

Orbital Exchange Calculations of Chemical Bonding in Some Molecules Containing Carbon

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Abstract

The purpose of this paper is to extend the application of the orbital exchange method to a series of molecules containing carbon. The paper describes the calculation of bond length, bond strength and dipole moment in ethane, ethylene, acetylene, benzene, allene, hydrogen cyanide, formaldehyde, fluoromethane, tetrafluoromethane and fluoromethyldyne (CF). This work explains how the s bonding orbital coefficients in such molecules as ethylene and acetylene are maximized to enable shorter and stronger carbon-carbon bonds. Pi orbital resonance of the form [C-C+,CC,C+C-] in ethylene, acetylene, and benzene is described and quantified. Pi orbital resonance in HCN [CN,C+N-] and H₂CO [CO,C+O-] and sigma orbital resonance in H₃CF [H₃CF, H₃C+F-], CF₄ and CF is quantified. Except for HC bonds, calculated bond lengths are within 0.005Å of observed values. Calculated molecular energies are within 2%.

I. INTRODUCTION

The orbital exchange method¹ for calculating the chemical bond does not assume that the bonding electrons can be completely distinguished. That the overlapping electrons cannot be completely distinguished in the overlap region has implications beyond a straightforward reduction in kinetic energy. A bonding orbital need only to be made orthogonal to the core electrons of the atom to which it is bonding to the extent that it can be identified as representing an electron on an opposing atom. Similarly, non-bonding electrons need only be made orthogonal to the bonding orbital from an opposing atom to the extent that the bonding orbital is identified as from an opposing atom. The orbital exchange method permits significant latitude in the selection of hybrid orbital coefficients, since, at maximum overlap, a bonding atom can only be unambiguously identified to the extent of 0.5. For example, a traditional sp³ hybrid orbital can be treated as an sp hybrid orbital.

The orbital exchange method permits the summation of all interactions with a given bonding orbital provided that account is taken for simultaneous overlaps. This provides for seamless treatment of interactions with the once-removed, twice-removed, and etc. atoms in a molecule or lattice.

The orbital exchange methods utilized in the calculation of bonding in some simple molecules were described in detail in an earlier paper¹. The purpose of this paper is to expand the application of orbital exchange method to some somewhat more complex molecules and to introduce some new concepts.

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II. METHODS

A. Hybrid Orbital Coefficients

Hybrid orbitals are of the form $\phi = f_{sb} 2s + f_{pb} 2p_z$. The s orbital coefficient is maximized since this generally has the effect of lowering the overlap with the opposite bonding orbital. Lower overlaps are associated with increased bond energy since the maximum of overlap (overlap = 1.0) is reached at a shorter bond length. Typically, shorter bond lengths imply higher bond energy.

As mentioned above, the extent that a given electron can be identified as associated with one of the two bonding atoms impacts the range of possible s orbital coefficients. At maximum overlap, a given electron can only be unambiguously associated with a given atom to the extent of 0.5. Traditional sp^3 orbitals, associated with 4 coordination, can be considered as sp orbitals with $f_{sb} f_{sb} = 0.5$ at overlap = 1.0. Traditional sp^2 orbitals, associated with 3 coordination, have $f_{sb} f_{sb} = 0.667$ at overlap = 1.0.

For multi-coordinate atoms, all bonding hybrid orbitals need not be identical. One or more of the bonding orbitals can acquire s character from the other orbitals if this results in maximizing the total energy. For example, in HCCH, it is energetically favorable for the CC bond to be as short as possible. Therefore, the CC bonding orbitals acquire s character from the CH bonding orbitals. Such acquisition is limited. The CC bonding orbital can only acquire s character from the CH bonding orbitals to the extent that both bond simultaneously. Table I illustrates the logic for determining $f_{sb} f_{sb}$ when one bond of two is preferred in a two-coordinate situation, such as that for CC in HCCH. Notice that $f_{sb} f_{sb}$ of the CC bonding orbital is limited because, to the extent that both the CC and CH bonds are both not bonding, $f_{sb} f_{sb}$ must equal 0.5 to meet orthogonality requirements. Table II illustrates the logic for determining $f_{sb} f_{sb}$ when one bond of three is preferred in a 3-coordinate situation, such as that for CC in H_2CCH_2 . Table III illustrates the logic for determining $f_{sb} f_{sb}$ when one bond of four is preferred in a 4-coordinate situation, such as that for C in H_3CCH_3 . Table IV illustrates the logic for determining $f_{sb} f_{sb}$ when two bonds of three are preferred in a 3-coordinate situation, such as that for CC in benzene.

Table I. Calculation of s bonding hybrid orbital coefficients f_{sb} for symmetries of the form XCY with Y favored.

		Probability	Fraction s for			$f_{sb} f_{sb}$ Contribution for		
Bonding Y	X		All same	Favored	Not Favored	All same	Favored	Not Favored
b	b	0.25	0.5	1.0	0.0	0.12500	0.25000	0.00000
b	nb	0.25	1.0	1.0	1.0	0.25000	0.25000	0.25000
nb	b	0.25	1.0	1.0	1.0	0.25000	0.25000	0.25000
nb	nb	0.25	0.5	0.5	0.5	0.12500	0.12500	0.12500
Totals		1.000				0.75000	0.87500	0.62500

Bonding(b). Not bonding(nb). Probability of a single bond bonding is 0.5. Probability of two bonding is $0.5 \times 0.5 = 0.25$. Opposing bonding(b) share s.

Table II. Calculation of s bonding hybrid orbital coefficients fs_b for symmetries of the form X_2CY with Y favored.

Bonding Y X	Probability	Fraction s for			fs_b fs_b Contribution for		
		All same	Favored	Not Favored	All same	Favored	Not Favored
b 2b	0.125	0.3333	1.0	0.0	0.04167	0.12500	0.00000
b 1b,1nb	2 0.125	0.5	0.75	0.375	0.12500	0.18750	0.09375
b 2nb	0.125	1.0	1.0	1.0	0.12500	0.12500	0.12500
nb 2b	0.125	1.0	1.0	1.0	0.12500	0.12500	0.12500
nb 1b,1nb	2 0.125	0.75	0.75	0.75	0.18750	0.18750	0.18750
nb 2nb	0.125	0.5	0.5	0.5	0.06250	0.06250	0.06250
Totals	1.000				0.66667	0.81250	0.59375

Bonding(b). Not bonding(nb). Probability of a single bond bonding is 0.5. Probability of all three bonding is $0.5 \times 0.5 \times 0.5 = 0.125$. Opposing bonding(b) share s. Opposing not bonding(nb) are half (0.5) s. In the pseudo-trigonal X_2CY geometry, adjacent bonds oppose to the extent of $1/2$ [$\cos(60^\circ) = 0.5$].

Table III. Calculation of s bonding hybrid orbital coefficients fs_b for symmetries of the form X_3CY .

Bonding Y X	Probability	Fraction s for			fs_b fs_b Contribution for		
		All same	Favored	Not Favored	All same	Favored	Not Favored
b 3b	0.0625	0.25	1.0	0.0	0.01563	0.06250	0.00000
b 2b,1nb	3 0.0625	0.3333	0.6667	0.2222	0.06250	0.12500	0.04167
b 1b,2nb	3 0.0625	0.5	0.6667	0.4444	0.09375	0.12500	0.08333
b 3nb	0.0625	1.0	1.0	1.0	0.06250	0.06250	0.06250
nb 3b	0.0625	0.5	0.5	0.5	0.03125	0.03125	0.03125
nb 2b,1nb	3 0.0625	0.4166	0.4166	0.4166	0.07812	0.07812	0.07812
nb 1b,2nb	3 0.0625	0.6666	0.6666	0.6666	0.12500	0.12500	0.12500
nb 3nb	0.0625	0.5	0.5	0.5	0.03125	0.03125	0.03125
Totals	1.000				0.500000	0.640625	0.453125

Bonding(b). Not bonding(nb). Probability of a single bond bonding is 0.5. Probability of all four bonding is $0.5 \times 0.5 \times 0.5 \times 0.5 = 0.0625$. Opposing bonding(b) share s. Opposing not bonding(nb) are half (0.5) s. In the pseudo-tetrahedral X_3CY geometry, adjacent bonds oppose to the extent of $1/3$ [$\cos(180^\circ - 109.47^\circ) = 0.3333$].

Table IV. Calculation of s bonding hybrid orbital coefficients f_{sb} for symmetries of the form X_2CY with X favored..

Bonding X Y		Probability	Fraction s for			f_{sb} f_{sb} Contribution for		
			All same	Favored (left of X)	Not Favored	All same	Favored	Not Favored
b,b	b	0.125	0.3333	0.5	0.0	0.04167	0.06250	0.00000
b,b	nb	0.125	0.5	0.75	0.0	0.06250	0.09375	0.00000
b,nb	b	0.125	0.5	0.75	0.0	0.06250	0.09375	0.00000
b,nb	nb	0.125	1.0	1.0	1.0	0.12500	0.12500	0.12500
nb, b		0.125	1.0	1.0	1.0	0.12500	0.12500	0.12500
b,nb	nb	0.125	0.75	0.75	0.75	0.09375	0.09375	0.09375
nb,b	nb	0.125	0.75	0.75	0.75	0.09375	0.09375	0.09375
nb,nb	nb	0.125	0.5	0.5	0.5	0.06250	0.06250	0.06250
Totals		1.000				0.66667	0.75000	0.50000

Bonding(b). Not bonding(nb). Probability of a single bond bonding is 0.5. Probability of all three bonding is $0.5 \cdot 0.5 \cdot 0.5 = 0.125$. Opposing bonding(b) share s. Opposing not bonding(nb) are half (0.5) s. In the pseudo-trigonal X_2CY geometry, adjacent bonds oppose to the extent of $1/2 [\cos(60^\circ) = 0.5]$.

B. Non-Coincident Bonding

Typically, primary and secondary bonds are coincident. Total overlap is found by summing primary and secondary overlaps while excluding the extent of coincidence. However, there are instances where the secondary bonds cannot be coincident. This occurs when the primary bond is partially dual.

Dual bonding occurs when there is more than one electron pair available for sigma bonding. Full dual bonding is observed in many di-atomics such as C_2 , N_2 and O_2 . Partial dual bonding occurs when a second electron pair is available to a partial extent. This occurs, for example, in the CC bond in H_2CCH_2 . C has the $2s^2 2p^2$ configuration. When bonding in the pseudo trigonal configuration, such as in H_2CCH_2 , one of the 2s does not have to be completely promoted to 2p to meet the orthogonality requirement. This leaves what can be described as a $2s^{1.125} 2p^{2.875}$ configuration. The 2s is not promoted to 2p to the extent that all three C bonds are not bonding ($0.5 \cdot 0.5 \cdot 0.5 = 0.125$). Each C 2s is available for CC dual bonding to the extent of 0.25 (when the CH bonds are bonding). Another example is the CC bond in $HCCH$. The 2s is not promoted to 2p to the extent that the two C bonds are bonding ($0.5 \cdot 0.5 = 0.25$). Here each C 2s is available for CC dual bonding to the extent of 0.5 (when the CH bond is bonding).

Consider the secondary bonding in the H_2CCH_2 example. The 2s orbital on the left-hand C cannot bond to the Hs on the right-hand C coincident with the bonding of right-hand C 2s to the Hs on the left. This is because the left-hand CH bonds are not necessarily bonding coincident with the bonding of the right-hand CH bonds. The left-to-right HC secondary bonds are only coincident with the right-to-left HC secondary bonds to the extent of 0.25. Both the left-to-right and right-to-left HC secondaries bond (and add to the total bond energy) but do not do so in a

coincident manner. The left-to-right and right-to-left HC secondaries cannot both contribute completely to the maximum overlap total. Only 0.25 of one side contributes to the total.

It should be noted that, when the primary bond is dual, there can be secondary bonding to each of the orbitals with sigma symmetry. In the H_2CCH_2 example, there can be a secondary bond between the H 1s and the C sp or a secondary bond between the H 1s and the C 2s. The secondary bond between the H 1s and the C 2s is to be favored since this secondary bond is not coincident with the primary to the extent of the secondary bond between the H 1s and the C sp (The C 2s to C 2s primary bond only occurs to the extent of 0.25). Less coincidence between the primary and secondary bonds implies a higher secondary bond energy.

Consideration of non-coincident bonding in the calculation of secondary interactions has a small, but significant, impact on the bond length results. For bonds that have a partial dual component, the assumption that all secondary bonds are coincident results in erroneously long calculated bond lengths.

C. Resonance

Both sigma and pi electrons can resonate. Resonance frequently takes the form $[\text{XY}, \text{X}^+\text{Y}^-]$ and sometimes $[\text{X}^-\text{Y}^+, \text{XY}, \text{X}^+\text{Y}^-]$. The relative population of uncharged and charged species need not be [0.5,0.5] or [0.25,0.5,0.25]. For resonances of the type $[\text{XY}, \text{X}^+\text{Y}^-]$ frequently the relative populations of neutral and anionic species are [0.75,0.25].

Adjacent bonds cannot both support resonance as this would result in the possibility of an energetically unfavorable doubly charged species. For example, in benzene, only two of the six bonds can host a pi resonance. Resonances which might result in the anionic and cationic species being separated by more than one bond also do not occur as these are also very energetically unfavorable.

A resonating electron has the kinetic energy of an electron in an orbital which overlaps totally (overlap = 1.0) with the opposite bonding orbital. This is particularly significant for pi resonance where overlap seldom approaches 1.0. Reduced kinetic energy, however, is not the only factor which makes resonance energetically favorable. The potential energy of the charged species, X^+Y^- , is also very important in determining the favorability of resonance. The potential energy associated with X^+Y^- depends on the electronic configuration of Y^- .

Atoms with non-bonding electrons typically have two configurations; a “bonding” configuration when all of the bonds to coordinated atoms are bonding and a “not-bonding” configuration when any of the bonds are not bonding. The latter configuration meets the orthogonality requirements (valence orthogonality). For example, N_2 has a bonding configuration of $2s^2 2p_z 2p_\pi^2$ (same as the atom) and a not-bonding configuration of $2sp_0 2s 2p_z 2p_\pi^2$, where sp_0 is the “opposing” hybrid orbital orthogonal to the bonding orbital on the opposite N. Since N_2 is bonding for 0.5 (fraction_bonding=0.5), the former configuration occurs to the extent of 0.5 and the latter to 0.5.

N in HCN has configurations the same as those of the N in N_2 . The CN in HCN has a pi resonance of the form $[\text{CN}, \text{C}^+\text{N}^-]$. The potential energy associated with the N bonding configuration acquiring an extra pi electron is more favorable than the not-bonding configuration acquiring an extra pi electron. Therefore, CN has a pi resonance when the CN sigma bond is bonding (i.e. for 0.5). The relative populations of CN and C^+N^- are [0.75,0.25]. The CO pi resonance in H_2CO is similar to the pi resonance in HCN.

The CF bonds in CF_4 and H_3CF exhibit sigma bond resonances. These occur when F is in the not bonding configuration.

III. RESULTS

The results are summarized in Table V. As in the previous work, the atomic orbitals of Duncanson and Coulson² have been utilized. The quantities Duncanson and Coulson call μ and μc (These are equivalent to the effective nuclear charge [or orbital scale factor] for 2s and 2p electrons.), are increased by factors (called fact herein) ranging from 1.01 to 1.055 consistent with previous work¹.

Table V. Orbital Exchange Calculation Results for Some Molecules Containing Carbon

Molecule	Observed/ Calculated	Configurations (1s ² omitted)	Resonance	Bonds
Ethane H ₃ CCH ₃	CC length 1.535/1.531 HC length 1.094/1.13 energy 29.18/28.98	C 2s2p _z 2p _⊥ ² C f _{s_{bc}} f _{s_{bc}} =0.641 C f _{s_{bH}} f _{s_{bH}} =0.453 fact _{2s,2p} =1.055 H:1s(polarized) H f _{s_b} f _{s_b} =0.983	no resonance	CC σ HC σ
Ethylene H ₂ CCH ₂	CC length 1.339/1.340 HC length 1.087/1.105 energy 23.35±0.16/ 23.54	C configurations: all bonds to C bonding 2s ² 2p _z 2p _⊥ any not bonding(0.875) C 2s2p _z 2p _⊥ 2p _π C f _{s_{bc}} f _{s_{bc}} =0.8125 C f _{s_{bH}} f _{s_{bH}} =0.5938 fact _{2s,2p} =1.050 H 1s(polarized) H f _{s_b} f _{s_b} =0.976	[C-C+,CC,C+C-] π _{resonance} fraction s⇒p on one side= 1.0-0.5·0.5·0.5= 0.875	CC σ , partial dual σ when both H on both sides are bonding 2 π _{resonance} when s⇒p on both sides. 1 π _{resonance} when s⇒p on just one side. HC σ H:1s polarized with 2p _z [2p fact=2.90,1s fact=1.09]
Acetylene HCCH	CC length 1.203/1.195 HC length 1.060/1.115 energy 17.01±0.14/ 17.20	C configurations: both bonds to C bonding 2s ² 2p _z 2p _π any not bonding(0.753) C 2s2p _z 2p _π ² C f _{s_{bc}} f _{s_{bc}} =0.875 C f _{s_{bH}} f _{s_{bH}} =0.625 fact _{2s,2p} =1.040 2 π bonding orbitals on C when any not bonding	[C-C+,CC,C+C-] π _{resonance} fraction s⇒p on one side=1.0-0.5·0.494= 0.753	CC σ , partial dual σ when H on both sides are bonding 2 π _{resonance} plus π when s⇒p on both sides . otherwise 1 π _{resonance} HC σ (bonding=0.494) HC bond does not reach bonding=0.5 H:1s polarized with 2p _z

Molecule	Observed/ Calculated	Configurations (1s ² omitted)	Resonance	Bonds
Benzene C ₆ H ₆	CC length 1.399/1.400 HC length 1.101/1.13 energy 57.25/57.61	C configurations: all σ bonding to C 2s ² 2p _z 2p _⊥ any not σ bonding(0.875) C 2s2p _z 2p _⊥ 2p _π C f _{sbc} f _{sbc} =0.7292 C f _{sbc} f _{sbc} reduced because favored orbitals are partially opposed C f _{sbH} f _{sbH} =0.5417 fact _{2s,2p} =1.050 H 1s(polarized) H f _{sb} f _{sb} =0.975	[C-C+,CC,C+C-][CC] ₂ 0.3333 π _{resonance}	CC σ, partial dual σ when both adjacent CC are bonding 2 π _{resonance} for 0.333 when s⇒p on both sides π _{resonance} for 0.333 when s⇒p on one side 2 π for 0.667 when s⇒p on both sides (reduced by common overlap) HC σ
Allene H ₂ CCCH ₂	CC length 1.308/1.312 HC length 1.087/1.10 energy 29.33/29.12	Central C: both bonding C 2s ² 2p _z 2p _π either not bonding (0.75) C 2s2p _z 2p _π ² C f _{sbc} f _{sbc} =0.75 End Cs: all bonding C 2s ² 2p _z 2p _⊥ any not bonding(0.875) C 2s2p _z 2p _⊥ 2p _π C f _{sbc} f _{sbc} =0.8125 C f _{sbH} f _{sbH} =0.5938 H 1s(polarized) H f _{sb} f _{sb} =0.976	No resonance	CC σ, partial dual σ when both H bonding and opposite CC bonding π for 0.75 0.875 (when s⇒p on both sides) 0.5 π for 0.25 0.875 when s⇒p on end C and s≠p on central C reduced by 0.5 π overlap
Hydrogen cyanide HCN	CN length 1.153/1.156 HC length 1.066/1.093 energy 13.25/12.98 Dipole moment (μ) (μ _{calc} =3.04 D μ _{expt} =2.985 D)	C configuration: both bonds to C bonding 2s ² 2p _z 2p _π any not bonding(0.757) C 2s2p _z 2p _π ² C f _{sbN} f _{sbN} =0.875 C f _{sbH} f _{sbH} =0.625 2 π bonding orbitals on C when any not bonding N configuration: CN bond bonding 2s ² 2p _z 2p _π ² not bonding(0.5) N 2sp _o 2s2p _z 2p _π ² N f _{sbc} f _{sbc} =0.591	[CN,C+N-] (0.75,0.25) π _{resonance} Resonance only when N configuration is 2s ² 2p _z 2p _π ² (s≠p on N) fraction s⇒p on C side=1.0-0.5·0.486= 0.757	CN σ, partial dual σ when H bonding on C HC σ (bonding=0.486) HC bond does not reach bonding=0.5 H:1s polarized with 2p when not resonating 2π when s⇒p on C, π when s≠p. when resonating π when s⇒p on C plus 0.5 π for 0.5 (when not C+)

Molecule	Observed/ Calculated	Configurations (1s ² omitted)	Resonance	Bonds
Formal- dehyde H ₂ CO	CO length 1.208/1.208 HC length 1.116/1.125 energy 15.59/15.76 (μ _{calc} =2.51 D μ _{expt} =2.332 D)	C configuration: both bonds to C bonding 2s ² 2p _z 2p _⊥ any not bonding(0.875) C 2s2p _z 2p _⊥ 2p _π C fs _{bo} fs _{bo} =0.8125 C fs _{bH} fs _{bH} =0.5938 π bonding orbital on C when any not bonding O configuration: CO bond bonding 2s ² 2p _z ² 2p _π ² not bonding(0.5) O 2sp _o 2s2p _z 2p _⊥ 2p _π ² O fs _{bc} fs _{bc} =0.600	[CO,C+O-] (0.7812,0.2188) (0.2188=0.875 0.25) π _{resonance} Resonance only when O configuration is 2s ² 2p _z ² 2p _π ² (s≠p on O) and s⇒p on C fraction s⇒p on C side=1.0-0.5 0.5 0.5=0.875	CO σ , partial dual σ when both H bonding on C π _{resonance} for 0.4375 π when s⇒p on C and not resonating (0.875-0.4375) plus, when resonating 0.5 π for 0.5 (when not C+)
Floro- methane CH ₃ F	CF length 1.382/1.377 HC length 1.095/1.100 energy 17.44/17.58 (μ _{calc} =1.73 D μ _{expt} =1.858 D)	C 2s2p _z 2p _⊥ ² C fs _{bF} fs _{bF} =0.5 C fs _{bH} fs _{bH} =0.5 H:1s(polarized) H fs _b fs _b =0.986 F configuration: CF bond bonding 2s ² 2p _z ² 2p _⊥ ³ not bonding(0.5) F 2sp _o 2s2p _z 2p _⊥ ⁴ F fs _{bc} fs _{bc} =0.591	[CH ₃ F,C+H ₃ F-] (0.75,0.25) σ _{resonance} for 0.5 fract _{ion} =0.25 Resonance only when F configuration is 2sp _o 2s2p _z 2p _⊥ ⁴ (s⇒p on F) s⇒p on F = 0.5	CF σ Overlap calculation: 0.5 fract _{ion} parallel bond when C+F-. serial overlap reduced by (1.0-0.5*fract _{ion}). Kinetic energy: 0.5 resonance 2 - 0.5 non-resonance
Tetrafloro- methane CF ₄ (T _d)	CF length 1.323/1.318 energy 5.089/5.06 (single CF bond)	C 2s2p _z 2p _⊥ ² C fs _{bF} fs _{bF} =0.5 F configuration: CF bond bonding 2s ² 2p _z ² 2p _⊥ ³ not bonding(0.5) F 2sp _o 2s2p _z 2p _⊥ ⁴ F fs _{bc} fs _{bc} =0.589	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> F F F- F [F-C+F,FC+F-,FC+F,FC+F] F F F F </div> <div style="text-align: center;"> fract_{ion} F- =0.25 Resonance only when F configuration is 2sp_o2s2p_z2p_⊥⁴ (s⇒p on F) s⇒p on F = 0.5 </div> </div>	CF σ Overlap calculation: 0.5 fract _{ion} parallel bond when C+F-. serial overlap reduced by (1.0-0.5*fract _{ion}). Kinetic energy: 2 0.5 resonance 2 - 0.75 non-resonance

Molecule	Observed/ Calculated	Configurations (1s ² omitted)	Resonance	Bonds
Floro- methyl- idyne (CF)	CF length 1.272/1.269 energy 5.33±0.11/5.40 ($\mu_{\text{calc}}=0.63$ D $\mu_{\text{expt}}=0.645$ D)	C configuration: bonding $2s^2 2p_z 2p_\pi$ not bonding(0.5) $2s p_o 2s 2p_z 2p_\pi$ C $f_{s_{bF}} f_{s_{bF}}=0.382$ F configuration: bond bonding $2s^2 2p_z^2 2p_\pi^3$ not bonding(0.5) $2s p_o 2s 2p_z 2p_\pi^4$ F $f_{s_{bC}} f_{s_{bC}}=0.636$	[CF,C+F-] (0.75,0.25) $\sigma_{\text{resonance}}$ for 0.5 fract_ion F- =0.25 Resonance only when F configuration is $2s p_o 2s 2p_z 2p_\pi^4$	σ overlap calculation: CF σ dual C+F- σ dual on C+ side single on F- side 0.5 fract_ion parallel bond Kinetic energy: 0.5 resonance 2 non-resonance π bond π orthogonalization when $s \Rightarrow p$ and when F-

Bond lengths are in Å. Energy is in eV. Except for CF₄, energy here is the total of the bond energies. This energy is calculated from data in the CRC Handbook³. Bond lengths are from the CRC Handbook⁴. Dipole moments are from the CRC Handbook⁵. $s \Rightarrow p$ indicates a 2s promoted to 2p. Fraction $s \Rightarrow p$ is typically $1.0-0.5*0.5 = 0.75$ for 2 coordinate atoms, $1.0-0.5*0.5*0.5=0.875$ for 3 coordinate atoms. Terms used in bond counting: a single σ or π bond entails the left electron bonding to the right as well as the right electron bonding to the left (so a 0.5 bond entails only the electron on one side bonding) , a single σ or π resonance entails only a single electron.

A. Ethane (H₃CCH₃)

The stability of ethane is maximized by making the CC bond as short as possible consistent with the possible hybrid orbital coefficients. Shorter bonds are associated with hybrid orbitals with larger s orbital coefficients. The s orbital coefficient for the CC bond in ethane is set to 0.641 consistent with the analysis summarized in Table III. This results in a calculated CC bond length of 1.531Å, in good agreement with the observed bond length of 1.535Å.

The bond lengths for the HC bonds are calculated to be 1.13Å vs. the observed value of 1.094Å. The calculated HC bond lengths for the molecules studied here are typically about 0.03Å higher than the observed values.

It is generally difficult to determine the core orthogonalization parameters for “soft” atoms such as H. This issue is discussed in Section IIIA of reference 1. The estimated uncertainty associated with the core orthogonalization of H is about 0.01 to 0.02Å. Difficulties associated with core orthogonalization do not account for the observed difference between the calculated and observed values for the HC bond length. Difficulties associated with core orthogonalization lead to uncertainties in the energy of the HC bond of about 0.05 to 0.08 eV (1 to 2%).

In bonding, H is polarized towards C by adding electron density of the form of a 2p orbital with an effective nuclear charge of 2.90 to the H 1s orbital. Typically, the best bond energy is found when the polarized H orbital has about 2% of the added 2p form. This is a relatively crude method of polarization. The radius of the 1s is varied to obtain the maximum bond energy. Polarization has a significant impact on the bond length. Arbitrarily reducing the added 2p function by half reduces the bond length by about 0.02Å and the energy by about 0.14 eV.

The calculated total of the bond energies in ethane is 28.98 eV. This is to be compared to the observed value of 29.18 eV. In this calculation, as well as other calculations discussed in this paper, the energy to promote a 2s to a 2p is the energy given in Table IV in reference 1.

B. Ethylene (H₂CCH₂)

The s orbital coefficient for the CC bond in ethylene is set to 0.8125 consistent with the analysis summarized in Table II. The CC bond in ethylene is dual to the extent that the two HC bonds on each C are both bonding ($0.5 \cdot 0.5 \cdot 0.5 \cdot 0.5 = 0.0625$). The calculated CC bond length is 1.340Å, in good agreement with the observed bond length of 1.339Å. The calculated total of the bond energies in ethylene is 23.54 eV. This is to be compared to the observed value of 23.35 eV. Detailed breakdowns of the CC and HC bond calculations in ethylene are shown in Tables VI and VII, respectively.

Each carbon in ethylene has a p_π electron to the extent that any of its three sigma bonds is not-bonding ($1.0 - 0.5 \cdot 0.5 \cdot 0.5 = 0.875$). These p_π electrons resonate. Although the kinetic energy of a resonating p_π electron is more favorable than that of a simple pi bond, resonance is driven primarily by the lower potential energy associated with the C⁻ C⁺ charge separation (electron-electron repulsions are less). That the lower potential energy associated with charge separation is the primary driver of resonance appears to be general.

Table VI. Components of the C=C bond in H₂CCH₂ Calculation at 1.3414 Å (Energy in electron volts)

The configuration of C is 1s²2s²2p². H₂C=C has a pseudo trigonal planar structure. The configuration of C in H₂CCH₂ is 1s²2s^{0.125}2p_z2p_{xy}^{1.875}. Terminology is as in reference 1. Orbital scale factor for C is 1.05. In the limit of complete bonding, fraction s to p is typically 1.0-0.5 0.5=0.75 for 2 coordination, 1.0-0.5 0.5 0.5=0.875 for 3 coordination.

Component	Value	Overlap change	Energy (eV) change
<i>Primary C = C Bond</i>			
overlap _{s-s}	0.4076		
overlap _{s-p} = overlap _{p-s}	0.5019		
overlap _{p-p}	0.5766		
sigma overlap of primary sp hybrid orbitals with s up (overlap _{sp/sp})			
$\text{overlap}_{\text{sp/sp}} = f_{\text{s}_b} f_{\text{s}_b} \text{overlap}_{\text{s-s}} + f_{\text{s}_b} f_{\text{p}_b} \text{overlap}_{\text{s-p}+}$ $f_{\text{p}_b} f_{\text{s}_b} \text{overlap}_{\text{p-s}+} + f_{\text{p}_b} f_{\text{p}_b} \text{overlap}_{\text{p-p}}$ $f_{\text{s}_b} = \text{sqrt}(0.8125), f_{\text{p}_b} = \text{sqrt}(1.0 - 0.8125)$			
fraction_bonding when single sp/sp bond (s up)	0.4539		
fraction_bonding _{sp/sp} = overlap _{sp/sp} / (1 + overlap _{sp/sp})			

*Calculation of Bonding when two σ bonding electrons
(s down dual bond)*

$$\text{overlap}_{\text{sp/s}} = \text{overlap}_{\text{s/sp}} = f_{\text{s}_b} \text{overlap}_{\text{s-s}} + f_{\text{p}_b} \text{overlap}_{\text{s-p}}$$

$$\text{and } \text{overlap}_{\text{s/s}} = \text{overlap}_{\text{s-s}}$$

$$\text{average bonding of each of two pairs } \text{fraction_bonding}_{\text{ave}} = 0.25 \quad 0.3703$$

$$(\text{fraction_bonding}_{\text{sp/sp}} + 2.0 \text{fraction_bonding}_{\text{sp/s}} + \text{fraction_bonding}_{\text{s/s}})$$

$$\text{sum of overlaps of both bonding pairs} = 2.0 (\text{fraction_bonding}_{\text{ave}} / (1.0 - \text{fraction_bonding}_{\text{ave}}))$$

$$\text{simultaneous overlap of sp/sp and s/s} = \text{fraction_bonding}_{\text{sp/sp}}$$

$$\text{fraction_bonding}_{\text{s/s}} / (1.0 - \text{fraction_bonding}_{\text{sp/sp}})$$

$$\text{fraction_bonding}_{\text{s/s}}$$

$$\text{simultaneous overlap of sp/s and s/sp} = \text{fraction_bonding}_{\text{sp/s}}$$

$$\text{fraction_bonding}_{\text{s/sp}} / (1.0 - \text{fraction_bonding}_{\text{sp/s}})$$

$$\text{fraction_bonding}_{\text{s/sp}}$$

$$\text{overlap of two pair exclusive of coincident bonding} = \quad 0.8674$$

$$\text{sum of overlap of both pairs} - \text{overlap of sp/sp and s/s} -$$

$$\text{overlap of sp/s and s/sp}$$

$$\text{dual fraction_bonding } (\text{fraction_bonding}_{\text{dual}}) \quad (\text{s down dual}) \quad 0.4645$$

$$\text{factor} = \text{fraction_bonding}_{\text{dual}} / \text{fraction_bonding}_{\text{ave}} \quad 1.2542$$

$$\text{primary fraction_bonding } (\text{fraction_bonding}_{1\text{st}}) \quad 0.4545$$

$$\text{fraction_bonding}_{1\text{st}} = (1.0 - 0.25) 0.25 \text{fraction_bonding}_{\text{sp/sp}} +$$

$$(0.25) 0.25 \text{fraction_bonding}_{\text{dual}}$$

$$\text{primary overlap } (\text{overlap}_{1\text{st}}) \quad 0.8333 \quad 0.8333$$

$$\text{overlap}_{1\text{st}} = \text{fraction_bonding}_{1\text{st}} / (1.0 - \text{fraction_bonding}_{1\text{st}})$$

Calculation of Sigma Bonding Kinetic Energy Contributions

$$\text{kinetic energy of hybrid orbital sp-sp bond } (2 \text{KE}_{\text{sp/sp}}) \text{ with s up} \quad 6.8654$$

$$\text{KE}_{\text{sp/sp}} = (1 / (1 + \text{overlap}_{\text{sp/sp}})) (f_{\text{s}_b} f_{\text{s}_b} \text{overlap}_{\text{s-s}} \text{KE}_{\text{net s-s}} +$$

$$f_{\text{s}_b} f_{\text{p}_b} \text{overlap}_{\text{s-pz}} \text{KE}_{\text{net s-pz}} + f_{\text{p}_b} f_{\text{s}_b} \text{overlap}_{\text{pz-s}} \text{KE}_{\text{net pz-s}} +$$

$$f_{\text{p}_b} f_{\text{p}_b} \text{overlap}_{\text{pz-pz}} \text{KE}_{\text{net pz-pz}})$$

$$\text{kinetic energy of hybrid orbital s-sp bond } (2 \text{KE}_{\text{s/sp}}) \quad 5.0857$$

$$\text{KE}_{\text{s/sp}} = (1 / (1 + \text{overlap}_{\text{s/sp}})) (f_{\text{s}_{br}} \text{overlap}_{\text{s-s}} \text{KE}_{\text{net s-s}} +$$

$$f_{\text{p}_{br}} \text{overlap}_{\text{s-pz}} \text{KE}_{\text{net s-pz}})$$

$$\text{KE}_{\text{sp/s}} = \text{KE}_{\text{s/sp}}$$

$$\text{kinetic energy of s-s bond } (2 \text{KE}_{\text{s/s}}) \quad 3.6605$$

$$\text{KE}_{\text{s/s}} = (1 / (1 + \text{overlap}_{\text{s/s}})) \text{overlap}_{\text{s-s}} \text{KE}_{\text{net s-s}}$$

$$\text{kinetic energy of dual bond } (2 \text{KE}_{\text{dual}})$$

$$\text{KE}_{\text{dual}} = \text{factor} (0.25 \text{KE}_{\text{s/s}} + 0.25 \text{KE}_{\text{s/sp}} + 0.25 \text{KE}_{\text{sp/s}} + 0.25 \text{KE}_{\text{sp/ps}})$$

$$(\text{factor defined above})$$

$$\text{primary kinetic energy } (2 \text{KE}_{1\text{st}}) \quad 6.8392 \quad 6.8392$$

$$\text{KE}_{1\text{st}} = (1.0 - 0.25) 0.25 \text{KE}_{\text{sp/sp}} + (0.25) 0.25 \text{KE}_{\text{dual}}$$

Orthogonalization Energies

$$\text{energy to make C sp orbital orthogonal to opposite C } 1s^2 \quad -7.2312$$

$$(\text{KE}_{\phi} - \text{KE}_{\phi}) \text{ where } \phi \text{ is C sp made orthogonal, } \phi \text{ is C sp}$$

energy to make C sp orbital orthogonal to opposite 1s ² when not bonding	-3.6156	-3.6156
$KE_{core_ortho} = (KE_{\phi} - KE_{\phi}) (1 - 0.5)$		
energy to make C 2s orbital orthogonal to opposite C 1s ²	-4.4257	
$(KE_{\phi} - KE_{\phi})$ where ϕ is C 2s made orthogonal, ϕ is C 2s		
energy to make C 2s orbital orthogonal to opposite 1s ² when not bonding	-0.5132	-0.5132
$KE_{core_ortho} = (KE_{\phi} - KE_{\phi}) (1 - 0.5 \text{ } 0.5 \text{ fraction_bonding}_{s/s}) \text{ } 0.5 \text{ } 0.5 \text{ } 0.5$		
<i>Calculation of Pi Bonding Kinetic Energy Contributions</i>		
$KE_{net \text{ } p\pi - p\pi}$	3.8520	
energy of resonating π electron $0.5 KE_{net \text{ } p\pi - p\pi}$	1.9260	
total π resonance energy = resonance when both C have s up (to $p\pi$) + resonance when one C has s up and the other has s down = $2.0 (1.0 - 0.5 \text{ } 0.5 \text{ } 0.5) (1.0 - 0.5 \text{ } 0.5 \text{ } 0.5) \text{ } 0.5 KE_{net \text{ } p\pi - p\pi} +$ $2.0 (1.0 - 0.5 \text{ } 0.5 \text{ } 0.5) (0.5 \text{ } 0.5 \text{ } 0.5) \text{ } 0.5 KE_{net \text{ } p\pi - p\pi}$	3.3706	3.3706
<i>Potential Energy Terms</i>		
C nuclear- C nuclear repulsion energy	-386.4341	-386.4341
C nuclear to opposite C 1s orbitals energy (4 of these)	64.4058	257.6231
C nuclear to opposite 2s orbital energy $2.0 (1.0 + 0.5 \text{ } 0.5 \text{ } 0.5)$ of these	71.7966	143.5932
C nuclear to opposite 2p _z orbital energy (2 of these)	73.1481	146.2962
C nuclear to opposite 2p _{xy} orbital energy [$2.0 (2.0 - 0.5 \text{ } 0.5 \text{ } 0.5)$ of these]	58.8807	220.8026
C electron-C electron repulsions energy	-369.9797	-369.9797
C electron affinity when s is down (0.5^3)	1.262	
when s is up (estimated)	0.0	
net affinity	0.0776	0.0776
resonance except when both 2s are down ($1.0 - 0.5^6$)		
C- for half of resonance		
C ionization potential	-11.2601	
C+ when both s are down and for half of resonance		-5.5421
energy to raise C 2s to 2p	-7.50	
when in resonance, 2s is promoted to 2p on each C when s is up $(1.0 - 0.5^3)$ on both Cs [$2.0 (1.0 - 0.5^3) (1.0 - 0.5^3)$] and when one C has s up and the other down [$2.0 \text{ } 0.5^3 (1.0 - 0.5^3)$]		
net energy to raise C 2s to 2p after allocating 1.0 C 2s to 2p to HC bonds (allocation is arbitrary)	-5.625	-5.625

energy to compress C orbitals (orbital scale factor = 1.05)	-0.66	-0.66
Total primary energy		6.30
<i>Secondary H – C Bond</i> <i>Assumes primary HC bond length is 1.10Å</i> <i>Angle between the primary CC bond and the HC bond is 26.17°</i> <i>cos 26.17° = 0.8975</i> <i>Secondary bond length is 2.1313Å</i>		
secondary H 1s – C 2s overlap component along primary axis	0.1279	
overlap _{s/s_2nd} = 0.8975 0.8975 overlap _{s-s}		
secondary H 1s – C sp overlap component along primary axis	0.1830	
overlap _{s/sp_2nd} = 0.8165 0.8165 (fs _b overlap _{s-s} + 0.8165 fp _b overlap _{s-p})		
secondary 1s to 2s fraction_bonding (fraction_bonding _{s/s_2nd})	0.1134	
fraction_bonding _{s/s_2nd} = overlap _{s/s_2nd} / (1 + overlap _{s/s_2nd})		
secondary 1s to sp fraction_bonding (fraction_bonding _{s/sp_2nd})	0.1547	
fraction_bonding _{s/sp_2nd} = overlap _{s/sp_2nd} / (1 + overlap _{s/sp_2nd})		
<i>Secondary fraction_bonding is reduced by previous, coincident</i> <i>1st order bonding and previous coincident 2nd order bonding.</i>		
s-sp fraction_bonding increment (fraction_bonding _{s/sp_2nd_inc})		
fraction_bonding _{s/sp_2nd_inc} =		
0.5 0.75 (1- fraction_bonding _{1st+prev2nd}) fraction_bonding _{s/sp_2nd}		
0.75 because s is up for 0.25		
0.5 because increment is for component in one direction		
fraction_bonding _{1st+prev2nd} adds previous secondary overlap		
increments to fraction_bonding _{1st}		
s-sp overlap increment (overlap _{s/sp_2nd_inc})		
overlap _{s/sp_2nd_inc} = fraction_bonding _{s/sp_2nd_inc} /		
(1.0- fraction_bonding _{s/sp_2nd_inc})		
s-s fraction_bonding increment (fraction_bonding _{s/s_2nd_inc})		
fraction_bonding _{s/s_2nd_inc} =		
0.5 0.25 (1- 0.25 fraction_bonding _{s/s_1st}) fraction_bonding _{s/s_2nd}		
0.25 because s down for 0.25		
s-s overlap increment (overlap _{s/s_2nd_inc})		
overlap _{s/s_2nd_inc} = (0.5+0.5 0.25) fraction_bonding _{s/s_2nd_inc} /		
(1.0- fraction_bonding _{s/s_2nd_inc})		
for rationale for (0.5+0.5 0.25) see discussion of asynchronous bonding.		
Sum of secondary overlap increments over all four H C secondary bonds	0.1657	0.1657
kinetic energy of secondary s-sp bond (2 KE _{s/sp}) with s up		
KE _{s/sp} = 0.75 (1.0- fraction_bonding _{1st+2nd}) (1 / (1+ overlap _{total}))		
(fs _b overlap _{s-s} KE _{net s-s} + 0.8165 fp _b overlap _{s-p} KE _{net s-p})		
kinetic energy of H – C secondary bond (KE _{bond_2nd})	0.4841	0.4841
potential energy terms are included in H C primary bond calculation		

Totals	0.9994	6.78
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Table VII. Components of the Primary HC bond in H₂CCH₂ Calculation at 1.1060 Å
(Energy in electron volts)

Terminology as in reference 1. Orbital scale factor for H is 1.09 and 1.05 for C.

Component	Value	Overlap change	Energy (eV) change
<i>Primary H – C Bond</i>			
H 1s bonding orbital is polarized as indicated in Table ? above.			
overlap _{s-s}	0.6038		
overlap _{s-p}	0.6815		
sigma overlap of primary orbitals (overlap _{1st}) overlap _{1st} = fs _b overlap _{s-s} + fp _b overlap _{-p} fs _b fs _b = 0.59375 fp _b fp _b = 1.0-0.59375	0.8996	0.8996	
fraction_bonding (fraction_bonding _{1st}) fraction_bonding _{1st} = overlap _{1st} / (1 + overlap _{1st})	0.4736		
kinetic energy of sigma orbital pair (2 KE _{bond}) KE _{bond} = (1 / (1 + overlap _{1st})) (fs _{br} overlap _{s-s} KE _{net s-s} + fp _{br} overlap _{s-p} KE _{net s-pz})	6.8019		6.8019
energy to make H 1s orthogonal to opposite C 1s ² (KE _φ - KE _φ) where φ is H 1s made orthogonal, φ is H 1s	-10.2454		
energy to make H 1s orthogonal to opposite 1s ² when not bonding KE _{core_ortho} = (KE _φ - KE _φ) (1 - 0.5)	-5.1227		-5.1227
nuclear-nuclear repulsion energy	-78.1189		-78.1189
C nuclear to H 1s energy	83.8000		83.8000
H nuclear to opposite two C 1s orbitals energy	26.0397		26.0397
H nuclear to opposite 2s orbital energy	14.2464		14.2464
H nuclear to opposite 2p _z orbital energy	14.9261		14.9261
H nuclear to opposite two 2p _{xy} orbital energy	21.4100		21.4100
H electron-C electron repulsions energy	-77.7397		-77.7397
energy to compress/polarize H	-0.641		-0.641
energy to raise C 2s to 2p 0.25 of s to p energy (allocation to bonds arbitrary, see Table?)	-1.87		-1.87

Total primary energy	3.73	
<i>Secondary H – H Bond</i>		
<i>cos ∠ between the HH bond and the primary HC bond=0.854</i>		
<i>Secondary bond length is 1.890Å</i>		
secondary H 1s – H 1s overlap (secondary overlap _{s-s})	0.2762	
secondary H – H sigma overlap along primary axis (overlap 2 _{nd})	0.2014	
overlap _{2nd} = 0.854 0.854 overlap _{s-s}		
secondary fraction_bonding (fraction_bonding _{2nd})	0.1676	
fraction_bonding 2 _{nd} = overlap _{2nd} /(1+overlap _{2nd})		
secondary fraction_bonding increment (fraction_bonding _{2nd_inc})	0.0441	
fraction_bonding _{2nd_inc} = 0.5 (1- fraction_bonding _{1st})		
fraction_bonding _{2nd} .		
secondary fraction_bonding is		
reduced by previous, coincident 1 st order bonding.		
0.5 because secondary spans 2 primary.		
secondary overlap increment	0.0462	0.0462
secondary overlap =		
fraction_bonding _{2nd_inc} /(1- fraction_bonding 2 _{nd_inc})		
kinetic energy of H – H bond (KE _{bond_2nd})	0.3061	
KE _{bond_2nd} = (secondary overlap _{s-s} /(1.0+overlap _{total})) KE _{net s-s}		
overlap _{total} = overlap _{1st} +overlap _{2nd}		
[not (2.0 KE _{bond_2nd}) as this energy is shared with the other HC bond]		
secondary kinetic energy increment (KE _{bond_2nd_inc})	0.1740	0.1740
KE _{bond_2nd_inc} = (1- fraction_bonding _{1st}) KE _{bond_2nd}		
Secondary KE _{bond_2nd} is reduced by previous, coincident		
1 st order bonding.		
H nuclear-H nuclear repulsion energy	-7.6193	
H nuclear to opposite H 1s (2 single nuclear to opposite)	16.1965	
total H 1s to H 1s electron - electron repulsion	-8.4946	
total potential energy terms	0.0826	
net potential energy	0.0413	0.0413
0.5 total because energy is shared with adjacent HC bond		
total secondary energy		0.2153
<i>Secondary H – C Bond</i>		
<i>cos ∠ between the C=C bond and this HC bond=0.844</i>		
<i>cos ∠ between the primary HC bond and this HC bond=0.897</i>		
<i>Secondary bond length is 2.134Å</i>		
sigma overlap along primary axis (overlap _{2nd})	0.1612	
overlap _{2nd} = 0.844 0.844 (f _{s_b} overlap _{s-s} + 0.897 f _{p_b} overlap _{s-p})		
f _{s_b} f _{s_b} = 0.8125 f _{p_b} f _{p_b} = 1.0-0.8125		

secondary fraction_bonding (fraction_bonding _{2nd})	0.1388	
fraction_bonding _{2nd} = overlap _{2nd} / (1 + overlap _{2nd})		
secondary fraction_bonding increment (fraction_bonding _{2nd_inc})	0.0357	
fraction_bonding _{2nd_inc} = 0.5 (1 - fraction_bonding _{1st,HH2nd})		
fraction_bonding _{2nd}		
secondary fraction_bonding is		
reduced by previous, coincident 1 st and HH 2 nd order bonding.		
0.5 because secondary spans 2 primary		
secondary overlap increment	0.0370	0.0370
secondary overlap =		
fraction_bonding _{2nd_inc} / (1 - fraction_bonding _{2nd_inc})		
kinetic energy of secondary bond (KE _{bond})	0.2167	
KE _{bond} = (1 / (1 + overlap _{total})) (f _{Sbr} overlap _{s-s} KE _{net s-s} +		
f _{pbr} overlap _{s-p} KE _{net s-pz})		
overlap _{total} = overlap _{1st} + overlap _{HH2nd} +		
0.844 0.844 (f _{Sb} overlap _{s-s} + 0.897 f _p overlap _{s-p})		
secondary kinetic energy increment (KE _{bond})	0.1114	0.1114
KE _{bond_2nd} = (1 - fraction_bonding _{1st,HH2nd}) KE _{bond}		
secondary KE _{bond} is reduced by previous, coincident bonding.		
energy to make H 1s orthogonal to opposite 1s ² when not bonding	-0.0565	-0.0565
KE _{core_ortho} = (KE _φ - KE _ψ) (1 - 0.5)		
net potential energy terms	0.1622	0.1622
<i>Tertiary H – H Bond (adjacent, straight across)</i>		
<i>cos ∠ between the HH bond and the primary HC bond = 0.52</i>		
<i>Tertiary bond length is 2.489Å</i>		
tertiary H 1s – H 1s overlap (secondary overlap _{s-s})	0.0984	
tertiary H – H overlap along primary axis (overlap _{3rd})	0.0266	
overlap _{3rd} = 0.52 0.52 overlap _{s-s}		
tertiary fraction_bonding (fraction_bonding _{3rd})	0.0259	
fraction_bonding _{3rd} = overlap _{3rd} / (1 + overlap _{3rd})		
tertiary fraction_bonding increment (fraction_bonding _{3rd_inc})	0.0066	
fraction_bonding _{3rd_inc} = 0.5 (1 - fraction_bonding _{previous})		
fraction_bonding _{3rd}		
tertiary overlap increment	0.0066	0.0066
tertiary kinetic energy increment (KE _{bond_3rd})	0.0199	0.0199
KE _{bond_3rd} = (1 - fraction_bonding _{previous}) (1 / (1 + overlap _{total}))		
(overlap _{s-s} KE _{net s-s})		
net of potential energy terms	0.0043	0.0043
<i>Tertiary H – H Bond (opposite)</i>		
<i>cos ∠ between the HH bond and the primary HC bond = 0.930</i>		
<i>cos ∠ between the HH bond and the CC bond = 0.797</i>		
<i>Tertiary bond length is 3.125Å</i>		

tertiary H 1s – H 1s overlap (secondary overlap _{s-s})	0.0483	
tertiary H – H overlap along primary axis (overlap _{3rd})	0.0418	
overlap _{3rd} = 0.93 0.93 overlap _{s-s}		
tertiary fraction_bonding (fraction_bonding _{3rd})	0.0401	
fraction_bonding _{3rd} = overlap _{3rd} / (1 + overlap _{3rd})		
tertiary fraction_bonding increment (fraction_bonding _{3rd_inc})	0.0101	
fraction_bonding _{3rd_inc} = 0.5 (1 - fraction_bonding _{previous})		
fraction_bonding _{3rd}		
tertiary overlap increment	0.0102	0.0102
tertiary kinetic energy increment (KE _{bond_3rd})	0.0045	0.0045
KE _{bond_3rd} = (1 - fraction_bonding _{previous}) (1 / (1 + overlap _{total}))		
(overlap _{s-s} KE _{net s-s})		
net of potential energy terms		
Totals	0.9996	4.19

C. Acetylene (HCCH)

The s hybrid orbital coefficient for the CC bond in acetylene is set to 0.875 consistent with the analysis summarized in Table I. The CC bond in acetylene is dual to the extent that the HC bonds on each C are both bonding. The calculated CC bond length is 1.195Å, in good agreement with the observed bond length of 1.203Å. The calculated total of the bond energies in ethylene is 17.20 eV. This is to be compared to the observed value of 17.01 eV.

When either of the two C sigma bonds is not bonding the C configuration is 2s2p_z2p_π². When both Cs have this configuration there are two pi resonances and a pi bond. When either or both Cs have the 2s²2p_z2p_π configuration there is a single pi resonance. (See note on Table V concerning the counting of bonds.)

D. Benzene (C₆H₆)

The s orbital coefficient for the CC bond in benzene is set to 0.729. Were there no geometric constraints, the s hybrid orbital coefficient would be 0.75 as described in Table IV. In benzene, however, the two favored C bonding orbitals have a geometric component which faces the other. Favored hybrid orbitals acquire s character by taking it from an opposite hybrid orbital. The common component of favoritism between facing orbitals must be omitted. The two favored orbitals face each other (depart from the normal) by 30 degrees (120-90 = 30). The normal component is 60 degrees. The asymmetry is limited by 0.25 since cos30 cos30=0.25. 0.6667+ 0.75 (0.75-0.6667) = 0.72917. (0.6667 would be the s hybrid orbital coefficient were no C bond preferred.)

The CC bond in benzene is dual to the extent that the two adjacent CC are both bonding (adjusted for the extent that the s s bonds are simultaneous with the s s bonds of the adjacent

bonds). The calculated CC bond length in benzene is 1.400Å, in good agreement with the observed bond length of 1.399Å.

Pi resonance in benzene is limited to 1/3 because adjacent bonds cannot resonate. Adjacent resonance raises the possibility of a doubly charged species that is very energetically unfavorable. Non-resonance pi bonds form for 2/3. Both pi resonance and non-resonance pi bonds require that C have the $2s2p_z2p_{\perp}2p_{\pi}$ configuration (any sigma bond not-bonding). For a non-resonance pi bond both sides must have this configuration. Non-resonance pi bonds are reduced to account for simultaneous pi bonding from both sides of the C. The calculated total of the bond energies in benzene is 57.61 eV. This is to be compared to the observed value of 57.25 eV.

E. Allene (H_2CCCH_2)

The s hybrid orbital coefficient for the end Cs in the CC bonds in allene is set to 0.8125 consistent with the analysis summarized in Table II (same as in ethylene). The s hybrid orbital coefficient for the central C in the CC bonds in allene is set to 0.75 consistent with the analysis summarized in Table I. The CC bond in allene is dual to the extent that the two adjacent HC are both bonding and the adjacent CC bond is also bonding. The calculated CC bond length in allene is 1.312Å, in good agreement with the observed bond length of 1.308Å.

Each CC bond in allene has a pi bond to the extent that both Cs have the $2s2p_z2p^2$ configuration. The central C has this configuration when either CC sigma bond is not bonding. The end C has this configuration when either of the HC bonds or the CC bond is not bonding. There is a half pi bond when the end C has the $2s2p_z2p^2$ configuration and the central C has the $2s^22p_z2p$ configuration. (Half here because there is only a single p orbital in the central C's x-y plane.) The half pi bond is reduced to account for simultaneous pi bonding from both sides of the central C. The calculated total of the bond energies in allene is 29.12 eV. This is to be compared to the observed value of 29.33 eV.

F. Hydrogen Cyanide (HCN)

The C s hybrid orbital coefficient for the CN bond in hydrogen cyanide is set to 0.875 consistent with the analysis summarized in Table I (the same as the C in acetylene). The N s hybrid orbital coefficient is set to meet the valence orthogonality requirements (0.59). The CN bond in hydrogen cyanide is dual to the extent that the HC bond is bonding (similar to acetylene). The calculated CN bond length in hydrogen cyanide is 1.156Å, in good agreement with the observed bond length of 1.153Å.

CN has a pi resonance of the form $[CN,C+N^-]$. Since the potential energy associated with the N^- configuration $2s^22p_z2p_{\pi}^3$ in $C+N^-$ is more favorable than the potential energy associated with the N^- configuration $2sp_o2s2p_z2p_{\pi}^3$ ($2sp_o$ is the opposing orbital which forms to the extent that the CN sigma bond is not bonding.), the pi resonance only occurs to the extent that the CN sigma bond is bonding (0.5) and N^- has the favorable configuration. The relative populations of the two species $[CN,C+N^-]$ are [0.75,0.25]. To the extent that the CN bond is resonating there is a second half pi bond (only one side bonds) bond for 0.5 (when not $C+N^-$). There is an additional (non-resonating) pi bond when the C configuration is $C 2s2p_z2p_{\pi}^2$. To the extent that the CN bond is not resonating (0.5), there is a pi bond plus a second when the C configuration is $2s2p_z2p_{\pi}^2$.

The energy of the resonance species $[C+N^-]$ is taken as the sum of the first ionization potential of C plus the electron affinity of N. The electron affinity of N is taken as -0.15 eV.

The calculated total of the bond energies in hydrogen cyanide is 12.98 eV. This is to be compared to the observed value of 13.25 eV.

If one assumes that the CN π resonance is unconstrained by the N^- configuration, and the relative populations of the two species $[CN, C+N^-]$ are [0.5,0.5], the resulting molecular energy would be reduced by about 0.55 eV.

The calculated dipole moment is 3.04 D. This is to be compared to the observed value of 2.985 D. The dipole moment is the sum of the HC bond dipole and the CN bond dipole. The HC bond has an associated dipole moment because the H is polarized in the bond.

G. Formaldehyde (H_2CO)

The C s hybrid orbital coefficient for the CO bond in formaldehyde is set to 0.8125 consistent with the analysis summarized in Table II (the same as the C in ethylene). The O s hybrid orbital coefficient is set to meet the valence orthogonality requirements (0.60). The CO bond in formaldehyde is dual to the extent that both HC bonds are bonding (similar to ethylene). The calculated CO bond length in formaldehyde is 1.208 Å, in good agreement with the observed bond length of 1.208 Å.

CO has a π resonance of the form $[CO, C+O^-]$. Since the potential energy associated with the O^- configuration $2s^2 2p_z 2p_\pi^4$ in $C+O^-$ is more favorable than the potential energy associated with the O^- configuration $2sp_\sigma 2s 2p_z 2p_\pi$, the π resonance only occurs to the extent that the CO sigma bond is bonding (0.5) and the O^- thus has the favorable configuration. This resonance is analogous to the resonance in HCN. The CO resonance only occurs to the extent that C has the $2s 2p_z 2p_\pi$ configuration which occurs when any of the three sigma bonds to C are not bonding (0.875). To the extent that the CO π bond is resonating there is also a second half π bond (only one side bonds) bond for 0.5 (when not $C+O^-$). To the extent that the CO π bond is not resonating, and when the C configuration is $2s 2p_z 2p_\pi^2$, there is a π bond (0.875-0.4375).

The energy of the resonance species $[C+O^-]$ is the sum of the first ionization potential of C plus the electron affinity of O. The electron affinity of O is taken as 1.46 eV.

The calculated total of the bond energies in formaldehyde is 15.76 eV. This is to be compared to the observed value of 15.59 eV.

The calculated dipole moment is 2.51 D. This is to be compared to the observed value of 2.33 D. The dipole moment is the sum of the HC bond dipoles and the CO bond dipole. The HC bonds have an associated dipole moment because the H is polarized in the bond. The dipole moment calculation is subject to any error in the HC polarization.

H. Fluoromethane (H_3CF)

The C s hybrid orbital coefficient for the CF bond in fluoromethane is set to 0.5, the same as in methane. The CF bond consists of overlaps of sp hybrid orbitals on C with sp hybrids on F. The CF bond in H_3CF has a sigma resonance of the form $[CF, C+F^-]$. The CF bond resonates

only to the extent that the F has the configuration $2s^0 2s^2 2p_z 2p_\perp^4$ (0.5). The relative populations of the two species $[H_3CF, H_3C+F^-]$ are [0.75,0.25].

The sigma resonance has an effect on the overall sigma bond overlap. When $C+F^-$, the F^- has two sigma orbitals, the C^+ none. The two F^- orbitals bond, F^- to C^+ , in parallel. Since this is an overlap only in one direction, right to left, there is one-half serial bond and one-half in parallel (parallel bond). When CF , there is the typical, serial, CF bond. Combining the CF and $C+F^-$ contributions, there results a bond which is 1.0-0.125 serial and 0.125 parallel. The distinction between serial and parallel is important because, in the determination of overall overlap, the serial overlaps are summed, serial fraction_bonding calculated, which is then added to the parallel fraction_bonding (See reference 1.). Because, when bonds are parallel, two fraction_bonding contributions are summed, rather than the overlaps summed, parallel bonding has the effect of increasing the overall overlap, thereby increasing the bond length. The calculated CF bond length in fluoromethane is 1.377\AA , in good agreement with the observed bond length of 1.382\AA . Consistent with resonance description above, the CF bond in H_3CF has the resonance kinetic energy associated with the 0.5 sigma resonance (2×0.25). (The resonance kinetic energy is calculated as if the overlap were 1.0. See reference 1.) The balance of the kinetic energy is that of a non-resonance bond (2.0) less the kinetic energy associated with the fraction as $C+F^-$ and the complementary resonance species CF (2×0.25).

The energy of the resonance species $[C+F^-]$ is the sum of the first ionization potential of C plus the electron affinity of F . The electron affinity of F is taken as 3.40 eV. It is important to note that the energy required to promote s to p in C^+ must be increased by $f_{sbc} f_{sbc}$ times the C stop value for C^+ . This is because a p orbital is removed in C ionization whereas an sp orbital is removed to form C^+ in H_3C+F^- . The calculated total of the bond energies in fluoromethane is 17.58 eV. This is to be compared to the observed value of 17.44 eV.

The calculated dipole moment is 2.73 D. This is to be compared to the observed value of 2.858 D. The dipole moment is the sum of the HC bond dipoles and the CF bond dipole. As mentioned with respect to formaldehyde, the dipole moment calculation is subject to any error in the HC polarization.

I. Tetrafluoromethane (CF_4)

The C s hybrid orbital coefficient for the CF bond in tetrafluoromethane is set to 0.5, the same as in methane. As in H_3CF , the CF bonds consist of overlaps of sp hybrid orbitals on C with sp hybrids on F . The CF bonds in CF_4 have a sigma resonance of the form $[C+F^-FFF, C+FF^-FF, C+FFF^-F, C+FFFF^-]$. The CF bond resonates only to the extent that the F has the configuration $2s^0 2s^2 2p_z 2p_\perp^4$ (0.5). The central C has a single positive charge. Each F has a negative charge of 0.25. An electron resonates among the four F s.

The sigma resonance has the same effect on the sigma bond overlap of each of the CF bonds in CF_4 as it did on the CF bond in H_3CF . As with the CF bond in H_3CF , there results a sigma bond which is 1.0-0.125 serial and 0.125 parallel. The calculated CF bond length in tetrafluoromethane is 1.318\AA , in good agreement with the observed bond length of 1.323\AA .

The resonance electron resonates from one F to another F . Therefore, the CF bond in CF_4 has twice the resonance kinetic energy as that associated with the sigma resonance for the CF bond in H_3CF . The resonance kinetic energy is $2 \times 2 \times 0.25$. The balance of the kinetic energy is that of a non-resonance bond (2.0) less the kinetic energy associated with the fraction as $C+F^-$ and

the two complementary resonance species CF (3 0.25). The calculated bond energy in tetrafluoromethane is 5.06 eV. This is to be compared to the observed value of 5.089 eV.

J. Fluoromethyldiyne (CF)

The bond in CF is different from the CF bonds in H_3CF and CF_4 for several reasons: the extra s sigma bonding electron on C permits dual bonding, the additional sigma bonding orbital must be made orthogonal to the F- bonding orbitals, and the axial symmetry of CF permits pi interactions. CF has a sigma resonance of the form $[\text{CF}, \text{C}^+\text{F}^-]$. As in H_3CF and CF_4 , the CF bond resonates only to the extent that the F has the configuration $2s^0 2s^2 2p_z^2 p_\perp^4$ (0.5). The relative populations of the two species $[\text{CF}, \text{C}^+\text{F}^-]$ are [0.75, 0.25]. When CF (0.75) there is a dual bond made up of sp to sp and s to sp hybrid orbital components. When C^+F^- , there is a left to right (0.5 contribution) dual bond made up of two s to sp hybrid orbital components. Also, there is a right to left (0.5 contribution) single s to sp hybrid orbital bond. As in H_3CF and CF_4 , there is also a one-half (left to right) parallel sp to sp bond when C^+F^- . The calculated CF bond length in fluoromethyldiyne is 1.269 Å, in good agreement with the observed bond length of 1.272 Å.

Consistent with resonance description above, the CF bond has the resonance kinetic energy associated with the 0.5 sigma resonance (2 0.25). The balance of the kinetic energy is that of a non-resonance bond consistent with the overlaps described above.

Because CF has axial symmetry there are pi interactions. CF has a single pi bond. When F has the configuration $2s^0 2s^2 2p_z^2 p_\pi^4$ one of the F p_π orbitals must be made orthogonal to the C p_π orbital. One of the F- p_π orbitals must be made orthogonal to the C p_π orbital when F-.

To meet the valence orthogonality requirements when C^+F^- , one of the F- sigma orbitals must be made orthogonal to the residual s orbital on the C+ to the extent that the bond is not bonding (0.5) (An $2s^0 2s^2$ configuration is energetically unfavorable.). The calculated bond energy in fluoromethyldiyne is 5.40 eV. This is to be compared to the observed value of 5.33 ± 0.11 eV.

The calculated dipole moment is 0.63 D. This is to be compared to the observed value of 0.645 D.

IV. CONCLUSION

The results presented here as well as previous results^{1,6} provide strong support for the efficacy of combined orbital theory of chemical bonding. The combined orbital theory does not assume that the bonding orbitals of two bonding atoms are completely distinguishable. When quantum chemical calculations were initially performed in the 1930's, calculations which did not assume that the bonding orbitals were distinguishable were not possible. It is only in the last ten or fifteen years that the sufficient processing power has been available to accurately perform the numerical calculations which are an essential part of combined orbital calculations. Independent research is needed to validate, or refute, the combined orbital approach.

¹ P.B. Merrithew, ChemRxiv. [Preprint] <https://doi.org/10.26434/chemRxiv.13049927> (2020).

² W.E. Duncanson and C.A. Coulson, Proc.Roy.Soc. (Edinburgh), **62**, 37 (1944).

³ W.M. Hayes, Editor-In-Chief, CRC *Handbook of Chemistry and Physics 95th Edition*, Section 5 pp 18-42, CRC Press (2014).

⁴ W.M. Hayes, Editor-In-Chief, *CRC Handbook of Chemistry and Physics 95th Edition*, Section 9 pp 31-47, CRC Press (2014).

⁵ W.M. Hayes, Editor-In-Chief, *CRC Handbook of Chemistry and Physics 95th Edition*, Section 9 pp 51-59, CRC Press (2014).

⁶ P.B. Merrithew, ChemRxiv. [Preprint] <https://doi.org/10.26434/chemRxiv.13013936> (2021).