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On the Nature of C−Li Bonding in Lithiated Hydrocarbons and Lithiocarbons

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The nature of C−Li bonding in CH_3Li and CLi_6 was reconsidered using two recently proposed new methodologies, namely the AIM generalized population analysis and Fermi hole analysis. The calculations were performed at HF level of the theory using 6-311G** basis sets. The main issue was the realistic estimation of the polarity of C−Li bonds. The analysis confirms that C−Li bonds in CH_3Li are predominantly ionic but some slight modifications of the contemporary picture of bonding in CLi_6 is proposed.

Introduction

Much attention has been paid in recent years to the investigation of the nature of carbon−lithium bond in simple organolithium compounds. The main issue in these studies is the degree of covalency vs ionicity of C−Li bond.[1] The most puzzling feature of this bond is that although the electronegativity difference between carbon and lithium allows one to expect the bond to be highly polar,[2,3] the solubility of simple organolithium compounds in nonpolar solvents such as benzene, the phenomenon by which these compounds differ from other alkali−alkyls, has been for a long time considered as the manifestation of essentially covalent nature of C−Li bond[4−6] The solution of this apparent discrepancy has attracted the interest of many theoreticians and during past years a lot of studies have been performed aiming at the quantitative determination of the ionicity and/or covalency of C−Li bond.[7−23]

Although earlier studies[7,9] reported relatively low ionicity of C−Li bond (27% according to[4,9]), the more recent calculations clearly suggest much higher polarity[10−21] and now it is rather well established that C−Li bond is even much more polar than expected on the basis of electronegativity arguments.[2,3] The main factor that contributed to this dramatic change is predominantly due to considerable improvement of the methodologies for the analysis of wave functions and charge densities.[10,14,24−30] The first studies that attributed to C−Li bond relatively strong covalent character were based mainly on the comparison of Mulliken atomic charges and C−Li bond populations. This type of analysis is known, however, to suffer from serious deficiencies[31,32] arising from artificial 1:1 partitioning of charge density, which makes the atomic charges and bond populations necessarily biased, and this bias increases with increasing polarity of the molecule. This, of course, is the case for many organolithium compounds and is why most of the earlier estimates of C−Li bond polarity cannot be regarded as realistic.

Most of the deficiencies of Mulliken population analysis can naturally be remedied using virial partitioning of charge density[24,25] and most of the arguments in favor of essentially ionic character of C−Li bond are based on the comparison of Bader's atomic charges or related, but slighly different, integrated spatial electron populations ISEP.[10a] Another strong argument against the covalent character of C−Li bond, that is also closely related to Bader's virial partitioning of electron density $\rho(r)$, was proposed some time ago by Streitwiesser et al.[10] (Another procedure to suppress the bias of Mulliken-like population analysis is the so-called NPA.)[29] This argument operates with extremely low value of electron density at C−Li bond critical point (BCP). The typical value for several different C−Li bonds is around 0.03−0.04 which is much lower than the analogous value for covalent C−C or C−H bonds (0.3). This difference clearly suggests that the extent of electron sharing in C−Li bond is considerably lower that in typical covalent C−C and C−H bonds and that the C−Li bonding interactions for example in CH_3Li are rather characteristic of closed-shell ionic species $CH_3^-...Li^+$.

This picture of bonding was subsequently questioned by Graham, Marynick, and Lipsomb[22] who argued that similarly low values of electron density at BCP can be found also in some other molecules such as Li_2, Be_2H_2, etc., where considerable ionicity can be excluded due to homopolar nature of these species. Similarly, the nonnegligible covalent character of C−Li bond in methyllitium was advocated by Schiffer et al.[23] Their conclusions were, however, also criticized[1] and most of the authors now agree with C−Li bond being essentially ionic.

Our aim in this study is to contribute to the existing debate and to discuss the nature of C−Li bond in terms of two recently

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proposed new methodologies, the so-called generalized population analysis[33,34] and the analysis of domain averaged Fermi holes.[35,36] Both these methodologies were recently applied to the elucidation of the structure of molecules with complex bonding patterns,[37−39] and we believe that they can throw some new light also on this old problem. Moreover, the advantage of these two methodologies is that they can be formulated either exactly, in terms of strict Bader's AIM theory, or approximately, using Mulliken-like partitioning of the charge density. The conclusions of both forms (exact vs approximate) of both the above methodologies can thus be straightforwardly compared. Such comparison can not only show the origin of the deficiency of approximate analyses based on Mulliken-like partitioning of the charge density, but also allows one to estimate how large is the bias arising from this approximation compared to exact AIM based theory. The analysis was applied to the molecules of CH_3-Li, and CLi_6 at ab initio HF level of the theory.

Theoretical

As the theoretical background underlying both above methodologies was sufficiently described in previous studies,[33−37] we confine ourselves here only to a brief recapitulation of basic principles and formulas to the extent necessary for the purpose of this study.

The so-called nonlinear or generalized population analysis is a simple new methodology allowing one to detect the existence of both classical 2-center and nonclassical multicenter bonding interactions in a molecule. The method relies on the idempotency property of SCF density matrix expressed by the identity

$$\frac{1}{2^{k-1}}\,\mathrm{Tr}(PS)^k = N \tag{1}$$

where P is the usual charge density bond order matrix, and S is the overlap one. The analysis was first introduced in the approximate form based on the Mulliken-like partitioning of identity (1) for various values of k into contributions which can be attributed a clear physical or chemical meaning

$$\frac{1}{2^{k-1}}\mathrm{Tr}(PS)^k = \sum_A \Delta_A^{(k)} + \sum_{A<B}\Delta_{AB}^{(k)} + ... \sum_{A\,<\,B....\,<\,K}\Delta_{ABC...K}^{(k)} \tag{2}$$

Thus, for example, in the case of $k = 1$, the partitioning reduces to the well- known Mulliken-population analysis[40] and the results are (Mulliken) atomic charges Q_A on individual atoms. Another useful partitioning of the identity (1) is for $k = 2$, which yields mono- and biatomic terms that are equivalent to the well-known Wiberg indices.[41−42] Although these indices that often reproduce classical bond multiplicities[43] are often sufficient to describe the bonding in "normal" molecules well described by classical Lewis formula, the description of molecules with more complex bonding patterns, like for example multicenter bonding requires to scrutinize higher powers of (PS) product. Thus, for example, the most common type of multicenter bonding, the 3-center bonds, can be detected and localized by the values of the populations $\Delta_{ABC}{}^{(3)}$ that, just for this reason, are called 3-center bond ndices[44−48]

$$\Delta_{ABC}^{(3)} = \frac{3}{2}\sum_{\mu}^{A}\sum_{\nu}^{B}\sum_{\lambda}^{C}(PS)_{\mu\nu}(PS)_{\nu\lambda}(PS)_{\lambda\mu} \tag{3}$$

In view of the known deficiencies of Mulliken-like partitioning of the identity (1), the extension of the generalized population analysis into the framework of Bader's AIM theory was recently reported.[32,49−52] As the full details of this generalization can again be found in the original literature we will not go into details here, but just for a brief information we remind only the final formulas for AIM generalized equivalents of Mulliken charge, Wiberg index, and 3-center bond index

$$Q_A \approx \Omega_A^{(1)} = N(A) = 2\sum_i^{occ}\langle i|i\rangle_A \tag{4}$$

$$W_{AB} \approx \Omega_{AB}^{(2)} = 4\sum_i^{occ}\sum_j^{occ}\langle i|j\rangle_A\langle j|i\rangle_B \tag{5}$$

$$\Delta_{ABC}^{(3)} \approx \Omega_{ABC}^{(3)} = 2\sum_i^{occ}\sum_j^{occ}\sum_k^{occ}\{\langle i|j\rangle_A\langle j|k\rangle_B\langle k|i\rangle_C + \langle i|j\rangle_A\langle j|k\rangle_C\langle k|i\rangle_B + ...\} \tag{6}$$

As it is possible to see, the AIM generalized equivalent of Mulliken charge is the Bader's charge $N(A)$, whereas equivalents of Wiberg and 3-center indices are the quantities $\Omega_{AB}{}^{(2)}$and $\Omega_{ABC}{}^{(3)}$,resulting from the partitioning

$$N = \sum_A \Omega_A^{(k)} + \sum_{A\,<\,B}\Omega_B^{(k)} + ... \sum_{A\,<\,B...\,<\,K}\Omega_{ABC..K}^{(k)} \tag{7}$$

that represents nothing but the AIM generalization of the original formula (2) for $k = 2$ and 3.

The other general methodology we are going to apply in this study is the analysis of domain averaged Fermi holes. The concept of Fermi hole has been introduced long time ago by Wigner and Seitz[53] in solid-state physics, but the applications to chemistry have been so far rather scarce.[54−58] Some time ago, the interest in the chemical exploitation of these holes was revived and the concept of the so-called domain averaged, or closely related charge-weighted Fermi hole was introduced and applied.[35−39] These holes, defined by the formula (8), are closely related to the quantities $F(\Omega,\Omega')$ introduced some time ago by Bader[59]

$$g_\Omega(r) = \rho(r_1)\int_\Omega \rho(r_2)dr_2 - 2\int_\Omega \rho(r_1,r_2)dr_2 \tag{8}$$

$$F(\Omega,\Omega') = \int_{\Omega'} g_\Omega(r_1)dr_1 \tag{9}$$

These holes satisfy the universal normalization condition (10), where N_Ω is the total number of electrons in the region Ω

$$\int g_\Omega(r_1)dr_1 = N_\Omega \tag{10}$$

Although the validity of this normalization does not depend on the size and the shape of the region Ω, the actual choice of this region affects the form of the hole itself. Consequently, the structural information that can be extracted from these holes also depends on the actual form of this region. In our studies, we have tested just one particular choice of such regions where they coincide with atomic domains of Bader's partitioning. In this case, the analysis provides the information about the valence state of a given atom in a molecule and this information was recently exploited for the detection of the valence shell expansion in hypervalent molecules.[37] The analysis of these holes consists of the diagonalization of the matrix G^Ω that represent the hole in AO basis for each particular choice of the region Ω and in the subsequent inspection of the corresponding eigenvalues and eigenvectors. As the detailed procedure of this analysis is sufficiently reported in the studies, we will not go into further details here but refer the reader to the original literature.[35−39]

Before presenting the results of our Fermi hole analysis it is, however, fair to say, that although its formalism was formulated from the very beginning quite generally, the practical applications were so far restricted by certain additional approximations. First of them, concerns the pair density required for the construction of conditional probabilities. In general, this pair density could be generated by quantum chemical calculations at any level of the theory (both HF and post-HF). Unfortunately, the correlated pair density is not at present easily available from standard quantum chemical programs so that we had to confine ourselves to SCF level of the theory. In this case, the formula for "charge-weighted" Fermi holes (8) transforms to (11)

$$g_{\Omega}(r_1) = 2\sum_{i}^{occ}\sum_{j}^{occ}\langle i|j\rangle \varphi_i^*(r_1)\varphi_j(r_1) \tag{11}$$

The second approximation which we have adopted in previous studies concerns the integration over Bader's atomic regions. This integration was replaced by a simple Mulliken-like approximation according to which the electron is expected to be in a region of the atom A, if it resides in an orbital localized on this atom. Within this approximation, the integrals of the type $\langle i|j\rangle_{\Omega}$, that appear in (11) are approximated as (12)

$$\langle i|j\rangle_{\Omega A} = \sum_{\mu}^{A}\sum_{\nu} c_{\mu i}c_{\nu j}S_{\mu\nu} \tag{12}$$

This formula is not, however, symmetrical in μ and ν as it is in the case of explicit Bader's integration so that the matrix G^{Ω} which represents the hole (20) in AO basis is not symmetrical. To remedy this artifact of the approximation (12), the matrix of the Fermi hole must have been artificially symmetrized. The symmetrization of the hole can be avoided working with symmetrically orthogonalized basis sets and in this case, the normalization factor N_{Ω} equals to Löwdin charge of the region.

Although interesting and useful structural information have been obtained from the analysis of approximate domain averaged Fermi holes[35−39] it is nevertheless probable that Mulliken-like approximation (12) can bias the conclusions of the approximate Fermi hole analysis similarly as it is known to affect the population analysis. As this bias can be especially important for polar systems, it is evident that obtaining reliable picture of bonding, especially in the case of organolithium compounds, relies on the application of the approach at highest possible level of the theory. With this in mind we have generalized our original codes so that now "exact" Fermi holes averaged over real Bader's atomic domains can be generated and analyzed and in this study we are going to present the results of such analysis. But in order to estimate also the bias arising from the Mulliken-like partitioning of the charge density, the results of "exact" AIM generalized Fermi hole and population analysis will be confronted with the picture of bonding emerging from earlier approximate formulations. In the following part, the results of our calculations will be reported.

Calculations

Having presented the theoretical background of the above methodologies, let us specify, in the following part, the technical details of our calculations. The calculations performed in this study were of two types. In the first step, the geometry of all the studied molecules was completely optimized at ab initio HF level of the theory in 6-311G** basis. These standard calculations were performed using Gaussian 94 program.[59] The aim of these calculations was to generate density matrices and molecular orbitals that were used, in the second step, for the construction and analysis of Fermi holes and for the population analysis. These analyses, in both approximate and "exact" AIM generalized form, were performed using our own codes which can be obtained upon request. These programs are at present interfaced with Gaussian and PC−Gamess[60] and require as an input the standard Gaussian and/or Gamess output files. In addition to these files, which are sufficient to perform the Mulliken-like approximate form of both analyses, an additional file containing the so-called AOM matrix is required in the case of "exact" analysis. In our case, this file was produced by Gaussian program appropriately modified by one of us (R.B.), but similar modification could in principle be introduced also into other programs such as PROAIM.[12] This was in fact necessary in the case of CLi_6, for which the AOM file could not be generated by Gaussian. The results of our calculations are summarized in Tables 1-4.

TABLE 1: Mulliken and AIM Generalized Atomic Charges and Bond Indices for CH_3Li

CH_3Li			
Mulliken		AIM generalized	
Q_C	6.667	$N(C)$	6.578
Q_{Li}	2.519	$N(Li)$	2.086
Q_H	0.938	$N(H)$	1.112
Q_{CH3}	9.481	$N(CH_3)$	9.914
$\Delta^{(2)}_{Li-C}$	0.798	$\Omega^{(2)}_{C-H}$	1.060
$\Delta^{(2)}_{C-H}$	0.966	$\Omega^{(2)}_{C-Li}$	0.178
$\Delta^{(3)}_{LiCH}$	0.000	$\Omega^{(3)}_{LiCH}$	0.015

TABLE 2: Fermi Hole Analysis of CH_3Li for Different Choices of the Region Ω

	CH_3Li		
Ω	approximate	AIM generalized	interpretation
C	1.996	2.000	1s
	1.431	1.789	σ_{C-Li}
	0.952 (3x)	0.927 (3x)	σ_{C-H}
	0.007	0.009	neglected
H	0.903	1.019	σ_{C-H}
	0.003 (2x)	0.055, 0.030	neglected
Li	1.992	1.991	1s
	0.531	0.090	σ_{C-Li}
	0.052 (3x)	0.002 (2x)	neglected

TABLE 3: Mulliken and Bader Atomic Charges and Bond Indices for CLi_6

Mulliken		AIM	
Q_C	6.977	$N(C)$	10.545
Q_{Li}	2.873	$N(Li)$	2.241
$\Delta^{(2)}_{LiC}$	0.586	$\Omega^{(2)}_{LiC}$	0.368
$\Delta^{(2)}_{LiLi}$	0.167	$\Omega^{(2)}_{LiLi}$	0.020
$\Delta^{(3)}_{LiCLi}$	0.084	$\Omega^{(3)}_{LiCLi}$	0.070

In the following section, the results of our calculations will be discussed.

Results and Discussion

CH_3Li. The simplest representative of organolithium compounds is the molecule of methyllithium, CH_3Li. Although this molecule is known to exist in the form of tetrameric aggregate $(CH_3Li)_4$,[61−63] most of the existing theoretical analyses were performed for simple monomeric species. (IR spectra of

TABLE 4: Fermi Hole Analysis of CLi_6 for Various Choices of Regions Ω

Ω	approximate	interpretation	AIM generalized	interpretation
			2.000	1s
	1.999	1s	1.934	2s
C	0.940 (4x)	sp^3-like hybrids	1.784 (3x)	p_x, p_y, p_z
	0.012	neglected	1.205	metallic cage
			0.009 (6x)	neglected
6Li	1.999	metallic cage	1.991 (6x)	1s
	1.993 (6x)	1s	0.790	metallic cage
	1.061 (4x)	sp^3-like hybrids	0.215 (3x)	(p_x, p_y, p_z)
	0.001	neglected	0.066	2s

monomeric methyllithium in argon matrix was reported in ref 64). For this reason and for the sake of comparison with previous studies, we also report the results of our analysis for the simple molecule CH_3Li. The wave functions generated using primary HF/6-311G** calculations were subsequently analyzed using the above-reported methodologies in both approximate "Mulliken-like" and exact AIM generalized form and the results of these calculations are summarized in Tables 1−2. Let us discuss now these results and let us first start with the more familiar Mulliken population analysis. The values of "approximate" 2-center bond populations (equivalent to Wiberg indices) and Mulliken atomic charges are summarized, together with the corresponding AIM generalized counterparts, in Table 1. The comparison of the values is very instructive and straightforwardly elucidates the discrepancy between earlier studies that admitted nonnegligible covalent character of C−Li bond and more recent ones, that rather suggest the bond to be predominantly ionic. The first indication of the contradiction between the conclusions of approximate and "exact" analysis comes from the comparison of atomic charges. Although the difference between Bader's and Mulliken charges is only marginal for C and to some extent also for H, the difference for Li atom is much higher and attains roughly 0.5e. As a consequence of this difference, the Bader's atomic charge of Li is only 2.086, which agrees with the results of the earlier study by Ritchie and Bachrach[27] (N(Li) = 2.09 in 3-21G basis) and which is not too far from the limit 2.0 corresponding to completely ionic CH_3^- ... Li^+ bond. On the other hand, the analogous comparison of Mulliken charges is rather consistent with the structure $CH_3^{-0.5}$... $Li^{+0.5}$. This contradiction between the conclusions of approximate and "exact" population analysis finds its reflection also in the values of 2-center bond indices. Thus, for example, the reduced polarity of C−Li bond, suggested by lower Mulliken atomic charges, necessarily implies a nonnegligible covalent character of C−Li bond, and this covalency is consistently reflected by the values of Wiberg indices for C−Li bond (Table 1). On the other hand, the analogous values of "exact" AIM generalized 2-center bond indices are much lower and, consistent with the expectation based on Bader's atomic charges, clearly suggest that the covalent character of C−Li bond is very low.

The same picture of bonding also emerges from the complementary approach based on the analysis of domain averaged Fermi holes. The results of this analysis are summarized in Table 2. As it is possible to see the picture of bonding resulting from both "exact" and approximate, analysis is qualitatively very similar and the main difference concerns again the underestimation of the polarity of C−Li bond in the approximate approach. Let us discuss now the results of this analysis, and let us start first with "exact" hole associated with Bader's atomic region of carbon atom. In this case, the analysis yielded 5 (essentially) nonzero eigenvalues. One of them exactly equals 2.00, and the inspection of the associated eigenvector shows that it corresponds to completely filled ($1s^2$) core electron pair on carbon. In addition to this electron pair, which is irrelevant for bonding, there are 4 additional (essentially) nonzero eigenvalues that characterize valence state of the carbon atom in the molecule. Three of them are equal to 0.927, and the corresponding eigenvectors are reminiscent of localized orbitals of C−H bonds of sp^3 hybridized CH_3 group. (Figure 1a). These eigenvectors are interpreted as "broken valences " of C−H bonds.[35−37]

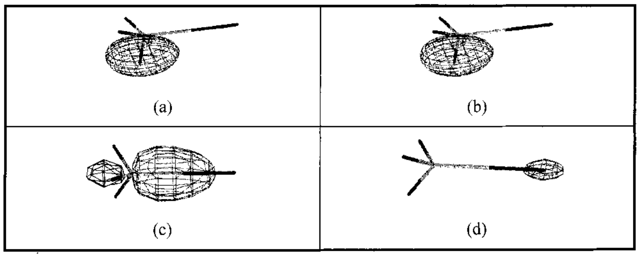

Figure 1. Fermi hole analysis of CH_3Li Hole associated with C atom, eigenvector corresponding to broken valence of C−H bond Hole associated with one of H atoms, eigenvector corresponding to broken valence of C−H bond (complementary to 1a). Hole associated with C atom, eigenvector corresponding to broken valence of C−Li bond Hole associated with Li atom. Eigenvector corresponding to ($1s^2$) core electron pair on Li.

This interpretation is straightforwardly supported by the results of the analysis of the Fermi holes associated with H atoms. Thus, for example, the analysis of the hole associated with one of the hydrogens yields only one essentially nonzero eigenvalue equal to 1.019 and the associated eigenvector (Figure 1b) is again very reminiscent of the eigenvector corresponding to the "broken valence" of C−H bond from the previous analysis. On the basis of this parallel, it is possible to interpret the eigenvalues corresponding to this "common" eigenvector of the Fermi holes associated with C and H atoms as the contributions of these two atoms to C−H bond electron pair. As it is possible to see, the actual value of the sum 1.019 + 0.927 is indeed very close to 2 so that C−H bond in CH_3Li retains to very good approximation the character of localized 2c−2e bond. Moreover, the fact that the values are not very different from unity clearly suggests that the electron pair of this bond is shared more or less uniformly.

Let us analyze the C−Li bond in a similar way. As expected, such analysis requires us to scrutinize the eigenvalues and eigenvectors of the Fermi holes associated with C and Li atoms. A crucial role in this respect is played by the eigenvector of the carbon Fermi hole corresponding to the nonzero eigenvalue equal to 1.789. As it is possible to see (Figure 1c), this eigenvector is reminiscent of the localized orbital of C−Li bond, and we interpret it as the "broken valence" of C−Li bond. This interpretation is completely consistent with the results of the analysis of the Fermi hole associated with Li atom. This analysis yields two (essentially) nonzero eigenvalues, of which one is very close to 2, and the remaining one equals 0.090. The first eigenvector, corresponding to ($1s^2$) core electron pair (Figure 1d) is not important for bonding, but the second one is very similar to the "broken valence" of C−Li bond from Figure 1c. The situation is thus very similar to what was observed for C−H bonds and the only, but important, difference concerns the considerable difference in the amount of electrons that both atoms contribute to C−Li bond electron pair. The fact that both eigenvalues differ strongly from unity clearly suggests that the contributions of C and Li atoms to the electron pair of C−Li bond are dramatically different, and the electron sharing in this bond is very far from even.

The picture of bonding resulting from the approximate analysis of the Fermi holes is qualitatively very similar except for strongly underestimated polarity of C−Li bond whose electron pair is now formed by the contributions 1.468 and 0.531 from CH_3 group and Li atom, respectively. This result is not again very surprising because it only once again demonstrates the well-known bias characteristic for all types of analyses based on Mulliken-like partitioning schemes. The realistic picture of bonding, based on the “exact” AIM generalized quantities is thus clearly consistent with the conclusions of the majority of modern studies of C−Li bond that characterize this bond as predominantly ionic.

CLi_6. Another interesting molecule that we are going to discuss in this study is the molecule of CLi_6. A remarkable feature of this molecule is its extraordinary thermodynamic stability. To explain this stability, the bonding in CLi_6 was often the subject of numerous theoretical studies.[17,18,29,65−69] The main problem addressed in these studies is, where the stability of this molecule comes from. On the basis of these studies, the stability of hyperlithiated molecules was attributed to the presence of Li....Li bonding interactions that effectively produce a “metallic cage” surrounding the central atom.[65] Although this picture of bonding can still be considered as qualitatively correct, one must be aware of the fact that most of early studies of ab initio wave functions of hyperlithiated molecules were based on Mulliken population analysis, whose inability to provide a realistic picture of carbon−lithium bonding is now well recognized. It is thus quite probable that some modifications of the above picture of bonding could be expected if the analysis was based on a more realistic partitioning scheme. An example of such a scheme is the so-called natural population analysis (NPA)[15] designed to provide a more realistic alternative to Mulliken population analysis. The main difference that this analysis brought for the picture of bonding in CLi_6 was the dramatic increase of polarity, which roughly corresponds to the situation where the central C atom in the oxidation state (−IV) is surrounded by the cage of six Li^+ ions held together by two electrons. Bonding between the central carbon and the metallic cage is expected to be predominantly ionic. This result is very important because the same trend of increasing the polarity of C−Li bonds is also characteristic of the results of Bader’s AIM theory and in order to estimate the corresponding increase of polarity quantitatively, the results of approximate “Mulliken-like” and “exact” AIM based analysis will be reported.

The calculations were again performed at ab initio HF level of the theory in 6-311G** basis, and the results are summarized in Tables 3 and 4. Let us attempt now to discuss the conclusions of our analyses, and let us start with the comparison of atomic charges. These values are summarized in Table 3, and, as it is possible to see, the transition from Mulliken to Bader’s charges is accompanied, as expected, by a dramatic increase of polarity. Thus, for example, the atomic charge on lithium decreases from the Mulliken value 2.873 to AIM value 2.241, which again closely corresponds to the charge $N(Li) = 2.28$ reported by Ritchie and Bachrach.[27] Although this increase of polarity is in complete agreement with the results on other C−Li bonds, the situation with CLi_6 is nevertheless slightly more complex. This is due to the fact that Bader’s atomic charge of carbon exceeds the limiting value of 10, characteristic of completely filled K and L shells, and for this reason, it was criticized as overestimated.[70] This criticism is not, however, justified because the more detailed inspection that we are going to report clearly shows that the exaltation of the atomic charge of C cannot be regarded as a violation of the Lewis octet rule. Such an inspection shows namely that this exaltation is due to interference of two contributions. One of them involves the electrons of the valence shell and, as it will be shown, this contribution strictly confirms the Lewis octet rule. The formal exaltation of the charge is thus due to the second contribution that comes from the electron pair forming the “metallic cage” surrounding the central atom. This electron pair was of course detected already in previous studies based on Mulliken population analysis,[17,29,65] but in these studies, it was always completely associated with the lithium cage. Our study shows that the interpretation of the electron pair of “metallic cage” as being completely associated with lithium is also very probably biased by the well-known failure of Mulliken population analysis to describe the partitioning of electron charge in polar bonds. As it will be shown, the second contribution to the charge density on carbon comes from the part of the electrons in diffuse orbitals on Li that are inside the cage close to C and that Mulliken population analysis artificially attributes to lithium. Theoretical support for the above picture of bonding straightforwardly follows from the analysis of domain averaged Fermi holes. The results of this analysis are summarized in Table 4. Let us start with the analysis of the “exact” AIM averaged Fermi hole associated with the central C atom. As it is possible to see in Table 4, the analysis of this hole yields 6 essentially nonzero eigenvalues, of which 5 are nearly equal or close to 2. The inspection of the corresponding eigenvectors shows, that first two of them, associated with the eigenvalues 2.00 and 1.934, correspond to 1s and 2s orbitals of carbon. In addition to this, there is a group of 3 degenerated eigenvalues equal to 1.784, and the inspection of the associated eigenvectors shows (Figure 2a) that they correspond to p_x, p_y, and p_z orbitals, respectively. These orbitals thus evidently form the core and valence shell of C. On the basis of this assignment, it is possible to calculate the total charge density in the valence shell and the resulting value 7.286 clearly suggests that Lewis octet rule is not violated. The exaltation of the electron density of C is thus due to the contribution of remaining nonzero eigenvalue. As it is possible to see from the inspection of the corresponding eigenvector (Figure 2b), this contribution does not come from the valence shell of carbon but from the diffuse “metallic cage”. At first sight this result may seem quite surprising since this cage was usually associated only with lithium atoms. However, according to our results, such an interpretation of the “metallic cage” is apparently oversimplified because it very probably reflects the well-known bias of Mulliken-like partitioning of charge density in polar bonds. That this is indeed the case can be clearly seen

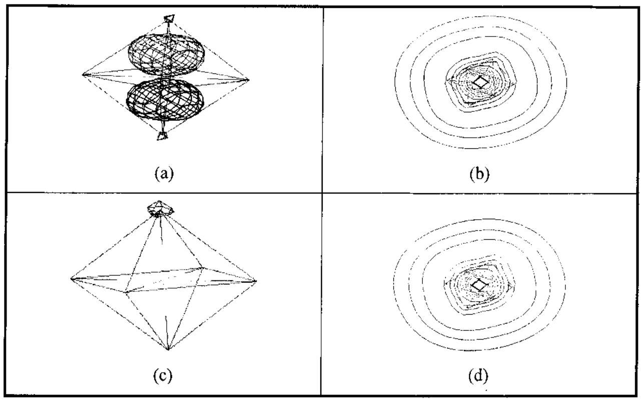

Figure 2. Fermi hole analysis for CLi_6 Hole associated with C atom. Eigenvector corresponding to one of practically filled core (2p) orbitals on C. Hole associated with C atom. Eigenvalue corresponding to “metallic cage” Hole associated with Li_6 fragment. Eigenvector associated with ($1s^2$) core electron pair on one of Li atoms. Hole associated with Li_6 fragment. Eigenvector corresponding to “metallic cage“ (complementary to 2b).

from the results of "exact" AIM based analysis, and the eigenvalue 1.205 just represents the contribution of C to the electron pair describing the bonding of this cage. The support for the above interpretation straightforwardly comes from the analysis of the complementary Fermi hole associated with the fragment of 6 Li atoms. This analysis yields 10 essentially nonzero eigenvalues but, despite this apparent complexity, the interpretation of this hole is extremely simple and transparent. Thus, as it is possible to see, 6 of 11 nonzero eigenvalues are very close to 2 and the inspection of the corresponding eigenvectors shows that they correspond to ($1s^2$) core electron pairs on individual Li atoms (Figure 2c). In addition to these core electrons, there is one additional nonzero eigenvalue equal to 0.790 and the inspection of the corresponding eigenvector shows that it is again very reminiscent of the diffuse orbital of the "metallic cage" detected in the Fermi hole of carbon (Figure 2d). This result is very important since the similarity of this "common" eigenvector, as well as the complementarity of the corresponding eigenvalues ($1.205 + 0.790 \cong 2$) suggests that these eigenvalues can be interpreted as the contributions of C and Li to the shared electron pair holding together the "metallic cage" of six Li^+ ions. In this connection, it is perhaps interesting to stress that similar analysis of the approximate Fermi holes does not associate any contribution to the metallic cage with carbon and, consistent with the bias of Mulliken population analysis, the whole electron pair of this "metallic cage" is attributed to lithium.

The interpretation of remaining nonzero eigenvalues of the Fermi hole associated with the fragment region of 6 Li atoms is also very simple. The inspection of the corresponding eigenvectors shows namely that they are again very reminiscent of 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals found in the previous analysis of the Fermi hole of carbon. (In the case of the "approximate" Fermi hole this analysis yields the set of 4 degenerated sp^3-like hybrid orbitals that are in fact equivalent to the set of s, p_x, p_y, and p_z orbitals obtained in the case of the "exact" analysis.) Taking into account this similarity as well as the near complementary values of the corresponding occupation numbers ($1.784 + 0.215 \cong 2$, $1.934 + 0.066 \cong 2$) it is possible to conclude that carbon−lithium bonding in CLi_6 is due to 4 very unevenly shared electron pairs. The polarity of C−Li bonds can be roughly estimated from the comparison of the corresponding eigenvalues. Such an estimate shows that roughly 90% of the eight valence electrons (7.286) involved in C−Li bonding is contributed by carbon and only the remaining 10% by lithiums. This result more or less corresponds to the polarity of other C−Li bonds, for example in CH_3Li. The estimate based on the analogous data from the approximate analysis is, of course, correspondingly lower but this decrease of the polarity is again expected because of the well-known bias of Mulliken population analysis.

On the basis of the above results the final picture of bonding in CLi_6 can be described as follows:

(a) C−Li bonding is due to 4 very unevenly shared electron pairs. The realistic estimate of this polarity based on the analysis of AIM averaged Fermi holes gives the value of valence charge density at carbon equal to 7.286, which is more or less comparable with the estimate of NPA 7.44. Consequently, one cannot speak of the violation of Lewis octet rule in this molecule.

(b) In addition to these 4 valence electron pairs responsible for C−Li bonding, there is another electron pair involved in the formation of the "metallic cage" of six Li^+ ions surrounding the central carbon. This electron pair was so far interpreted as being involved solely in Li...Li bonding interactions but, as it was discussed above, such an interpretation in fact only reflects the bias of Mulliken population analysis. According to our AIM generalized analysis, this electron pair is also shared and the contributions of C and Li are roughly equal to 1.2 and 0.8, respectively. This result is very interesting because it suggests that although oxidation state of the central carbon is indeed close to NPA estimate (−IV), the interactions between this central atom and the surrounding cage need not be purely ionic as expected so far. This conclusion seems to be supported also by the results of generalized population analysis (Table 3). Such an analysis namely detects the presence of nonnegligible 3-center bonding interactions in LiCLi fragments that can arise only from covalent interactions between central atom and the metallic cage. As it is possible to see on the values of the corresponding indices, such C...Li_{cage} interactions do indeed exist.

(c) The bonding in the metallic cage has the character of 6-center 2-electron bond, but the contribution to the electron pair of this bond comes more or less evenly from both C and Li. Consistent with this sharing are also the values of Li...Li bond indices whose values drop from 0.167, corresponding to approximate Mulliken-like analysis, to AIM generalized value 0.020. This result is very interesting because the dramatic decrease of Li...Li bonding interactions is straightforwardly consistent with the absence Li...Li bond paths reported by Ritchie and Bachrach.[27]

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