Localized Orbitals for Polyatomic Molecules. II. The C–H Bond Transferability in Unsaturated Systems

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Abstract: Examination of ethylene and acetylene, as well as prior work on methane, ethane, and methanol, has shown that the C–H bond orbital is essentially the same in these different molecular environments. In addition, the "observed" bond moment of the C–H bond may be attributed to a net bond moment due to molecular formation.

In a previous paper[1] (hereafter referred to as I), the Edmiston–Ruedenberg localized orbitals[2] (LMO) for the C–H bond were found to be practically identical in methane, ethane, and ethanol. This transferability was found to be valid for a variety of basis sets and for a number of molecular conformations. [This paper focuses on the first part of the transferability issue: "Is it possible to find a set of orbitals that are similar from molecule to molecule?" The second part of the issue: "What limitations are there in their use?" assumes that they do exist and requires an affirmative answer to the first part. Recent work on this second part has been reported by O. J. Sovers, *et al.*, *J. Chem. Phys.*, **49**, 2592 (1968), and J. R. Hoyland, *ibid.*, **50**, 473 (1969).] Since all the molecules in I would traditionally be considered sp^3 hybridization cases, it is of interest to examine molecules which nominally have a different hybridization.

The acetylene and ethylene molecules were chosen for this study as representatives of these other classes. Since the only previous studies[3,4] of these types of systems used localized orbitals for a minimal STO basis set, it is useful to examine the transferability question with more accurate wave functions contracted from a more flexible basis.

Results

The wave functions for this study were constructed from basis functions which give almost "double-ζ" quality atomic SCF results. Each basis function is a linear combination of primitive Gaussian functions. The initial work used the Whitten[5] Gaussian-lobe functions (GLF) for the s- and p-type orbitals and the remainder of the work used the Cartesian Gaussian functions (CGF) of Huzinaga[6] for the p-type orbitals. These bases are referenced in the table as the "minimal" bases. This basis consists of ten s-type primitive Gaussians contracted to three group functions (basically a group to represent the 1s, the 2s, and the cusp-labeled 0s) and five p-type Gaussians contracted to one group function. "Extended" bases are obtained from the minimal bases by splitting off the smallest component of the 2s and 2p group function for carbon and the 1s group functions for hydrogen. The "extended + d" basis is obtained by adding a single d-type CGF to each carbon (with an exponent of 1.0—used by a number of authors and actually rather close to the optimal value[7] for CH_4). The molecular geometries used in this study are the more recent experimental ones and are also shown in Table I. All computations reported here used the MOLE Quantum Chemistry System[8] on the University Computing Co. 1108 computer system.

Table I. Calculations and Basis Sets for C_2H_2 and C_2H_4

Energy	Ref	Basis sets used[a]
		A. C_2H_2
−76.6165	*b*	Minimal STO basis, scaled
−76.6190	*c*	Minimal STO basis, scaled
−76.7218	*d*	Minimal GLF basis ($3s^{10}$, $1p^5/1s^5$)
−76.7224	*e*	Minimal GLF basis ($3s^{10}$, $1p^5/1s^5$): M
−76.7418	*f*	CGF basis ($9s^9$, $3p^3/3s^3$)
−76.7911	*e*	Extended GLF basis ($4s^{10}$, $2p^5/2s^5$): X
−76.7916	*d*	Extended GLF basis ($4s^{10}$, $2p^5/2s^5$): X
−76.8194	*e*	Extended + d CGF basis ($4s^{10}$, $2p^5$, $1d^1/2s^5$): X + D
−76.8495	*g*	Very extended STO basis ($12\sigma_g$, $12\sigma_u$, $6\pi_u$)
−76.8539	*g*	Very extended STO basis ($15\sigma_g$, $15\sigma_u$, $8\pi_u$)
		B. C_2H_4
−77.8343	*b*	Minimal STO basis, scaled
−77.8355	*h*	Minimal STO basis, scaled
−77.9390	*i*	Minimal GLF basis ($3s^{10}$, $1p^5/1s^4$)
−77.9402	*e*	Minimal GLF basis ($3s^{10}$, $1p^5/1s^5$): M
−77.9502	*f*	CGF basis ($9s^9$, $3p^3/3s^3$)
−77.9890	*e*	Minimal + d CGF basis ($3s^{10}$, $1p^5$, $1d^1/1s^5$): M + D
−78.0012	*i*	Extended GLF basis ($4s^{10}$, $2p^5/1s^4$)
−78.0031	*e*	Extended CGF basis ($4s^{10}$, $2p^5/2s^5$):
−78.0062	*j*	CGF basis ($9s^9$, $5p^5/3s^3$)
−78.0330	*e*	Extended + d CGF basis ($4s^{10}$, $2p^5$, $1d^1/2s^5$): X + D

[a] Notation for basis set description: as^b means a total of "*b*" s-type primitive functions were grouped (contracted) to "*a*" functions. [b] W. E. Palke and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2384 (1966). [c] U. Kaldor, *J. Chem. Phys.*, **46**, 1981 (1967). [d] R. J. Buenker, S. D. Peyerimhoff, and J. L. Whitten, *ibid.*, **46**, 2029 (1967). [e] This work. The C_2H_2 geometry is linear with R(C–H) = 2.002, R(C–C) = 2.281. The C_2H_4 geometry is planar with R(C–H) = 2.0235, R(C–C) = 2.551, and ∠HCH = 117°. [f] J. Moskowitz, *J. Chem. Phys.*, **43**, 60 (1965). [g] A. D. McLean and M. Yoshimine, "Tables of Linear Molecule Wave Functions," IBM Corp., Yorktown Heights, N. Y., 1967, p 211. [h] U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968). [i] J. L. Whitten, *ibid.*, **44**, 359 (1966). [j] J. M. Schulman, J. W. Moskowitz, and C. Hollister, *ibid.*, **46**, 2759 (1967).

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(4) (a) R. H. Pritchard and C. W. Kern, *J. Amer. Chem. Soc.*, **91**, 1631 (1969); (b) M. D. Newton, E. Switkes, and W. N. Lipscomb, *J. Chem. Phys.*, **53**, 2645 (1970).

(5) J. L. Whitten, *ibid.*, **44**, 359 (1966).

(6) S. Huzinaga, *ibid.*, **42**, 1293 (1965).

(7) S. Rothenberg and H. F. Schaefer, unpublished results.

(8) S. Rothenberg, P. Kollman, M. Schwartz, E. F. Hayes, and L. C. Allen, *Int. J. Quantum Chem.*, *Symp.*, **No. 3**, 715 (1969).

Table II. Calculated Properties[a] of the C–H Bond Orbital

Molecule[b]	Basis	R_{C-H}	T	$4/r_C$	$1/r_H$	J	E_{C-H}[c]	μ_{el}
CH_4	M-GLF	2.0665	0.8690	2.6012	0.9296	0.6671	4.6565	1.341
CH_4	X-GLF	2.0665	0.8680	2.6024	0.9344	0.6736	4.6640	1.375
CH_4	BF-GLF	2.0665	0.8734	2.6094	0.9438	0.6864	4.6732	1.348
C_2H_2	M-GLF	2.002	0.8354	2.7063	0.9031	0.6768	4.8712	1.305
C_2H_2	X-GLF	2.002	0.8876	2.7674	0.9318	0.7023	4.9209	1.307
C_2H_2	X + D-CGF	2.002	0.8842	2.7640	0.9399	0.7131	4.9263	1.306
C_2H_6 (e)	M-GLF	2.0825	0.8872	2.6106	0.9318	0.6723	4.6381	1.352
C_2H_6 (s)	M-GLF	2.0825	0.8860	2.6097	0.9314	0.6720	4.6381	1.344
C_2H_4	M-GLF	2.0236	0.8753	2.6508	0.9329	0.6795	4.7373	1.337
C_2H_4	X-CGF	2.0236	0.8974	2.6792	0.9501	0.6960	4.7678	1.357
C_2H_4	M + D-CGF	2.0236	0.8786	2.6540	0.9457	0.6941	4.7481	1.355
C_2H_4	X + D-CGF	2.0236	0.8970	2.6782	0.9576	0.7068	4.7708	1.373
C_2H_4	X + D-CGF (σ only)	2.0236	0.8916	2.6807	0.9574	0.7080	4.7850	1.376
CH_3OH (s)	M-GLF	2.071	0.8914 (2)[d] 0.8908 (1)	2.6162 (2) 2.6275 (1)	0.9253 (1)	0.6737 (2) 0.6720 (1)	4.6519 (1)	1.358
CH_3OH (e)	M-GLF	2.071	0.8927 (2) 0.8890 (1)	2.6299 (2) 2.6149 (1)	0.9319 (1)	0.6727 (2) 0.6737 (1)	4.6424 (1)	1.347
CH_3OH (e)	X-GLF	2.071	0.9046 (2) 0.9120 (1)	2.6381 (2) 2.6573 (1)	0.9457 (2)	0.6897 (2)	4.6687 (2)	

[a] All values are in atomic units. The C_2H_4 and C_2H_2 results are new. The other values are from ref 1 and are included for ready comparison. The column headings T and J represent the kinetic energy and self-coulomb expectation value. [b] All molecules reported are calculated from a ($3s^{10}$, $1p^5$) basis except for the X basis (extended by splitting out long-range s and p on both C and H), for the BF basis (obtained by placing floating s functions along the C–H bond axis), and for the X + D basis (adding to the X basis a single d-type orbital on carbon). The s and e are used to indicate staggered and eclipsed conformation, respectively. [c] $E_{C-H} = 2[T - 4/r_C - 1/r_H] + J$. [d] There are three C–H bond orbitals in CH_3OH, of which two are identical by symmetry and the third is different. They do have slightly different properties; the values pertaining to the two identical ones are indicated by (2) and those pertaining to the third by (1).

The localization calculations were straightforward, as described in I. The acetylene results showed two C–H bond orbitals, two carbon 1s orbitals, one C–C σ bond, and two equivalent C–C banana bonds. The ethylene results were similar with four C–H bond orbitals, two carbon 1s orbitals, and two equivalent C–C banana bonds above and below the molecular plane. The SCF orbitals, transformation coefficients to LMO, and coulomb and exchange orbitals over the LMO are available as a supplement to this paper from the author.

Transferability

The question about the similarity of the C–H bond orbital in different molecular environments can be answered by an examination of the data in Table II. This table summarizes the numerous one-electron properties of the C–H bond as well as the self-coulomb integral (a two-electron property), including molecules from I for comparison. Overall, the results in Table II show that environment affects the bond properties less than 3%. In fact, basis-set quality appears to be more important than the environment, even though the variation as a function of basis set seems to be only about 7% in the worst case (kinetic energy, which involves the derivative of the basis function and certainly accentuates the differences in the orbitals). One should also notice that these results are for molecules having different C–H atomic distances.

It was suggested[9] that different C–H bond orbitals might be produced in ethylene if the localization procedure were carried out holding the π orbital fixed (*i.e.*, only localize the σ electrons). The results are shown in Table II as (σ only) and clearly do not produce a different C–H bond orbital.

Bent Bonds

As was observed in I and by Kaldor,[3] the C–H bond orbitals do not have to lie along the C–H nuclear axis. In fact, the C–H bond orbital was found[1] to lie slightly (<1.5°) outside the dihedral angle formed by the CH_3 group for both ethane and methanol. The results for ethylene show the same behavior; that is, they lie 1.0° outside the C–H axis for the minimal basis and 0.5° for the extended basis. This, however, is still far less than was found[3,10] for NH_3, where the N–H bond orbital points some 5–14° inside the molecular axis.

The C–H Bond Dipole Moment

The concept of the additivity of bond dipole moments has been used successfully by chemists for many years. The value in saturated systems has been estimated[11] to be about 0.4 D (with the polarity being uncertain between C^+H^- or C^-H^+). The value in sp^2 and sp systems was thought to have the carbon be more electronegative. For the concept of a localizable, transferable C–H bond orbital to have meaning, it ought to be capable of quantitatively showing these trends.

An explanation was offered in I, based on a finding of an "effective" nuclear contribution to this moment, that could account for a value of 0.4 D. With the data now available for unsaturated systems (Table II), it seems that an alternative explanation may lie in *interpreting the reported bond moment* value of 0.4 D *as a net bond moment due to bond formation.* This possibility was mentioned qualitatively by Pritchard and Kern,[4a] but can be quantified as shown below. If one assumes that the C–H bond orbital consists of a linear combination of an sp^n hybrid atomic orbital on the carbon and a hydrogen 1s orbital

$$b(\text{C–H}) = \lambda_1\chi(sp^n) + \lambda_2\chi(H_{1s})$$

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(9) M. Schwartz, personal communication.

(10) S. Rothenberg, unpublished minimal-basis GLF results, 1967.

(11) W. L. Gent, *Quart. Rev., Chem. Soc.*, 2, 383 (1948); see also C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, N. Y., 1955, pp 239–245.

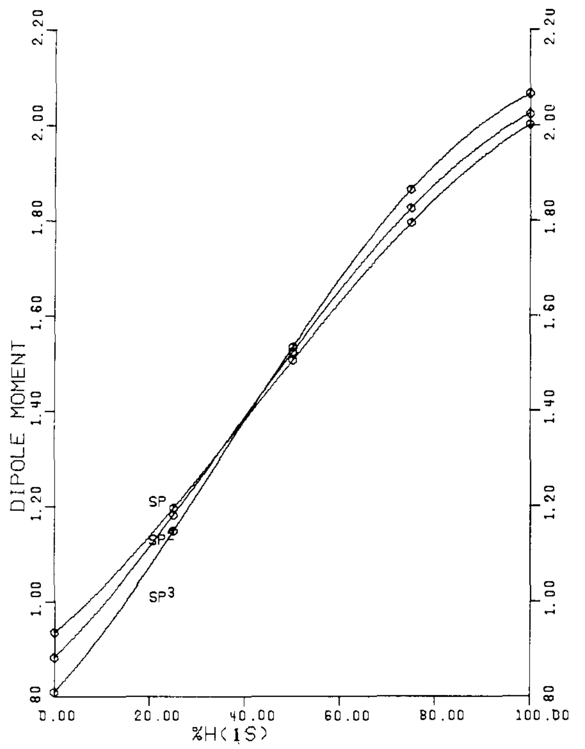

Figure 1. C-H bond dipole moment as a function of hydrogen 1s character for sp, sp^2, and sp^3 carbon hybrids.

Table III. Bond Moment of the C-H Orbital[a] as % (H_{1s})

Hybridization	% H				
	0	25	50	75	100
sp	0.9340	1.1956	1.5061	1.7953	2.0020
sp^2	0.8806	1.1805	1.5229	1.8253	2.0235
sp^3	0.8089	1.1482	1.5337	1.8645	2.0665

[a] The C-H orbital used here consists of a 2s AO and a 2p AO on carbon hybridized as shown and a 1s hydrogen orbital scaled by 1.414. The 2s AO is formed from the three s-type group functions as 2s AO = 1.0275 (2sG) − 0.2351 (1sG) − 0.0110 (0sG).

then the data in Table III and Figure 1 illustrate the bond moment as a function of per cent $\chi(H)_{1s}$ and hybridization character. Furthermore, if one assumes one electron from an sp^n orbital of carbon (*cf.* Table III) and one electron from the 1s orbital of hydrogen ($\mu = R_{CH}$), then an *atomic* moment for the pair of electrons is 2.87 (sp^3), 2.90 (sp^2), or 2.93 (sp). Subtracting this from the value shown in Table II for the total bond moment (sp^3, 2 × 1.37; sp^2, 2 × 1.37; sp, 2 × 1.30) gives a *net bond moment* of −0.32 (sp^3), −0.40 (sp^2) or −0.66 D (sp). This means that relative to noninteracting carbon and hydrogen atoms at the C-H bond distance, the C-H bond in molecular systems has a net sign of C^-H^+. Furthermore, this shows that removal of atomic bond moments[12] from the bond moments computed with localized orbitals yields net moments of the same order as "observed" bond moments.[11]

Conclusions

The C-H bond orbital seems to be a consistently identifiable construct. Examination of ethylene and acetylene, as well as prior work on methane, ethane, and methanol, has shown that the C-H bond orbital is essentially the same in these different molecular environments. This now gives substantial hope to the possibility that they can prove to be computationally useful. In addition, the observed bond moment of the C-H bond is attributed to a *net* bond moment due to molecule formation.

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[12] The effect of the "atomic dipole" was first pointed out by C. A. Coulson, *Trans. Faraday Soc.*, 33, 388 (1937).