exopolyhedral boron–boron σ bond of 1:1′-$[B_5H_8]_2$ are oriented in a fashion suitable for multiple bonding. However, on the basis of the observed[20a] boron–boron bond distance of 1.74(6) Å it was concluded that no such π-type interactions are present.

The % *s* character at boron in the exopolyhedral boron–boron bonds as calculated above from eq 4 for the possible dimers of 2,4-$C_2B_5H_7$ are B3 (40.7%) $\simeq$ B5 (39.4%) > B1 (34.3%). The exopolyhedral % *s* character for the boron atoms in 2,4-$C_2B_5H_7$ may be calculated from the experimental values[52] of J_{BH} with the relationship[52,53] $\% s = 0.312 J_{BH}$, but the same ordering is not obtained: B3 (57%, J_{BH} = 182 Hz) $\simeq$ B1 (56%, J_{BH} = 179 Hz) > B5 (52%, J_{BH} = 169 Hz). In both cases, however, boron atom B3 has the highest s character. This is consistent with the higher electronegativity of the two neighboring carbons relative to boron which increases the p-orbital contribution of the B3 atom toward the cage B–C bonds, thereby increasing the s-orbital contribution of these borons toward the exopolyhedral bonds.[52] An additional observation is that the largest coupling constants ($J_{BB'}$ and J_{BH}) in these cage compounds involve boron atoms (B3 in 2,4-$C_2B_5H_7$, B1 in B_5H_9) which can be described as having *fractional* closed three-center, two-electron bonding in the skeletal bonds[45a] to the rest of the cage.

In summary, it has been shown that Kroner and Wrackmeyer's correlation[14] of J_{BB} with the degree of s character of the hybrid orbitals involved in the boron–boron bond can be empirically extended to boron–boron 2-center, 2-electron bonds. Large values of $J_{BB'}$ in the boron–boron linked boron hydride and carborane cages are found to be attributable to high degrees of s character in the hybrid orbitals involved in the exopolyhedral 2-center, 2-electron, boron–boron bond. Likewise, small values of $J_{BB'}$ are indicative of low s character as in the various three-center, two-electron intracage[11,46] boron–boron–boron bonds. This correlation now provides a probe of the various bonding situations of boron based on experimentally determined spin–spin coupling constants and, in special cases, allows a determination of the hybridization of a boron in a particular bond with a reasonable degree of confidence.

Acknowledgment. J.A.A. and J.D.O. gratefully acknowledge financial support from the National Science Foundation (CHE80-13694) and valuable assistance from Dr. Ron Garber in obtaining the relaxation time measurements and Dr. P. D. Ellis for the T_1 program. R.J.A. and L.G.S. thank the National Science Foundation and the Army Research Office for support. The use of the facilities of the University of South Carolina Regional NMR Center, funded by the National Science Foundation (CHE82-07445), is also gratefully acknowledged. J.D.O. thanks Dr. R. E. Williams for the gift of 2,5-$C_2B_5H_7$.

Registry No. 1:1′-$[B_5H_8]_2$, 71595-75-0; 1:2′-$[B_5H_8]_2$, 31831-99-9; 2:1′-$[1\text{-}(CH_3)B_5H_7][B_5H_8]$, 89017-48-1; 2:2′-$[B_5H_8]_2$, 28775-81-7; 2:2′-$[1\text{-}(CH_3)B_5H_7]_2$, 71605-80-6; 2:2′-$[1\text{-}(CH_3)B_5H_7][B_5H_8]$, 89017-49-2; 1:3′-$[2,4\text{-}C_2B_5H_6]_2$, 70480-12-5; 3:3′-$[2,4\text{-}C_2B_5H_6]_2$, 59419-84-0; 3:5′-$[2,4\text{-}C_2B_5H_6]_2$, 70513-48-3; 2:2′-$[1,5\text{-}C_2B_3H_4]_2$, 60569-26-8; 2:2′,3′:2″-$[1,5\text{-}C_2B_3H_4][1',5'\text{-}C_2B_3H_3][1'',5''\text{-}C_2B_3H_4]$, 74501-91-0; B, 7440-42-8.

---

(51) Moore, E. B., Jr. *J. Am. Chem. Soc.* **1963**, *82*, 676–679.

(52) Onak, T.; Wan, E. *J. Chem. Soc., Dalton Trans.* **1974**, 665–669.

(53) Williams, R. E.; Harmon, K. M.; Spielmann, R., J. *OTS, AD* **1964**, No. 603782.

Electron Density Superposition Errors in Ethynyllithium

Steven M. Bachrach and Andrew Streitwieser, Jr.*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received July 25, 1983*

Abstract: Typical ab initio calculations with modest basis sets of organolithium and related compounds juxtapose an electron-deficient center having many functions (lithium) and an electron-rich center with function deficiencies (carbanion), a situation that leads to superposition errors in both energy and electron density. Electron density study of ethynyllithium exemplifies the problem and shows that such errors are minimized by proper use of diffuse functions in the basis; diffuse functions are more effective in reducing electron density superposition errors than polarization functions (d orbitals).

1. Introduction

Much discussion in the recent literature has centered on the nature of the carbon–lithium bond, particularly with the growing use of organolithium reagents in organic synthesis. Schleyer and co-workers have argued that the C–Li bond, though largely ionic, contains significant covalent character supplied through lithium p orbitals.[1] This conclusion was drawn from structural aspects and Mulliken populations of various organolithium compounds. The structures of organolithium compounds have the unusual property of lithium atoms bridging anionic centers in an effort to minimize the electrostatic energy. Since Schleyer found definite Mulliken population in Li p orbitals and Mulliken bond population involving Li p orbitals, he concluded that Li p orbitals are used to describe the covalent bonding in organolithium compounds.

The Streitwieser group, on the other hand, has maintained that the C–Li bond is predominantly ionic and bases their argument on integrated spatial electron populations (ISEP).[2] ISEP differs from Mulliken populations in that ISEP assigns electrons to regions of space regardless of where the basis functions are centered; Mulliken populations assign electrons to atoms by determining the number of electrons in each basis function centered on each atom, totally neglecting the spatial extent of these functions.

There exists general agreement that organolithium compounds may be essentially viewed as simply ion pairs. The carbon of the

---

(1) (a) Clark, T.; Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 527. (b) Kos, A. J.; Schleyer, P. v. R. *Ibid.* **1980**, *102*, 7928. (c) Apeloig, Y.; Clark, T.; Kos, A. J.; Jemmis, E. D.; Schleyer, P. v. R. *Isr. J. Chem.* **1980**, *20*, 43. (d) Kos, A. J.; Jemmis, E. D.; Schleyer, P. v. R.; Gleiter, R.; Fischbach, V.; Pople, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4996. (e) Schleyer, P. v. R.; Kos, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 448. (f) Clark, T.; Rohde, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344. (g) Schleyer, P. v. R.; Kos, A. J.; Kaufmann, E. *J. Am. Chem. Soc.* **1983**, *105*, 7617. **Added in Proof**: Professor Schleyer now believes (personal communication) that the C–Li bond is essentially ionic.

(2) (a) Streitwieser, A., Jr.; Williams, J. E., Jr.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778. (b) Klein, J.; Kost, D.; Schriver, G. W.; Streitwieser, A., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3922.

C–Li bond will have definitie anionic character, which is well-known to require diffuse orbitals for adequate description.[3] Lithium basis sets generally include an extremely diffuse outer p orbital, having its maximum at a distance from lithium longer than the average C–Li bond length.[4] Organolithium compounds, by their very nature, are setup for having superposition problems, particularly with small basis sets. With the anionic carbon atom seeking additional functions to aid its description and the outer Li p function extending well into the region of the anion, the Li p function may be used to describe the anion itself, not any bonding interaction. The p function may, in fact, be acting only as a superposition function. However, the Mulliken population formalism has no ability to correct for superposition and may be yielding invalid results on the nature of the C–Li bond.

We develop in this paper a method for correcting electron density for superposition error, described in section 2. This method is then applied to lithium acetylide, the results of which are described in section 3. We anticipate that once superposition effects are removed from the wave function, a clearer understanding of organolithium compounds will result.

2. Electron Density Superposition Error

The use of truncated basis sets in ab initio calculations, though economical, may present hazards that severely cloud the interpretation of the results. In particular, truncated basis sets frequently cause a severe inability to predict interaction or dissociation energies. The energy of interaction of subsystem A with subsystem B is defined as

$$E_{\text{int}}{}^* = E_{\text{AB}} - E_{\text{A}}{}^* - E_{\text{B}}{}^*$$

where E_{AB} is the energy of the supersystem AB and $E_{\text{C}}{}^*$ (with C = A, B) is the energy of the isolated subsystem C. When calculated in this manner, $E_{\text{int}}{}^*$ will generally be too large due to basis set superposition error (BSSE).[5] Superposition error occurs since the supermolecule AB and the subsystems are not all calculated by using the same basis set. Alternatively, superposition may be described as, for example, the truncated basis set of A (i.e., far from the Hartree–Fock limit) using any available orbitals to supplement itself. In so doing, the orbitals of B will be used to aid in describing A itself as well as to describe B and the interaction of B with A. Similarly, subsystem B will supplement its basis set with the orbitals of A.

Boys and Bernardi[6] have proposed a method for elminating BSSE which has achieved much success.[5,7] The method is termed counterpoise and defines the interaction energy as

$$E_{\text{int}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}}$$

where E_{AB} is the energy of system AB, and E_{C} (with C = A, B) is the energy of subsystem C calculated with the full basis set, i.e., the basis sets of both A and B. This method, though somewhat more expensive, does reduce the superposition error defined above. Basis set superposition error is then defined as the difference between E_{int} and $E_{\text{int}}{}^*$. In this paper, we will define the superposition energy to be the difference in energy between subsystem A with the full basis set and subsystem A using only the orbitals of A, i.e., $E_{\text{A}} - E_{\text{A}}{}^*$. The ultimate method for eliminating superposition is to use basis sets that are at the Hartree-Fock limit, but this method is usually not practical. Hence, it is important to understand the effects of small basis sets.

Table I. Superposition Energy (kcal mol^{-1}) of Lithium Acetylide at 4-31G

system	$E_{\text{int}}{}^*$	E_{int}	BSSE
radical	−68.70	−67.17	1.53
anion/cation	−183.70	−166.71	16.99

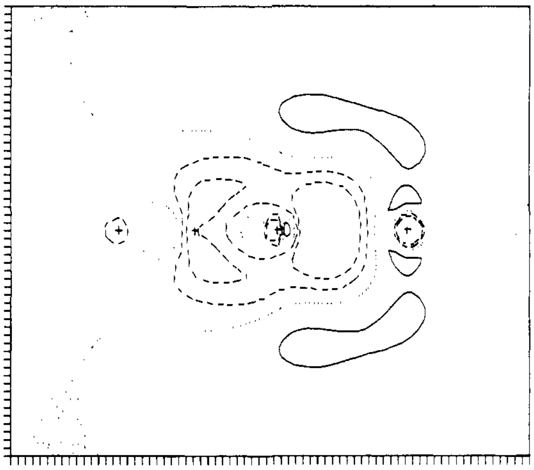

Figure 1. Projected electron density of Li radical with ghost CCH plus CCH radical with ghost Li minus the sum of Li radical and CCH radical at 4-31G with contour levels from −0.001 to 0.001 by 0.0005 e$^-$ au^{-2}. Nuclei indicated by + are arranged as HCCLi. Positive contours are solid lines, negative contours are dashed lines, and the zero contour is a dotted line.

Just as superposition affects energy, it must also affect electron density. When defined in terms of basis supplementation, it is clear that electrons may be placed in orbitals purely by superposition rather than interaction considerations. Normally, the electron density of interaction ($\rho_{\text{int}}{}^*$) would be defined as

$$\rho_{\text{int}}{}^* = \rho_{\text{AB}} - \rho_{\text{A}}{}^* - \rho_{\text{B}}{}^*$$

where ρ_{AB} is the density of AB and $\rho_{\text{C}}{}^*$ (C = A, B) is the electron density of the isolated subsystem C located at the position it occupies in the supermolecule. However, in an analagous fashion to the energy determination, we propose that the corrected electron density of interaction be defined as

$$\rho_{\text{int}} = \rho_{\text{AB}} - \rho_{\text{A}} - \rho_{\text{B}}$$

where ρ_{C} (C = A, B) is the electron density of subsystem C calculated with the full basis set.

3. Results and Discussion

Calculations were performed on lithium acetylide at the optimized geometry[8] using the 4-31G basis set.[9b] All calculations were run using either GAMESS[10] on the Lawrence Berkeley Laboratory CDC 7600 or a modified[11a] version of GAUSSIAN80[11b] on the Organic Chemistry Division VAX-11/750. Superposition calculations were run for two sets of subsystems

$$\cdot\text{Li} + \cdot\text{C}{\equiv}\text{CH} \qquad \text{(a)}$$

$$^{+}\text{Li} + {}^{-}\text{C}{\equiv}\text{CH} \qquad \text{(b)}$$

placing the ghost orbitals at the nuclear coordinates of LiCCH. All electron density maps were performed with the PROJ[12] program, which produces projected electron densities.

The superposition energy results for LiCCH are presented in Table I. Dividing lithium acetylide into lithium cation and

---

[3] Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609, 5612.

[4] Streitwieser, A., Jr.; Grier, D. L.; Kohler, B. A. B.; Vorpagel, E. R.; Schriver, W. G. In "Electron Distribution and the Chemical Bond", Coppens, P., Hall, M. B., Eds.; Plenum Press: New York, 1982.

[5] Kolos, W. *Theor. Chim. Acta* **1979**, *51*, 219.

[6] Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

[7] (a) Leclerq, J. M.; Allavena, M. *J. Chem. Phys.* **1983**, *78*, 4606. (b) Benzel, M. A.; Dykstra, C. E. *Ibid.* **1983**, *78*, 4052. (c) Allavena, M.; Silvi, B.; Capriani, J. *Ibid.* **1982**, *76*, 4573. (d) Bachrach, S. M.; Chiles, R. A.; Dykstra, C. E. *Ibid.* **1981**, *75*, 2270. (e) Bulski, M.; Chalasinski, G. *Theor. Chim. Acta* **1977**, *44*, 399. (f) Urban, N.; Hobza, P. *Ibid.* **1975**, *36*, 207, 215. (g) Johansson, A.; Kollman, P.; Rothenberg, S. *Ibid.* **1973**, *29*, 167.

[8] Hinchliffe, A. *J. Mol. Struct.* **1977**, *37*, 145.

[9] (a) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2607. (b) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *Ibid.* **1971**, *54*, 724. (c) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *Ibid.* **1972**, *56*, 2251.

[10] Dupuis, M.; Spangler, D.; Wendoloski, J. J. NRCC Program No. QG01.

[11] (a) Singh, U. C.; Kollman, P., unpublished results. (b) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406.

[12] Streitwieser, A., Jr.; Collins, J. B.; McKelvey, J. M.; Grier, D. L.; Sender, J.; Toczko, A. G. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2499.

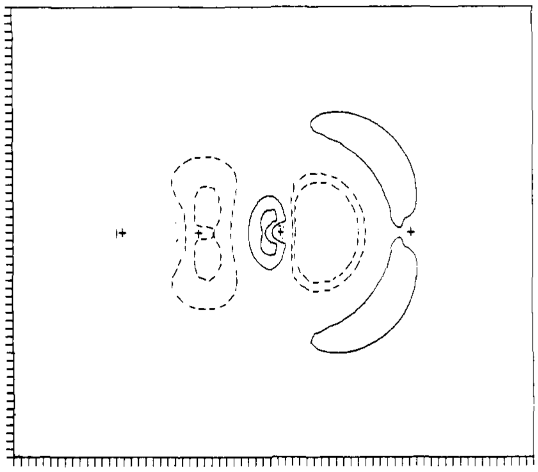

Figure 2. Projected electron density of Li cation with ghost CCH plus CCH anion with ghost Li minus the sum of Li cation and CCH anion at 4-31G with contour levels from −0.01 to 0.01 by 0.005 e⁻ au^{-2}.

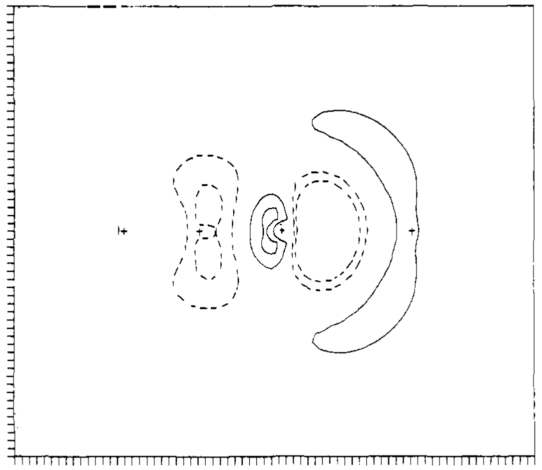

Figure 3. Projected electron density of CCH anion with ghost Li minus CCH anion at 4-31G with contour levels from −0.01 to 0.01 by 0.005 e⁻ au^{-2}.

acetylide anion leads to a superposition error a full order of magnitude larger than for the radical subsystems. This difference is explained by the electron density maps.

The difference in electron density due to superposition is obtained by forming the difference density map

$$\rho_A + \rho_B - (\rho_A{}^* + \rho_B{}^*)$$

The resulting maps for the radical and anion/cation systems are presented in Figures 1 and 2, respectively. Note that the contour levels of these two figures differ by a factor of 10; that is, the radical system shows an electron redistribution due to superposition of an order of magnitude less than the anion/cation system. Thus, the energy superposition error of the radical system is expected to be much less than for the anion/cation system.

The electron redistribution due to superposition results almost entirely from the acetylene subsystem. The superposition energy of lithium cation is only 0.02 kcal mol^{-1}, about 0.1% of the BSSE of LiCCH. This is not unexpected as lithium cation is very contracted and has the full split valence basis to describe only two electrons. With such a small superposition error for lithium cation, it is unlikely that the reverse superposition proposed by Schleyer[1g] would be significant. As seen by the nearly identical features of Figures 2 and 3, the superposition density of acetylide anion alone accounts for nearly all the redistribution of the supermolecule. In fact, this redistribution arises largely from one molecular orbital (MO). As seen in Figures 3, 4, and 5, the superposition occurring in the HOMO (lone-pair orbital) of acetylide anion alone accounts for nearly all of the superposition present in LiCCH. The remaining superposition mostly stems from the π system. The superposition evident in the lone-pair orbital can be described as a need to delocalize the anion beyond the capabilities of a simple split valence basis set, in order to minimize electron–electron repulsion within the lone pair. Since the lone pair is directed at lithium, the lithium orbitals may aid in diffusing the lone-pair electrons. Since the lithium p orbitals are quite diffuse, the lone pair is able to spread into a vastly larger region with the aid of the lithium orbitals. As seen in Figure 4, electron density is taken from the anionic center just to the right of carbon and moved outward toward lithium. A quantitative measure of the degree of electron movement is available through integration of the projected electron density. For acetylide anion with lithium ghost orbtials minus acetylide anion (Figure 4), integration of the area enclosed in the zero contour to the right of carbon indicates that 0.091 electron is removed from this region by superposition, a rather substantial electron redistribution.

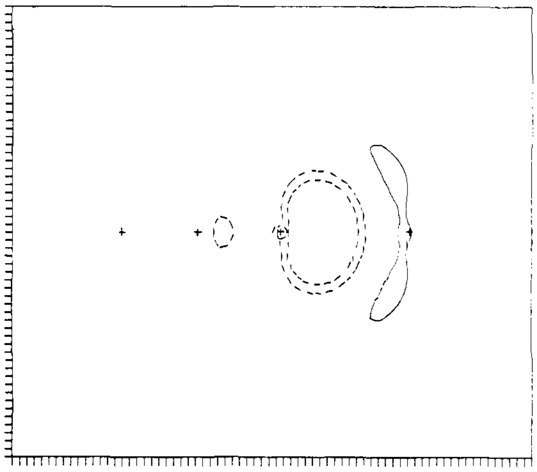

Figure 4. Projected electron density of MO 5 of CCH anion with ghost Li minus MO 5 of CCH anion at 4-31G with contour levels from −0.01 to 0.01 by 0.005 e⁻ au^{-2}.

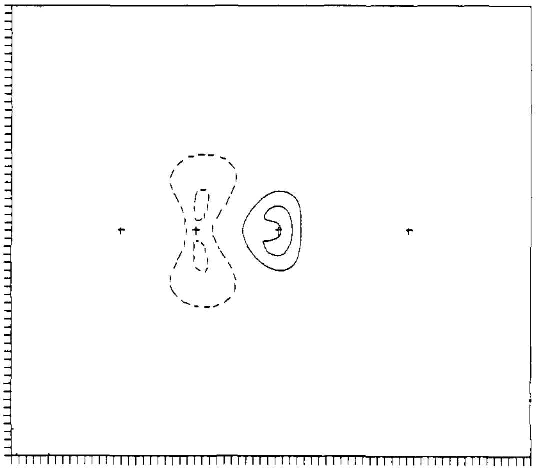

Figure 5. Projected electron density resulting from Figure 3 minus Figure 4 with contour levels from −0.01 to 0.01 by 0.005 e⁻ au^{-2}.

On the other hand, the acetylide radical has only one electron in the orbital directed toward lithium. The electron–electron repulsion within the anionic lone-pair orbital, which is the main reason for the anionic orbital to be diffuse, is not present in the radical. There is no urgent requirement for the radical orbital to be more diffuse, and, therefore, the use of lithium orbitals to aid in the description of this radical orbital is negligible, resulting in little superposition error.

The use of the superposition correction also provides a clean, graphical representation of the formation of a chemical bond. Figure 6 presents the uncorrected $\rho_{int}{}^*$ while Figure 7 presents ρ_{int} for LiCCH formed from the cation/anion subsystems. The superposition corrected map (Figure 7) clearly shows a closed region where electrons have been brought to form the bond

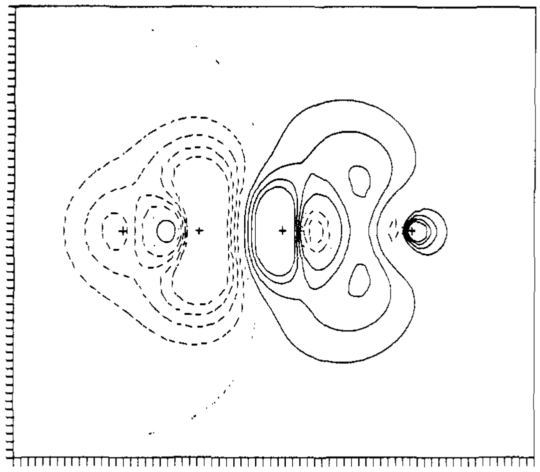

Figure 6. Projected electron density of lithium acetylide minus the sum of Li cation and CCH anion at 4-31G with contour levels from −0.02 to 0.02 by 0.005 e$^-$ au^{-2}.

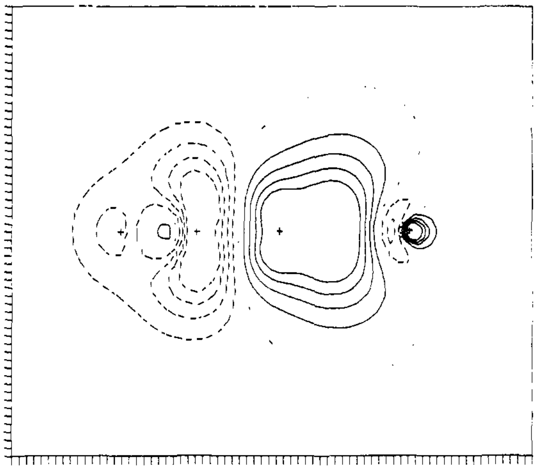

Figure 7. Projected electron density of Lithium acetylide minus the sum of Li cation with ghost CCH and CCH anion with ghost Li at 4-31G with contour levels from −0.02 to 0.02 by 0.005 e$^-$ au^{-2}.

Table II. Superposition Energy (kcal mol^{-1}) of Acetylide Anion at Various Basis Sets

basis set	superposition energy
STO-3G[9a]	72.63
4-31G[9b]	16.97
6-31G[9c]	16.13
4-31G* (no Li d)	15.66
4-31G* (Li d)	15.72
4-31G+	0.36
6-31G+	0.20

connecting acetylide anion and lithium cation, while the uncorrected density does not provide such a closed surface. Integration inside the zero contour of Figure 7 indicates that 0.269 electron has been moved into the bonding region.

The addition of polarization functions is expected to decrease superposition since, in general, larger basis sets are more complete and, therefore, do not require as much supplementation from adjacent centers as smaller basis sets. Polarization functions (α_d = 0.75) were added to carbon, and the superposition error was determined for acetylide anion. The superposition energy does decrease by slightly more than 1 kcal mol^{-1} with the addition of polarization functions, a relatively small amount (see Table II). The superposition density with polarization functions is presented in Figure 8. Integration inside the zero contour of this map indicates that 0.080 electron has moved from the anionic center due to superposition, which is only slightly less than the 0.091 electron moved for acetylene anion without polarization functions. Clearly, polarization functions are not sufficient for eliminating superposition error.

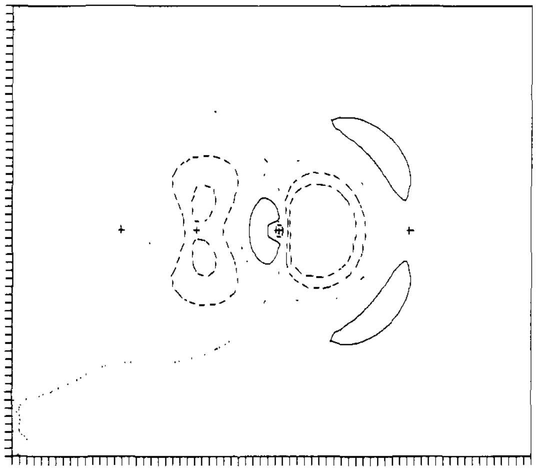

Figure 8. Projected electron density of CCH anion with ghost Li minus CCH anion at 4-31G* with contour levels from −0.01 to 0.01 by 0.005 e$^-$ au^{-2}.

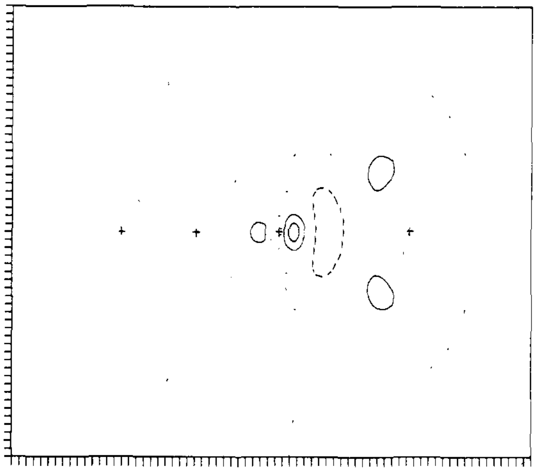

Figure 9. Projected electron density of CCH anion with ghost Li minus CCH anion at 4-31G+ with contour levels from −0.001 to 0.001 by 0.0005 e$^-$ au^{-2}.

The Schleyer group has recently emphasized the importance of diffuse s and p functions for adequate description of anions and has shown how small basis sets in common use can be effectively augmented by a set of such diffuse functions.[3] Since we model LiCCH as acetylide anion and lithium cation, diffuse orbitals on each carbon of acetylide may be necessary in the description of the anion and the overall description of lithium acetylide. Therefore, superposition calculations were obtained for LiCCH and acetylide anion using the 4-31G+ basis set.[3]

For energy considerations, the addition of diffuse s and p functions on carbon has essentially eliminated all superposition; the superposition error for acetylide anion is only 0.36 kcal mol^{-1}. As seen by the extremely small contour levels (a factor of 10 smaller than for Figure 3) of acetylide anion with lithium ghost orbitals minus acetylide anion at the 4-31G+ level (Figure 9), only a slight change in electron redistribution occurs due to superposition with this basis set. The map of acetylide anion at 4-31G+ minus acetylide anion at 4-31G (Figure 10) clearly demonstrates the ability of the diffuse orbitals to delocalize electrons into a vastly larger space, thereby not requiring the assistence of lithium orbitals to achieve this more stable electron distribution.

Table II lists the superposition energy of acetylide anion with lithium ghost orbitals with various basis sets. The intuitive trend that larger basis sets will exhibit smaller superposition error is borne out. Clearly, for organolithium compounds, the carbon basis

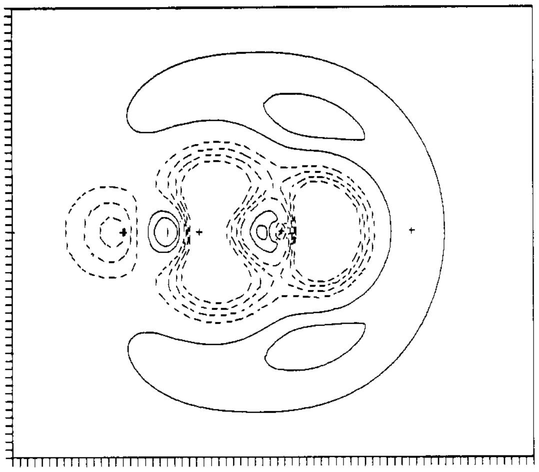

Figure 10. Projected electron density of CCH anion at 4-31G+ minus CCH anion at 4-31G with contour levels from −0.01 to 0.01 by 0.0025 $e^- au^{-2}$.

Table III. Coefficients of MO 6 and MO 7 of LiCCH at Various Basis Sets

function	4-31G	4-31G+ exponent[a]			4-31G+ no outer Li p
		0.04	0.06	0.08	
		MO 6 (p_z Only)			
C_1					
inner	−0.4147	−0.4168	−0.4402	−0.4372	−0.4408
outer	−0.3136	−0.3063	−0.3677	−0.4376	−0.3549
diffuse		0.1173	0.4329	0.3625	0.3875
Li					
inner	0.1938	0.2040	0.2171	0.2257	0.2217
outer	−0.0458	−0.0373	0.0288	−0.0062	
		MO 7 (p_x Only)			
C_1					
inner	0.3444	0.3453	0.3730	0.3735	0.3731
outer	0.2729	0.2523	0.2332	0.2288	0.2329
diffuse		0.1067	0.0325	0.0277	0.0388
Li					
inner	0.0359	0.0563	0.0384	0.0353	0.0391
outer	0.0604	−0.0503	0.0016	0.0151	

[a] Exponent of the diffuse orbital used.

set must be supplemented with one set of diffuse s and p orbitals to reduce superposition.

Once diffuse functions have been added to carbon, analysis of the lithium basis set becomes meaningful, since the use of lithium basis functions as superposition functions has been essentially eliminated. Table III lists the coefficients for the basis functions of MO 6 (σ_{C-Li}) and MO 7 (π) for LiCCH at 4-31G and 4-31G+ with various diffuse orbital exponents. In the σ_{C-Li} bond, the coefficient of the outer Li p function essentially vanishes with $\alpha_{diffuse}$ = 0.08. For the π bond, the coefficient of the outer Li p function becomes negligible with $\alpha_{diffuse}$ = 0.06. However, the coefficient of the outer Li p function in the 4-31G basis set is significant. Combining the following three facts—(1) 4-31G has more superposition error than 4-31G+, (2) the Li outer p function is extremely diffuse, and (3) the Li outer p function is not used at the 4-31G+ level—leads us to conclude that the Li outer p function serves only as a superposition function in small basis sets.[13]

Moreover, we find that with sufficiently large basis sets (i.e., basis sets including diffuse functions) the outer Li p function is not needed at all. The coefficients for MO 6 and MO 7 (listed in Table III) for LiCCH at 4-31G+ (α = 0.06) without Li outer p functions are nearly identical with the coefficients at 4-31G+. The complete 4-31G+ energy is only 0.125 kcal mol^{-1} lower in energy than the energy obtained with the basis set without the Li outer p functions. Thus, Li outer p functions are insignificant in terms of both energy and electron distribution when diffuse orbitals are placed on carbon.

Lastly, it is clear that lithium inner p functions are required to obtain adequate description. The coefficients of these functions remain relatively unchanged with basis set variation. The significant p_σ coefficient indicates a polarization of lithium electrons by the adjacent anionic charge. The much smaller but definite p_π coefficient undoubtedly represents the tiny but not zero carbon–lithium π bonding.

4. Conclusion

The superposition error manifested in electron density distribution has been shown to be graphically described by a formalism analogous to BSSE. This method has led to the conclusion that adequate basis sets for organolithium compounds must have diffuse orbitals on carbon, and lithium outer p functions are not required. Past descriptions invoking any usage of outer lithium p functions in bonding via Mulliken populations or related functions are erroneous. These functions are being used only to supplement an inadequate description of the carbanion center. However, lithium inner p functions are required to properly describe organolithium compounds.

Acknowledgment. This research was supported in part by N.I.H. Grant GM-30369. The VAX 11/750 used in this work was purchased with the assistance of N.S.F. equipment grant No. CHE-8214313.

---

[13] This conclusion is also reached for dilithiomethane where the same analysis shows the outer Li p function coefficient vanishing with the addition of diffuse orbitals on carbon. See: Bachrach, S. M.; Streitwieser, A. Jr. *J. Am. Chem. Soc.*, in press.