Table V. Extended Hückel Parameters

			orbital exponent[a]	
atom	orbital	H_{ii}	1	2
Cr	4s	−8.66	1.700	
	4p	−5.24	1.700	
	3d	−11.20	4.95	1.800
			(0.505 79)	(0.674 72)
Re	6s	−9.36	2.398	
	6p	−5.96	2.372	
	5d	−12.66	5.343	2.277
			(0.635 91)	(0.567 71)
P	3s	−18.60	1.600	
	3p	−14.00	1.600	
Cl	3s	−26.30	2.033	
	3p	−14.20	2.033	
C	2s	−21.40	1.625	
	2p	−11.40	1.625	
O	2s	−32.30	2.275	
	2p	−14.80	2.275	
H	1s	−13.60	1.30	

[a] In parentheses, the coefficients in the double ζ expansion of the d orbitals.

d^8–d^8. Now a superlative bridging acceptor, such as a carbene, allows a structure in which there is no metal–metal bonding.

Stereochemical variety, isomerism, is what makes all of chemistry interesting. Inorganic molecules often provide isomeric richness by making choices between bridged and unbridged structures. We believe that we have achieved a certain degree of understanding of the factors that influence that choice.

Acknowledgments. We are grateful to R. A. Walton, F. A. Cotton, W. C. Trogler, S. J. Lippard, and P. L. Watson for bringing some references to our attention, and to the members of our group for discussion. The typing was expertly done by E. Stolz and our drawings by J. Jorgensen, both of whom we thank. The work at Cornell was supported by the National Science Foundation through Research Grant CHE 7828048 and an Undergraduate Research Program that made the participation of R. Fisel possible.

Appendix

Extended Hückel calculations[38a] were used, with a weighted H_{ij} formula.[38b] The parameters taken from previous calculations[16a,17i] are listed in Table V.

The geometric parameters of the model compounds were the following.

$Cr_2(CO)_8(\mu\text{-}PH_2)_2$. Cr···C = 1.85 Å, C···O = 1.15 Å, Cr–P = 2.35 Å, P···H = 1.438 Å, angle HPH = 100°, all CCrC angles were taken as 90 and 180°.

Re_2Cl_{10}. ReCl = 2.34 Å; all ClReCl angles were taken as 90 and 180° for the bridged structure. The ReRe bonded structure had optimized 160 and 70° ClReCl angles.

$Re_2(CO)_{10}$. Re–C(terminal) = 1.9 Å, Re–C(bridged) = 2.1 Å, C–O(terminal) = 1.15 Å, C–O(terminal) = 1.18 Å, all CReC angles were taken as 90 and 180° for the bridged and the MM bonded structure.

$Re_2(CO)_8(\mu\text{-}CH_2)_2$. Re–C(terminal) = 1.9 Å, Re–C(bridged) = 2.26 Å, HCH angle = 109.47°, C–H = 1.08 Å, all CReC angles for the terminal ligands were taken as 90 and 180°.

Supplementary Material Available: A summary of experimental data on donor and acceptor bridged M_2L_{10} complexes, with discussion (7 pages). Ordering information is given on any current masthead page.

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(38) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 3179; **1962**, *37*, 2872. (b) Ammeter, J. H.; Bürgi, H. B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

Effects of Basis Set and Configuration Interaction on the Electronic Structure of Methyllithium, with Comments on the Nature of the C–Li Bond

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Abstract: Ab inito calculations have been performed for methyllithium, employing a variety of Slater atomic orbitals in order to assess the basis set dependence of the wave functions of methyllithium and related molecules. Modifications to the electronic structure with changes in basis set are monitored through variations in the total energy, dipole moment, and total electron density, studied with the aid of electron density and density difference maps. The effects of electron correlation are examined by performing a large configuration interaction calculation starting from the most elaborate Hartree–Fock wave function. Previously used criteria for assessing the relative ionic or covalent character of chemical bonds are criticized, on the basis of a comparison of test calculations performed on a series of small molecules. The question of the amount of charge separation involved in C–Li bonding is reexamined by using our more complete wave function.

It has long been recognized that the accuracy of quantitative and even qualitative predictions formulated from the results of ab initio quantum mechanical calculations depends strongly upon the basis set employed. In light of this fact, it is surprising that relatively few studies of the variation in the description of molecular electron density with changes in basis set have been carried out. The majority of the reported investigations of the computational characteristics of various basis sets have tended to focus on the deployment of a limited range of sets of orbitals in the study of a wide collection of molecules.[2-4] The accuracy of the various

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(1) (a) Harvard University. (b) The University of Texas at Arlington.

(2) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(3) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

0002-7863/80/1502-4572$01.00/0

approximations has been generally estimated from a comparison of numerical quantities such as the total molecular energy, dipole moment, or optimized structural parameters. More recently, the effects of the choice of basis set have been approached through the examination of changes in the total molecular electronic density, monitored by using electron density contour maps.[5] Such an approach augments comparisons of numerical quantities with comparisons of total electronic density and density difference maps that provide a detailed picture of the molecular electronic structure and can pinpoint the effects of the addition of extra basis function to specific regions of a molecule. Electron density maps themselves have been extensively used as aids in the visualization and interpretation of computed electronic distributions.[6-17] The total electronic density is preferable to the use of plots of single-orbital densities, atomic or ionic difference maps, or atomic charges as a criterion of comparison, as the total density, which depends only on the square of the molecular wave function, is rotationally invariant and independent of any arbitrary partitioning of charge between atoms or orbitals.

A prior study used a comparison of electron density maps to explore basis set and electron correlation effects in two molecules prototypical of covalent molecules in common bonding modes, H_2O and H_2S, and examined inner-shell correlation corrections for the diatomic molecule BH.[5] This paper represents an extension of that approach to the organometallic compound methyllithium. Several aspects of the bonding of methyllithium make it an interesting and generally illustrative target for study. The presence of low-lying unoccupied 2p orbitals on lithium make CH_3Li an "electron-deficient" molecule,[18] so that trends uncovered might also apply to other electron-deficient species such as the boron hydrides and carboranes. Due to the large electronegativity differences between carbon and lithium, it is expected that the C–Li bond will be highly polar or perhaps even totally ionic, so that methyllithium is also exemplary of molecules with significant charge separation in bonding. Further, recent experimental[19-21] and theoretical[22-27] interest in novel lithium-containing substances such as the alkyllithium oligomers and polylithiated hydrocarbons makes the development of adequate sets of orbital exponents for lithium a necessity.

The exact nature of the bonding between lithium and carbon atoms in organic molecules has recently become a subject of some controversy. Traditionally, organic chemists have tended to view alkyl- and aryllithium compounds as ionic Li^+ salts of the corresponding carbanion, and have rationalized the reactions of organolithium reagents accordingly.[28] However, both experimental[19,20] and nonempirical theoretical studies[22-24] confirm that the alkyllithiums condense to form oligomers exhibiting elaborate multicentered electron-deficient bonding schemes that would not normally be anticipated on the basis of a full-charge separation model. In addition, lithium has been found to be capable of replacing many or all of the hydrogen atoms for a wide variety of hydrocarbon structures.[21,25] Recent theoretical studies of various polylithiated carbon compounds have predicted the existence of highly ideosyncratic networks of multicenter bonds in the optimized structures.[25-27] The near Hartree–Fock basis set plus configuration interaction (CI) calculation reported here represents the most complete and elaborate theoretical treatment of the methyllithium molecule performed to date, and we hope to elucidate the nature of the C–Li bond through an analysis of the CI wave function. In particular, we consider the claim of Streitwieser et al.[29] that the bonding in methyllithium is purely ionic, on the basis of electronic densities and electron projection functions derived from a Gaussian split-shell plus carbon d and hydrogen p orbital basis set calculation.

Computational Methods

Wave functions for all of the molecules and basis sets considered in this paper were determined by using the program POLYCAL,[30-32]coordinated by Dr. R. M. Stevens. POLYCAL is a fully ab initio SCF-CI package computing all of the Hartree–Fock integrals to a specified accuracy (in this case five decimal places) over Slater oribtals. To the basic routines, the authors have added coding to perform standard analyses of SCF and, most recently, CI wave functions and to calculate molecular dipole moments.

SCF calculations on methyllithium were performed by using a series of basis sets possessing increasing numbers of Slater functions, designed to elucidate the changes in molecular properties with the variation of basis set. The smallest set contained only single-orbital exponents for the carbon 1s, 2s, and 2p, lithium 1s and 2s, and hydrogen 1s functions. Although technically a minimal basis set, as the Li 2p orbitals are formally unoccupied in the free atom, we label this a subminimum (SM) basis with respect to the frequent practice of including both 2s and 2p orbitals for all first-row elements in minimum basis set calculations.[33] The inner-shell Slater exponents were taken from Clementi and Roetti,[34] while the remaining exponents were determined by cyclic optimization. This set was augmented by the addition of lithium 2p functions to form a minimum (M) basis. All valence-shell orbital exponents used in this set were reoptimized. In all calculations, equivalent exponents were assumed for all components of the p orbitals, as prior calculations[5] have revealed that only minor improvements occur through the use of anisotropic p functions.

Two different extended basis sets at the double-ζ level were considered. The first, denoted DZ-1LiP, contains only a single lithium 2p shell with optimized exponent. The remaining carbon and lithium orbital exponents were taken from the atomic values of Clementi and Roetti,[34] with the Li 2s functions modified by partial optimization. Hydrogen exponents were taken from McDowell.[35] The single set of 2p functions on lithium was replaced by a pair of 2p orbitals to form the full double-ζ (DZ) basis. The results of exponent optimizations on the ^2P state of the lithium atom were used to estimate the magnitude of the Li 2p exponents, which are

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[4] Collins, J. B.; Schleyer, P. von R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142.

[5] Bicerano, J.; Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 732.

[6] Van Wazer, J. R.; Absar, I. "Electron Densities in Molecules and Molecular Orbitals"; Academic Press: New York, 1975.

[7] Owens, P. H., Streitwieser, A., Jr. "Orbital and Electron Density Diagrams; an Application of Computer Graphics"; Macmillan: New York, 1973.

[8] Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973.

[9] Steiner, E. "The Determination and Interpretation of Molecular Wave Functions"; Cambridge University Press: New York, 1976.

[10] Laws, E. A.; Lipscomb, W. N. *Isr. J. Chem.* **1972**, *10*, 77.

[11] Petke, J. D.; Whitten, J. L. *J. Chem. Phys.* **1972**, *56*, 830.

[12] Petke, J. D.; Whitten, J. L. *J. Chem. Phys.* **1973**, *59*, 4855.

[13] Støgård, A.; Strich, A.; Almlöf, J.; Roos, B. *Chem. Phys.* **1975**, *8*, 405.

[14] Imgartiner, H.; Hase, H.-L.; Schulte, K.-W.; Schweig, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 187.

[15] Hase, H.-L.; Schulte, K.-W.; Schweig, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 257.

[16] Hase, H.-L.; Schweig, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 258.

[17] Absar, I.; Van Wazer, J. R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 80.

[18] Wade, K. "Electron Deficient Compounds"; Appleton-Century-Crofts: New York, 1971.

[19] Brown, T. L. *Adv. Organomet. Chem.* **1965**, *3*, 365.

[20] Oliver, J. P. *Adv. Organomet. Chem.* **1977**, *16*, 235.

[21] West, R. *Adv. Chem. Ser.* **1974**, *130*, 211.

[22] Baird, N. C.; Barr, R. F.; Datta, R. K. *J. Organomet. Chem.* **1973**, *59*, 65.

[23] Guest, M. F.; Hillier, I. H.; Saunders, V. R. *J. Organomet. Chem.* **1972**, *44*, 59.

[24] Graham, G. D.; Richtsmeier, S.; Dixon, D. A., submitted to *J. Am. Chem. Soc.*

[25] Jemmis, E. D.; Poppinger, D.; Schleyer, P. von R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5796.

[26] Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. von R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419.

[27] Jemmis, E. D.; Chandrasekhar, J.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1979**, *101*, 2848.

[28] Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: New York, 1974.

[29] Streitwieser, A.; Williams, J. E.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778.

[30] Stevens, R. M. *J. Chem. Phys.* **1970**, *52*, 1397.

[31] Stevens, R. M. *J. Chem. Phys.* **1971**, *55*, 1725.

[32] Stevens, R. M. *J. Chem. Phys.* **1974**, *61*, 2086.

[33] Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58*, 1569.

[34] Clementi, E.; Roetti, C. *At. Data Nucl. Data Tables* **1974**, *14*, No. 3–4.

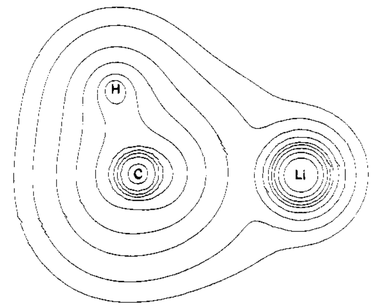

Figure 1. Total electron density of CH_3Li at the SM basis level. Contour values for all of the plots are listed in Table II.

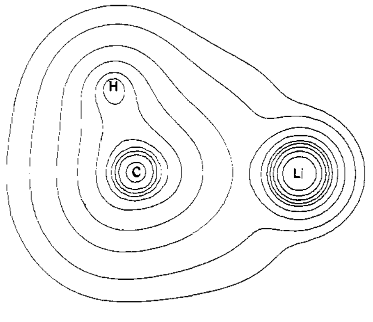

Figure 2. Total electron density of CH_3Li at the NHF-CI level.

found to be more contracted than the 2s orbials. The splitting of exponent values within the 2p shell had to be taken from the Li 2s splitting, as the atomic optimization yields functions inappropriate for valence orbitals involved in chemical bonding.

In order to achieve approximate s,p saturation, we formulated a close to triple-ζ (TZ) basis for carbon and lithium. The carbon exponents were those used by McDowell,[35] while the Li 2s and 2p ζ values were estimated by splitting the DZ quantities. The carbon and lithium inner shell and the hydrogen functions were held at the DZ values. Even though some of the parameters used in this and the other large basis calculations were not rigorously optimized, it is expected that the considerable variational flexibility inherent in the large basis sets should render the calculation rather insensitive to the exact orbital exponents used.[36,37]

To approach the Hartree–Fock limit, we successively added polarization functions to the TZ set for each atom. With the addition of a 3d orbital[35] on carbon (TZ-CD basis) plus a 3d function with assumed exponent on lithium (TZ-CLiD basis) plus finally a set of 2p orbitals[35] on hydrogen, the near Hartree–Fock (NHF basis) limit is reached. The values of the exponents used in all of the basis sets are collected in Table I.

The CI calculation was performed starting from the NHF wave function and is denoted NHF-CI. All symmetry-allowed single and double excitations from the valence MO's to virtual orbitals with eigenvalues less than 4.0 au were included, representing a total of 13 322 Slater determinants.

The molecular coordinates used in all of the methyllithium calculations were the optimized values found by Streitwieser et al.[29]

To provide a frame of reference for a discussion of the bonding in methyllithium, we performed SCF calculations at the double-ζ level for the small molecules Li_2, B_2, F_2, LiF, and Be_2H_2. Standard double-ζ exponents were used for the B,[34] F,[34] and H[35] atoms. The DZ values of Table I were used for Li. The basis for Be was constructed from optimized atomic functions[34] augmented by 2p functions with exponents assumed to be equal to the 2s quantities. The bond lengths of Li_2, F_2, and LiF were taken from experiment.[38] The interatomic distance in B_2 was determined for the excited $^1\Sigma_g{}^+$ state by optimization at the double-ζ level, and it is to this electronic state that all of the results for B_2 contained in this paper refer. The Be–Be distance in Be_2H_2 was optimized at the minimum basis set level by using standard exponents.[2]

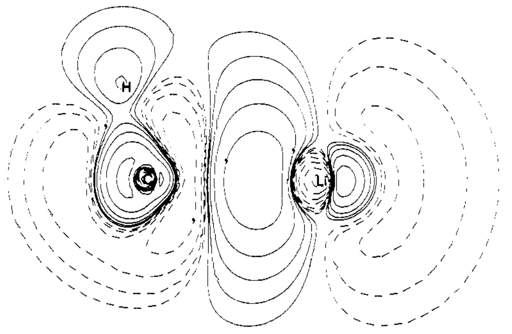

Figure 3. M minus SM density difference map.

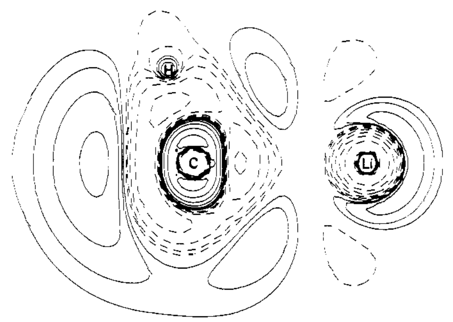

Figure 4. DZ-1LiP minus M density difference map.

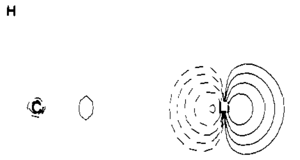

Figure 5. DZ minus DZ-1LiP density difference map.

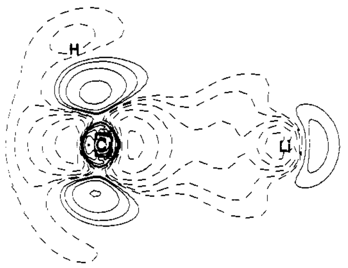

Figure 6. TZ minus DZ density difference map.

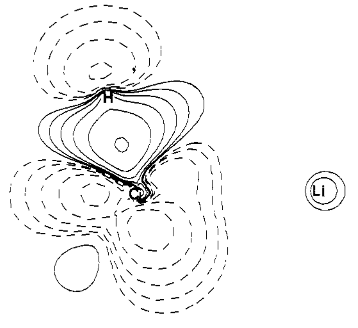

Figure 7. TZ-CD minus TZ density difference map.

Figure 8. TZ-CLiD minus TZ-CD density difference map.

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(35) McDowell, H. K. Ph.D. Thesis, Harvard University, 1972.

(36) Schaefer, H. F., III "The Electronic Structure of Atoms and Molecules. A Survey of Rigorous Quantum Mechanical Results"; Addison-Wesley: Reading, MA, 1972.

(37) Hurley, A. C. "Introduction to the Electron Theory of Small Molecules"; Academic Press: New York, 1976.

(38) Gray, H. B. "Chemical Bonds. An Introduction to Atomic and Molecular Structure"; W. A. Benjamin: Reading, MA, 1973.

Table I. Basis Sets for the Methyllithium Molecule

designation	slater orbital and exponent					
	carbon		lithium		hydrogen	
SM	1s	5.673	1s	2.691	1s	1.18985
	2s	1.68405	2s	0.76589		
	2p	1.58029				
M	1s	5.673	1s	2.691	1s	1.15510
	2s	1.70658	2s	0.77373		
	2p	1.67438	2p	0.89897		
DZ-1LiP	1s	7.522	1s	4.617	1s	1.50360
	1s'	5.123	1s'	2.462	2s	1.43410
	2s	1.831	2s	0.970		
	2s'	1.153	2s'	0.570		
	2p	2.730	2p	0.95883		
	2p'	1.257				
DZ	1s	7.522	1s	4.617	1s	1.50360
	1s'	5.123	1s'	2.462	2s	1.43410
	2s	1.831	2s	0.970		
	2s'	1.153	2s'	0.570		
	2p	2.730	2p	1.160		
	2p'	1.257	2p'	0.760		
TZ	1s	7.522	1s	4.617	1s	1.50360
	1s'	5.123	1s'	2.462	2s	1.43410
	2s	2.141	2s	1.340		
	2s'	1.354	2s'	0.770		
	3s	6.081	2s''	0.370		
	2p	5.152	2p	1.470		
	2p'	2.177	2p'	0.900		
	2p''	1.150	2p''	0.450		
TZ-CD	same as TZ basis set plus					
	3d	1.71680				
TZ-CLiD	same as TZ basis set plus					
	3d	1.71680	3d	1.000		
NHF	same as TZ basis set plus					
	3d	1.71680	3d	1.000	2p	1.74310

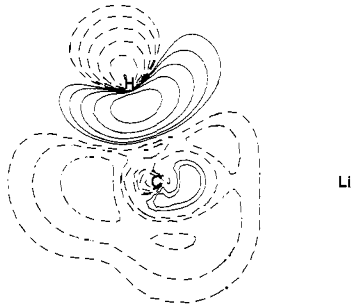

Figure 9. NHF minus TZ-CLiD density difference map.

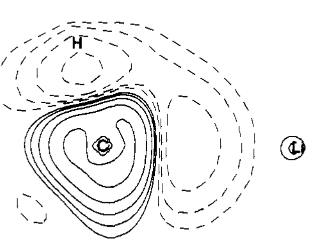

Figure 10. NHF-CI minus NHF density difference map.

Table II. Density Maps Contour Levels^a

total density maps	density diff maps	total density maps	density diff maps
10.000	0.032	0.046	−0.0005
1.050	0.016	0.014	−0.001
0.750	0.008	0.005	−0.002
0.450	0.004		−0.004
0.300	0.002		−0.008
0.210	0.001		−0.016
0.110	0.0005		−0.032

^{a} Contours in electrons/au^3 (e au^{-3}).

Table III. Total Molecular Energies and Dipole Moments for Methyllithium

level of approxmtn	energy^a	energy diff^{a,c}	dipole moment^b	dipole diff^{b,c}
SM	−46.880 342		3.627	
		−0.022 206		+1.047
M	−46.910 548		4.674	
		−0.092 368		+0.899
DZ-1 LiP	−47.002 916		5.573	
		−0.000 195		−0.003
DZ	−47.003 111		5.570	
		−0.010 073		+0.139
TZ	−47.013 184		5.709	
		−0.010 086		−0.029
TZ-CD	−47.023 270		5.680	
		−0.000 318		−0.004
TZ-CLiD	−47.023 588		5.676	
		−0.007 298		−0.058
NHF	−47.030 886		5.618	
		−0.181 887		−0.202
NHF-CI	−47.212 773		5.416	

^{a} Energies in atomic units (au). ^{b} Dipole moments in debye (D). ^{c} Differences between successive approximations.

Plots of the total electron density for each of the methyllithium bases were constructed from a grid of point density values, eight points per atomic unit in each dimension, for a plane containing the carbon, lithium, and one of the hydrogen atoms of the molecule. The changes in the total charge density between successive levels of approximation are relatively small and difficult to detect from these plots. Only the contours for the two most disparate calculations, those at the SM and NHF-CI levels, are reproduced here in Figures 1 and 2.

To reveal the subtle effects of basis set modifications, density difference maps were computed based on sets of grid points determined by subtracting densities for successive basis sets. These plots employ solid contours to denote increases and dashed contours to denote decreases in electronic density and are shown in Figures 3–10. The same contour levels, reported in Table II, were used for all of the drawings to facilitate comparisons among the different figures.

The plotting program was also used to compute electron densities for points along the first-row atom internuclear axes for CH_3Li and the group of comparison molecules.

Basis Set and Correlation Effects

The total energies and molecular dipole moments determined from each of the calculations on methyllithium are collected in Table III, along with the changes occurring in these values with each increasingly complete level of approximation. The most extensive theoretical treatment of methyllithium previously reported[29] is a double-ζ plus carbon d and hydrogen p calculation yielding a molecular energy of −47.0206 au. As revealed by Table III, our calculations using the TZ-CD and larger basis sets predict energies below this limit and are better upper-bound variational estimates of the true total molecular energy.

The addition of just a single 2p orbital to lithium in going from a subminimal to a minimal basis set is seen to have significant effects upon the description of the electronic structure, as shown by the M minus SM difference density plot of Figure 3. The variation in the energy and, especially, in the predicted dipole moment is also substantial. Occasionally, "unoccupied" 2p orbitals are omitted from minimum basis sets for lithium and beryllium. However, these results reveal that such omissions provide inadequate basis sets for Li and Be and may lead to large inaccuracies. The 2s and 2p orbitals of these elements are proximal in energy and both are expected to be important to even a basic description of the molecular bonding, more critical than, for example, higher energy 3d orbitals on carbon. In particular, results from calculations employing an SM "minimal" basis may not be comparable in accuracy to other minimal basis results and may tend to obscure any electron-deficient bonding of lithium, as such bonding is dependent on the presence of extra, formally unoccupied atomic orbitals.

The precise role of the 2p function on lithium is complex, and at least two effects are manifest. The first is that two of the lithium

2p orbitals are of the proper symmetry to interact with π-type symmetry orbitals on carbon and hydrogen. This π bonding is probably responsible for the density increases around the C–H bond region and for some of the increase in electronic charge in the C–Li internuclear zone, possibly those contours biased toward hydrogen. It appears that considerable charge transfer occurs through the π-type interaction, shifting electron density from the back of the Li atom toward carbon along the C–Li axis and shifting charge from the internuclear region near carbon toward the C atom. This mechanism probably accounts for most of the large jump in dipole moment in going from the SM to the M basis.

A second possible effect is that the Li 2p orbital, formally an "unoccupied" atomic orbital with a quantum number l one greater than the highest occupied orbital, may serve as a polarization function for Li, analogous to the effect of adding a 3d orbital to carbon or 2p functions to hydrogen. A comparison of Figure 3 with the plots illustrating the changes occurring upon the addition of such polarizing orbitals (Figures 7–9) reveals that all of these maps show increases in density within the internuclear zones. However, it is clear that the polarization mechanism does not predominate. The overall redistribution of electronic charge in the shift from the SM to the M basis set is far greater than for the addition of single polarization functions to the larger basis sets. Furthermore, the presence of orbitals on lithium that increase atomic polarizability should tend to reduce the total charge separation and, hence, the dipole moment. From an examination of Table III it may be seen that negative dipole differences are found for the addition of C and Li 3d and H 2p functions, whereas the dipole moment undergoes a large increase upon the addition of the Li 2p shell.

The decrease in energy upon shifting from the M to the DZ-1LiP basis is the largest observed for any change in computational procedure with the exception of the inclusion of CI corrections. The marked changes in the electron distribution (see Figure 4) and the dipole moment, far larger than for any subsequent modifications to the basis set, confirm previously noted trends,[5] showing that the largest basis set dependent improvements in calculated charge densities are realized in attaining the double-ζ level. The fact that the molecular dipole moment changes by less than 0.2 D in going from the DZ-1LiP to NHF-CI approximations demonstrates that double-ζ calculations should be fairly accurate for the prediction of gross electronic distributions. Calculations at the double-ζ level may often provide a judicious compromise between precision and computational cost.

As was found to be the case for molecules such as H_2O and H_2S,[5] the shift toward a double-ζ basis results in increases in electron density both directly around the atomic centers and in zones further from the first-row atomic centers along vectors directed away from the bonded atoms. This effect appears to be largely atomic in nature, arising as a natural consequence of the fact that, as shown in Table I, the DZ-1LP basis provides two orbitals per valence orbital of the M basis (except for the Li p), one more contracted about the atomic center (bearing a larger exponent) and the other more diffuse (smaller exponent). The shifting of charge away from the internuclear zones accounts for the increase in dipole moment. It appears that the limited subminimal and minimal bases involve all of the atomic orbitals in covalent bonding and it is only with the more variationally flexible double-ζ bases that the more polar nature of the bonding in this compound can be expressed.

Concomitant large decreases in charge density behind the hydrogen atoms reported for H_2O and H_2S[5] were not observed in this study.

The charge redistribution occurring upon the addition of a second lithium 2p shell to the DZ-1LiP basis to form the full DZ complement of orbitals is illustrated in Figure 5. The perturbation upon the molecular electronic structure is small, the only appreciable change being an increase in the displacement of charge from the C–Li bond region to the far side of the lithium atom, continuing the trend noted in going from the M to DZ-1LiP basis set. The variations in molecular energy and dipole moment are also minute. Thus, while it was shown that the inclusion of a single set of Li 2p orbitals was important in the formulation of a minimum basis set, it seems that the presence of multiple 2p exponents on lithium is not critical to an adequate description of the molecule and the errors introduced by retaining only a single Li 2p orbital in an extended basis set calculation should be small.

The redistribution of charge (see Figure 6) and decrease in molecular energy that accompany the addition of a third set of 2s and 2p orbitals to form the TZ from the DZ basis are significant, being of a comparable magnitude to the changes introduced by the addition of polarization functions. The increase in dipole moment in the TZ calculation is in fact greater than the decreases found for the addition of the high l quantum number orbitals. This underscores the previously reported[5] observation that a double-ζ basis is not synonymous with s,p saturation. The practice of adding polarization functions directly to a double-ζ basis to form the "complete" basis set may thus omit orbital interactions of comparable magnitudes to the corrections introduced.

The TZ minus DZ difference plot reveals that the C–H bonding regions of methyllithium are populated at the expense of the rest of the molecule, with charge coming primarily from the carbon–lithium internuclear zone, as is illustrated in Figure 6. This accounts for the modest increase in dipole moment. It is interesting to note that while the addition of a second group of atomic orbitals to form the DZ from the M basis set resulted in a depopulation of the bonding regions, the shift to the TZ basis selectively increases the C–H and decreases the C–Li shared electronic density and, hence, covalent character. It appears that, for methyllithium, the variationally inflexible minimum basis set includes all of the atomic orbitals significantly in the calculated wave function and tends to overestimate the covalent character of the bonding. The larger double-ζ basis compensates by unilaterally shifting electrons out of the internuclear zones, increasing and perhaps overestimating the amount of charge separation. It is only in the near s,p saturated TZ calculation that sufficient orbitals are present to allow the true nature of the bonding to be reflected in the selective shifting toward ionicity or covalency of different bonds in the molecule.

The addition of polarizing 3d functions centered at carbon to form the TZ-CD set of orbitals has the expected effect of shifting charge density from the carbon atom and surrounding nonbonding regions into the internuclear zone (see Figure 7), accompanied by a decrease in dipole moment. However, appreciable charge is polarized only toward the hydrogen atoms from carbon. A small increase in density is seen directly at the lithium center, but no shift in charge from carbon toward lithium occurs. Apparently, bonding interactions between the carbon 3d orbitals and the appropriate hydrogen symmetry orbitals are more favorable than corresponding interactions with the more diffuse lithium 2s and 2p functions. These results, however, are not necessarily contrary to those anticipated from simple ionic polarizability models, as while the lithium atom is predicted to bear a larger positive charge than the hydrogens (over twice as great at the TZ-CD basis level), it is also significantly farther from the carbon center. Further, there is a considerably higher electron density in the C–H bond than in the C–Li internuclear zone, so that a larger charge redistribution through polarization in this region is not surprising. The effects of the addition of a second set of diffuse d orbitals on carbon are expected to be minimal by analogy to previous findings.[5]

The decreases in energy and dipole moment upon the inclusion of a 3d shell on lithium to form the TZ-CLiD basis are negligible. Similarly, the difference map, shown in Figure 8, illustrates that only a miniscule rearrangement of the electron distribution occurs, shifting some charge from the carbon nuclear region to the C–Li internuclear zone. It is clear that the addition of 3d Li functions to the basis set is largely superfluous. While it was previously demonstrated that a single Li 2p shell is critical to a proper description of molecular bonding and serves as more than a polarization function, it appears that double- or triple-ζ lithium p orbitals are sufficient to allow the expression of the most important polarization effects. The fact that a small decrease in dipole moment occurs with the addition of a second Li 2p function in forming the DZ from the DZ-1LiP basis, in contrast to the increase in charge separation found in going from a minimal to double-ζ basis in the other orbitals, demonstrates that additional p functions act primarily as polarizing orbitals. It should be pointed out, however, that these results pertain to a lithium atom σ bonded to only a single nucleus and do not necessarily apply to the multicoordinated lithium centers that occur in the alkyl lithium oligomers and in polylithiated hydrocarbons, for which the inclusion of d orbitals may well be important, as is often the case for the central atoms of highly coordinated species.

With the inclusion of a 2p shell on the hydrogen atoms, the near Hartree–Fock basis is formed. As shown in Table III and Figure 9, the modifications to the description of the molecular electronic structure are of comparable magnitude to those found for the addition of 3d orbitals to carbon. The NHF minus TZ-CLiD plot reveals that a polarization of charge occurs from the area behind hydrogen away from carbon into the C–H internuclear zone. Also, charge is drawn from the nonbonding regions about carbon and redistributed primarily toward the hydrogens but also toward the lithium atom. The dipole moment decreases, as expected. These effects may be explained by using a simple charge cloud polarization model, but it should be noted that orbital interactions between the hydrogen 2p functions and the carbon orbitals, especially the 3d functions, may account for the specific charge rearrangement observed.

The improvement in the total energy found by performing a large single- and double-excitation CI calculation starting from the NHF wave function is substantial. The correction, –0.18189 au (–114.1 kcal/mol), is larger than the energy change found for the entire series of improvements in augmenting the SM to form the NHF basis set. In light of the large energy decrease, it at first may seem surprising that the overall redistribution of charge, illustrated in Figure 10, is not extensive, being on the order of changes introduced by the addition of the polarization functions to carbon or hydrogen. The change in dipole moment, while larger than that for the addition of polarizing orbitals, is far smaller than the variations induced in proceeding from the SM to M or the M to DZ-1LiP basis set. It must be remembered that configuration interaction involves the redistribution of electronic occupation within the space of the molecular orbitals, whereas basis set extension allows the charge distribution to expand into regions of physical space that were not previously accessible. In addition, the large energetic improvement with the inclusion of CI may arise from the fact that the changes in electronic density that do occur are all in the high-density, high-energy bonding regions of the molecule. These results confirm the well-documented rule that the determination of accurate molecular energies and other "second-order" properties require far more elaborate theoretical treatments than do calculations of electron density distributions or bonding properties.

It is anticipated that correlation corrections should be most important in molecular systems bearing negative charges or possessing regions of concentrated electron density. For methyllithium, the primary effect of the inclusion of CI appears to be a flow of charge density into the area around carbon from both the C–H and C–Li bonding regions and from the hydrogen atoms. These changes are similar, at least qualitatively, to those found for H_2O and H_2S,[5] both of which possess central atoms with a relatively high concentration of charge. No unique effects that might be associated only with a carbanion center are manifest. Curiously, the dipole moment decreases rather than increases, even though the charge is placed primarily into regions proximal to the carbon atom.

The Nature of the C–Li Bond

The minimum values of the total electronic density[29] of methyllithium along the C–Li internuclear axis for both the DZ and the NHF-CI basis sets are reported in Table IV. To facilitate the meaningful interpretation of these quantities, we also included the minimum point densities calculated for the central bond from a double-ζ wave function for the molecules Li_2, B_2, F_2, LiF, and Be_2H_2. For the sake of comparison, calculations on Be_2H_2 and LiF were carried out both with equilibrium bond lengths and with the Be–Be or Li–F bonds set to the C–Li internuclear distance. As demonstrated above, double-ζ calculations are reasonably accurate for the determination of charge distributions. Streitwieser et al.[29] find a minimum density of 0.038 e au^{-3} along the C–Li bond, which they contrast to the corresponding quantity of 0.275 e au^{-3} for the C–H bond as a means demonstrating that the bonding in methyllithium is highly ionic. Our wave function yields the slightly larger but comparable quantities of 0.044 e au^{-3} at the DZ and 0.041 e au^{-3} at the NHF-CI levels. However, by comparing these values to the others in Table IV, it is clear that minimum charge densities of these magnitudes are not in themselves indicative of pure or nearly pure ionic bonding. Li_2, of necessity a totally covalent diatomic, has a minimum internuclear charge less than that found for methyllithium in either study, while the minimum density for the ionic LiF at its equilibrium bonding distance is greater.

Table IV. Bond Lengths and Minimum Interatomic Electron Densities

molecule	bond	basis set	bond length^a	min density^{b,c}
Li_2	Li–Li	DZ	2.673^e	0.013
B_2^{d}	B–B	DZ	2.013^f	0.093
F_2	F–F	DZ	1.417^e	0.242
Be_2H_2	Be–Be	DZ	2.059^f	0.070
			2.021^g	0.073
LiF	Li–F	DZ	1.564^e	0.080
			2.021^g	0.025
CH_3Li	C–Li	DZ	2.021^h	0.044
		NHF-CI		0.041

^{a} Bond lengths in Å. ^{b} Densities in e au^{-3}. ^{c} Minimum density determined by computing point densities along the internuclear axis at 0.05 au intervals. ^{d} $^1\Sigma_g{}^+$ state. ^{e} Experimental distance. ^{f} Optimized (see text). ^{g} Set to the C–Li bond length. ^{h} Optimized value taken from ref 28.

Chemical bonds are phenomena occurring in all three spatial dimensions. Any index of ionicity or covalency based on a charge density criterion must take into account the integrated electronic density over a volume appropriate to the bond in question. This is demonstrated by the strong correlation between the minimum charge densities and bond lengths for the bonds listed in Table IV, the shorter bonds having the higher densities. In fact, the minimum density values for the purely covalent molecules are very approximately proportional to the inverse cube of the bond length. A further proof comes from a comparison of the minimum electron density for the C–Li bond of methyllithium calculated from the DZ vs. the NHF-CI wave function. Although the NHF-CI dipole moment is 0.154 D less than the DZ value, the minimum internuclear electron density for the NHF-CI basis set is smaller, contrary to what would be expected if a lower point density indicated an increase in charge separation. A comparison of Figures 1 and 2 reveals that the most noticeable effect of basis set improvement is a dispersion of charge over a larger area, particularly in the neighborhood of the C–Li bond. Thus, the NHF-CI point density is lower than the DZ becasuse the bonding electrons have been spread out over a greater effective volume, not because the bond ionicity has increased.

The nature of an individual chemical bond in a polyatomic molecule is not an invariant or well-defined molecular property. Many analytic indices are strongly basis set dependent and implicitly involve arbitrary and at times inappropriate partitioning schemes. The use of Mulliken overlap populations or atomic charges[39] has been criticized[29] for these reasons. Comparisons of minimum total charge densities fail to take into account the effects of varying bond volumes. In addition to this inadequacy, criteria based on a consideration of minimum charge densities computed from the valence molecular orbitals again rely upon an arbitrary assumed charge-partitioning scheme. Further, even purely covalent molecules may have regions of very low electron

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(39) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

density in the bonding orbitals occurring between the atomic nucleus and the bond center. Such behavior is found, for example, for the 3σ MO of Li_2. Projection functions,[29,40] in which electron density is projected into two dimensions by integrating the square of the wave function over the remaining coordinate, still fail to take into account the three-dimensional nature of bonding. In reality, only an integration of the electron density function over the full spatial extent of a chemical bond that could be compared to bonds in other molecules or, perhaps, to integrations over atomic zone volumes would provide the proper measure of the qualitative ionic-covalent classification. However, explicit rules for the determination of appropriate bond volumes have yet to be formulated and once again would most likely rely on arbitrary assumptions. At present, the most prudent course is either to limit oneself to the consideration of invariant molecular properties such as the dipole moment or to attempt to interpret data such as internuclear point densities in light of their observed dependence on bond length.

Some evidence that the bonding in methyllium is considerably less ionic than that in LiF comes from a comparison of the minimum charge densities in Table IV. As this quantity has been shown to be strongly bond length dependent, it is only appropriate to compare the charge density of the C–Li bond to densities of other bonds with very similar bond lengths. Both B_2 and Be_2H_2 have equilibrium central bond lengths close to the C–Li distance. To facilitate a quantitative comparison, we computed the minimum internuclear charge density for a Be_2H_2 geometry with the Be–Be bond shortened slightly to equal the C–Li bond length of 2.021 Å. The calculated value, 0.073 e au^{-3}, is taken to represent the minimum point density of a completely covalent bond at the C–Li distance. To estimate the expected minimum charge in the limit of totally ionic bonding, we performed a similar calculation for LiF with the Li–F distance lengthened to 2.021 Å. As expected, the dipole moment increases sharply with the increased bond distance and a minimum point density of 0.025 e au^{-3} is found, much smaller than the quantity of 0.080 e au^{-3} calculated for equilibrium LiF. Comparing the Be_2H_2 and LiF minimum densities at the C–Li bond length to the value of 0.044 e au^{-3} found for the C–Li bond in methyllithium with the DZ basis, it is seen that minimum density criteria reveal the bonding in CH_3Li to be approximately in between the ionic and covalent limits, perhaps a little biased toward ionic bonding. Thus, methyllithium appears to be about 60% ionic, but it clearly is far from the limit of complete ionicity expected for a molecule such as LiF.

If the dipole moment of CH_3Li is modeled by the presence of fractional point charges located at the carbon and lithium nuclei, our results predict about a 0.57+ charge on lithium. Here, the small contributions from the C–H bond moments directed along the C–Li bond axis are ignored. Curiously, this agrees well both with the above estimate based on the minimum point densities and with the charge of 0.56+ computed from a Mulliken analysis of the DZ wave function, although the NHF-CI calculation yields the smaller Mulliken charge of 0.44+. For comparison, the double-ζ calculation on the ionic LiF with its bond length set to the C–Li distance in methyllithium predicts a dipole moment of 8.000 D, which translates to about 0.82 electron of charge localized on each atom. A criticism of the point-charge model is that it fails to account for the reduction of the total dipole moment caused by a polarization of the anionic charge cloud toward the positively charged center. Thus, a predicted charge separation of 0.82 rather than 1.00 for LiF might be ascribed to a displacement of the F^- electrons. With the assumption that the polarizabilities of the CH_3^- and F^- anions are of approximately comparable magnitudes, the amount of charge necessary to correct for all polarization effects in LiF to give a unit charge separation, representing the most extreme correction possible, can be used to adjust the CH_3Li results as well. If this quantity (0.18 electron) is added to our estimate of the charge separation in methyllithium from the dipole moment, a maximum charge separation of about 0.75 electron is obtained for the latter molecule, slightly lower than the value of 0.8 given by Streitwieser et al.[29] for CH_3Li.

However, as previously indicated, the actual charge separation may be considerably less than this maximum quantity. The Mulliken population analysis[39] has been faulted for measuring the overlap between orbitals everywhere in a molecule, rather than only in bonding regions, possibly resulting in the misapportionment of charge, especially to centers possessing diffuse orbitals. The overlap among atomic orbitals is highly distance-dependent, and such errors should be far less severe for longer bonds, like the C–Li bond in methyllithium, than for short bonds. This is reflected in the excellent agreement between the dipole moment and Mulliken predictions of the Li atomic charge based on the DZ wave function, in contrast to the results for LiF at its normal bond length. Thus, even though arguments employing such analyses must be regarded as somewhat speculative and criteria based on the total molecular wave function are to be preferred, the validity of the Mulliken scheme cannot be totally discounted in this case, as it predicts atomic charges that are not inconsistent with the independent and more reliable criteria described above. The 0.44+ charge found from the NHF-CI calculation may be taken as a minimum estimate of the charge separation, with the minimum electron density and dipole estimate of approximately 0.57+ being a compromise between the Mulliken and polarized dipole approximations.

A predicted charge separation of 0.55–0.60 electron seems reasonable in light of the chemical evidence. This amount of charge polarization is sufficient to make ionic mechanisms believable, but not so complete as to rule out occasional radical behavior. The approximately half-covalent character of carbon–lithium bonding would not prohibit the existence of polylithiated species or organolithium oligomers with "electron deficient" bonding schemes. In fact, elaborate and unusual multicenter bond networks might be especially prevalent in such compounds, as both the presence of vacant p orbitals and the partial positive charge contribute to the lithium atom's electron deficiency.

Conclusions

Several trends from our study of the basis set dependence of ab initio molecular orbital calculations should be generally applicable to other molecules possessing highly polar bonds or electron-deficient centers. The role of p orbitals on lithium is found to be intermediary between that of bonding and polarization functions. The inclusion of at least one 2p shell is critical to even a minimal description of the electronic structure, but additional p functions may serve as polarization functions and the inclusion of 3d orbitals appears to be largely superfluous. Major improvements are attained in going from a minimal to a double-ζ basis, and the gross charge distribution obtained at the double-ζ level is subject to only small subsequent modifications. The double-ζ basis is found to fall short of full s,p saturation, and the changes predicted for the addition of a third set of valence s and p orbitals on the first row atoms are of comparable magnitudes to the effects of adding polarizing 3d functions to carbon and 2p functions to hydrogen. Finally, although only a modest redistribution of charge occurs upon performing a near full single-double excitation CI, the energy corrections are found to be very large.

By a comparison of the results of calculations on several small molecules, minimum internuclear charge densities and density projection functions are shown to be unreliable indices of molecular bonding. From a consideration of the molecular dipole moment of methyllithium, along with an examination of Mulliken charges and minimum charge densities in light of their dependence on molecular geometry, the charge separation along the C–Li bond can be set at between 0.45 and 0.75 electron, with a value of about 0.55–0.60 electron appearing to be the most reasonable estimate.

Acknowledgments. This research was supported in part by a grant from the National Science Foundation. One of the authors (G.D.G.) also thanks the National Science Foundation for a Predoctoral Fellowship.

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(40) Streitwieser, A.; Collins, J. B.; McKelvey, J. M.; Grier, D.; Sender, J.; Toczko, A. G. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2499.