hydrogen electron occurs onto a less electronegative bromine atom. Importantly, this simple molecular orbital interaction diagram provides a qualitative rationale for the large bond strength of H–F versus the smaller bond strength of H–Br despite the opposite trend in orbital overlap.

H–X ACIDITY TREND WITHOUT ORBITAL OVERLAP

Acidity and reactions involving proton transfer are classically rationalized by the resulting conjugate base stability. Within this

type of qualitative model, the acidity trend of hydrogen halides can be associated with the relative stability of halide anion valence orbitals. Larger and more diffuse valence orbitals are more stable due to less Coulombic repulsion between electrons.²¹ For halide anions, the relative stability of the valence HOMO orbitals is bromide > chloride > fluoride. This trend is opposite to the trend in HOMO orbital energies for neutral halogen atoms. This ordering of halide HOMO orbital energies translates into weaker HOMO–LUMO interactions with the empty proton 1s atomic orbital for more stable halide anion orbitals. Additionally, larger and more diffuse anions result in less electrostatic stabilization for interaction with a proton. Presentation of this type of model for H–X acidity to organic chemistry students does not require a discussion of orbital overlap but rather focuses on the stability of halide anions by a HOMO–LUMO interaction or a simple electrostatic interaction.²²

CONCLUSION

Several undergraduate organic chemistry textbooks and Internet Web sites explain the impact of halogen atom size on trends in bond strengths or acidity of hydrogen halides by decreasing orbital overlap with successively larger group 17 halogen atomic orbitals. However, quantum mechanical evaluation of orbital overlap for H–X and C–X bonds reveals that orbital overlap increases rather than decreases with larger halogen atoms. As an alternative to orbital overlap, three physically correct models were briefly discussed for H–X bond strengths that include relative orbital contribution, valence bond model, and molecular orbital interaction model. Each of these models indicates that the electronegativity difference across H–X bonds explains bond strengths. The acidity trend of hydrogen halides was discussed within the classic model of halide anion stability.

ASSOCIATED CONTENT

Supporting Information

Calculation details for evaluation of fragment orbital overlap in ADF, comparison of orbital overlap values calculated with DZ, DZP, and TZ2P basis sets, and calculated fragment orbital mixing coefficients. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (13) We have also considered π orbital overlap for halogen atoms in acyl halides. In contrast to σ orbital overlap, π orbital overlap decreases along the series F to Cl to Br. For example, the π orbital overlap values between the halogen atom and the doubly occupied CO π orbital for $\text{CH}_3\text{CO-F}$, $\text{CH}_3\text{CO-Cl}$, and $\text{CH}_3\text{CO-Br}$ are 0.049, 0.038, and 0.031. The π orbital overlap values between the halogen atom and the unoccupied CO π^* orbital for $\text{CH}_3\text{CO-F}$, $\text{CH}_3\text{CO-Cl}$, and $\text{CH}_3\text{CO-Br}$ are 0.183, 0.174, and 0.158.
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