

Integrated Spatial Electron Populations in Molecules: Application to Simple Molecules

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The electron projection function $P(x, z) = \int \rho(x, y, z) dy$ is used to evaluate charge transfer and covalency in two series of molecules, LiX and CH₃X (X = Li, BeH, BH₂, CH₃, NH₂, OH, and F), with wavefunctions derived from STO-3G, 4-31G, and, in some cases, 6-31* *ab initio* calculations. The precision of the method and comparison with Mulliken populations analysis are described. Particular attention is given to CH₃Li which by our criteria is wholly ionic.

INTRODUCTION

The analysis of electron distributions in molecules is of paramount importance in the chemical interpretation of molecular wavefunctions. Although the electron density function provides a complete description of electronic structure, it is a four-dimensional function that can be perceived only one plane at a time. As a consequence use is generally made of population functions. The simplest scheme, due to Mulliken,¹ suffers from numerous deficiencies (ref. 2 and citations therein) that limit its reliability. Direct integration of the electron density functions circumvents many of the problems inherent in the Mulliken method. Several authors have carried out these integrations, either by integrating the wavefunction over its angular coordinates³⁻⁵ in spherical polar space [eq. (1)],

$$P(r) = \int_0^{2\pi} \int_0^\pi \rho(r, \theta, \phi) r^2 \sin \theta d\theta d\phi \quad (1)$$

where $\rho(r, \theta, \phi)$ is the electron density in spherical polar space, or by integrating over two coordinates in Cartesian space^{3c,6-10} [eq. (2)],

$$P(z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(x, y, z) dx dy \quad (2)$$

The former function is most applicable to cen-

trosymmetric systems such as atoms, whereas the latter applies best to linear systems.

We have recently introduced² a projection function which extends these approaches to non-linear systems that are adequately represented by a plane [eq. (3)]:

$$P(x, z) = \int_{-\infty}^{\infty} \rho(x, y, z) dy \quad (3)$$

The principal advantage of this expression over that given in eq. (2) is that the added Cartesian dimension of eq. (3) permits the assignment of electrons to any region in x, z space, whereas eq. (2) permits only linear analysis. As shown below, eq. (3) can be integrated numerically over the x coordinate to yield the results obtainable by eq. (2).

Electron density plots of various types are increasingly common in the chemical literature but only relatively few studies have been made of integrated electron populations. Most of these studies are of small individual molecules⁶⁻⁸; only a few studies provide comparisons of a series of molecules.¹⁰⁻¹³ We report here an initial study that compares several features of the electron projection function by application to two series of simple molecules, CH₃X and LiX (X = Li, BeH, BH₂, CH₃, NH₂, OH, and F). In particular, we analyze the basis set dependence of charge distribution, σ vs. π effects in charge transfer, and the question of ionicity versus covalency in highly polar species. The descriptions that result are compared with

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corresponding estimates from Mulliken population analysis. It is intended that this study provide a framework for subsequent extension to other types of molecular system.

THEORETICAL METHOD

The main obstacle to the solution of eq. (3) is the provision of sufficient resolution in the numerical integration procedure to allow quantitatively meaningful charges to be assigned to any region in the x,z plane. This is a particularly severe consideration in regions encompassing atomic nuclei because here the wavefunction varies steeply. We have reported in detail elsewhere¹⁴ an efficient procedure by which $P(x,z)$ in eq. (3) can be replaced by its *average* value, $\bar{P}(x,z)$, in which this value is effectively the average of a large number (ca. 2000–10,000) of individual points in the neighborhood of (x,z) . The averaging procedure permits arbitrarily precise (generally <0.001 electron for all molecular orbitals) assignment of charge to various spatial regions without the necessity of a prohibitively expensive increase in the number of function evaluations. At present, intervals between sampling points of 0.2 a.u. (1 a.u. = $0.529 \times 10^{-10}M$) provide accurate charge assignments over spatial regions large enough (20×20 a.u.) to include fairly large organic molecules. In those instances in which an interval smaller than 0.2 a.u. is desired parabolic interpolation produces results nearly identical to those from a tenfold finer sampling grid (e.g., 0.02 a.u.).

In the applications below charges are associated with atoms or groups of atoms by first integrating $P(x,z)$ over x [eq. (4)] to obtain $P(z)$ [equivalent to eq. (2)], followed by

$$P(z) = \int_{-\infty}^{\infty} P(x, z) dx \approx \sum_{x_{\text{initial}}}^{x_{\text{final}}} P(x, z) \cdot \Delta x \quad (4)$$

partitioning of $P(z)$ at its minimum (z_0), according to eq. (5):

$$N_e = \int_{-\infty}^{z_0} P(z) dz \quad (5)$$

where N_e is the number of electrons in the region extending from $-\infty$ to z_0 and z_0 is the point at which $P(z)$ is a minimum. This minimum corre-

sponds approximately to Bader's "virial boundary"¹¹ and provides a simple albeit not unique basis for comparisons in our series.

The simplifying reduction to a single Cartesian coordinate is made in this initial application to establish points of reference for further studies. In later applications full use of the added versatility of eq. (3) will be applied to nonlinear systems.

RESULTS AND DISCUSSION

Basis Set Dependence

In view of the well-known basis set dependence of Mulliken population analysis, we chose to examine first the sensitivity of the wavefunction itself to gross changes in the quality of the basis set. Three systems that place the greatest demands on the basis were selected, namely, CH_3Li , LiF , and CH_3F . Projection function calculations were carried out with STO-3G,¹⁵ 4-31G,¹⁶ and 6-31G*,¹⁷ basis representations of Pople and co-workers, and with standard geometrical models.¹⁸ The projection function $P(x,z)$ was integrated according to eq. (4) and the difference plots are shown in Figures 1(a), (b), and (c) [$P(4\text{-}31\text{G}) - P(\text{STO-}3\text{G})$] and 2(a), (b), and (c) [$P(6\text{-}31\text{G}^*) - P(4\text{-}31\text{G})$].

Several features of the difference plots stand out. First, the differences are small. Indeed, when plotted on a scale that permits the individual functions to be displayed in their entirety, the differences are barely discernible. Second, the largest effects in enlarging the basis from the minimum STO-3G occur around the cores of the heavy atoms. This is not surprising in view of the behavior of Gaussian functions at the cusp. Third, in the change from STO-3G to 4-31G small net charge transfer occurs in all cases from the region behind (i.e., on the side away from the central bond) the more electropositive atom (or groups) to the region behind the more electronegative atom. Between these extremes there is what appears as a "polarization wave" which results from the displaced charge. The effect of adding polarization functions in the change from 4-31G to 6-31G* is primarily a reverse polarization at the heavy atoms; that is, the 4-31G basis overcorrects the STO-3G results and the 6-31G* basis provides

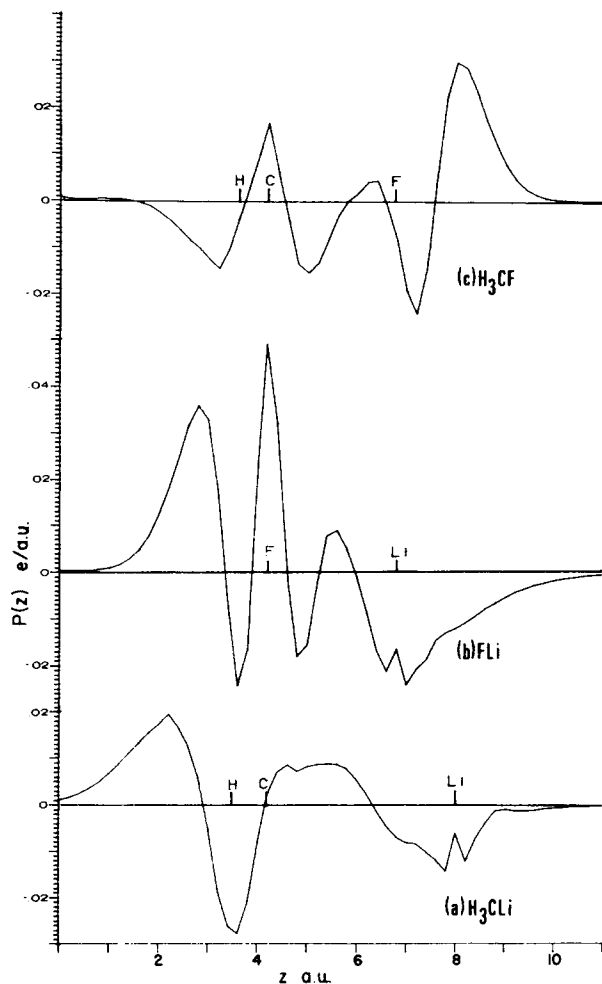


Figure 1. Difference of $P(z)$ calculated from two basis sets, $P(4-31G)-P(STO-3G)$: (a) CH_3Li , (b) FLi , (c) FCH_3 .

some readjustments. The amount of net charge transfer can be seen by examining the atomic charges in Table I calculated with the three basis sets. In the severest case (LiF) 0.24 electrons are transferred from Li to F when the basis is changed from $STO-3G$ to $4-31G$, whereas the average difference is ca. 0.1 electron. The differences between $4-31G$ and $6-31G^*$ are much smaller.

These comparisons demonstrate that the integrated populations derived from the minimum basis $STO-3G$ results are qualitatively reliable and, in fact, better than similarly derived Mulliken populations. The $4-31G$ integrated results differ but little from the larger basis $6-31G^*$ results. There is some dependency on the position of the

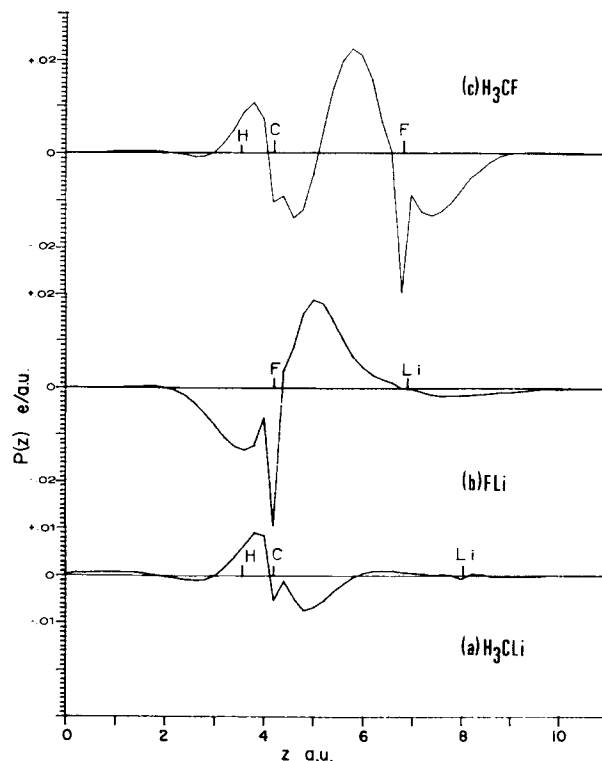


Figure 2. Difference of $P(z)$ for two basis sets, $P(6-31G^*)-P(4-31G)$: (a) CH_3Li , (b) FLi , (c) FCH_3 .

projection function minimum between atoms on basis set (Table II) that emphasizes the rather arbitrary nature of any scheme that assigns charges to molecules. Nevertheless, for those schemes in which the boundary occurs near the function minimum a split-shell type of basis such as $4-31G$ suffices to give a reasonable assignment of spatial electron populations.

Wiberg¹³ has recently discussed the effect of basis set on spatial hydrogen populations in bonds to hydrogen. He finds polarization or bond functions important in getting reasonable results. Bonds to hydrogen are especially difficult to dissect in any nonambiguous fashion. There is often little or no density minimum to provide a stationary region. Despite these problems, for a consistent definition and with a sufficient basis Wiberg does obtain useful correlations of his derived hydrogen charges. Nevertheless, we have chosen to consider the charge on the methyl group as a whole rather than to attempt to dissect it between carbon and hydrogen.

Table I. Comparison of calculated charges by the Mulliken population analysis with integrated spatial electron populations.

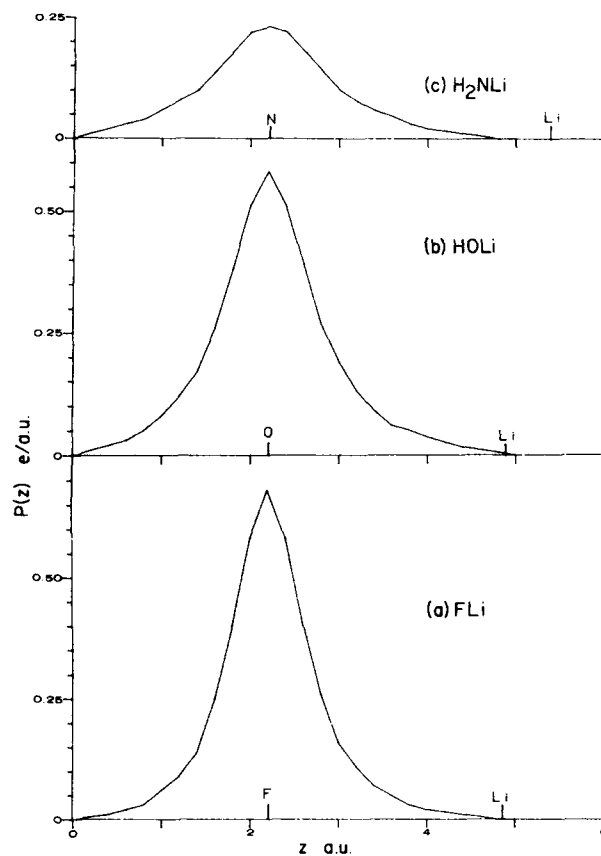
	STO-3G		4-31G		6-31G*	
	Mulliken	Integration	Mulliken	Integration	Mulliken	Integration
Charge on lithium						
LiF	+0.226	+0.615	+0.715	+0.859	+0.639	+0.874
LiOH	+0.177	+0.588	+0.650	+0.814		
LiNH ₂	+0.202	+0.634	+0.558	+0.793		
LiCH ₃	+0.146	+0.701	+0.451	+0.794	+0.416	+0.797
LiBH ₂	-0.090	+0.595	+0.201	+0.688		
LiBeH	-0.106	+0.554	-0.086	+0.593		
LiLi	0	0	0	0		
Charge on methyl						
CH ₃ F	+0.153	+0.425	+0.455	+0.549	+0.395	+0.617
CH ₃ OH	+0.119	+0.329	+0.345	+0.405		
CH ₃ NH ₂	+0.091	+0.238	+0.196	+0.240		
CH ₃ CH ₃	0	0	0	0		
CH ₃ BH ₂	-0.114	-0.568	-0.247	-0.561		
CH ₃ BeH	-0.141	-0.699	-0.388	-0.730		
CH ₃ Li	-0.146	-0.701	-0.451	-0.794	-0.416	-0.797

Table II. $P(z_0)$: Amplitude of $P(z)$ at its minimum z_0 [distance (a.u.) from C in CH₃X, from X in LiX]; 4-31G basis set (6-31G* basis).

	z_0 (a.u.)	$P(z_0)$ (e^- /a.u.)
LiF	1.774 (1.787)	0.084 (0.089)
LiOH	1.825	0.097
LiNH ₂	2.151	0.085
LiCH ₃	2.726 (2.727)	0.066 (0.066)
LiBH ₂	3.006	0.070
LiBeH	3.309	0.070
LiLi	2.525	0.066
CH ₃ F	1.166 (1.113)	0.223 (0.234)
CH ₃ OH	1.236	0.223
CH ₃ NH ₂	1.298	0.233
CH ₃ CH ₃	1.455	0.227
CH ₃ BH ₂	1.959	0.195
CH ₃ BeH	2.356	0.109
CH ₃ Li	2.726 (2.727)	0.066 (0.066)

σ vs. π Effects

One advantage of the projection function technique over orbital density diagrams is that it allows representation of all types of molecular orbital (i.e., σ , π , Δ) in the same plane. We chose to use this feature to examine the question of backbonding to an electropositive element, namely, Li. Some properties of lithium compounds have been attributed to the existence of low-lying, vacant p - π atomic orbitals.¹⁹ Consequently we examined the degree of π bonding to Li in LiF, LiOH, and LiNH₂. The projection functions $P(z)$ of the π molecular orbitals (HOMO) of the three species are

**Figure 3.** $P(z)$ π -MO of (a) LiF, (b) LiOH, and (c) LiNH₂.

plotted in Figure 3. The results are for the 4-31G basis, but the 6-31G* result is virtually identical. It is clear that in all three compounds the value

$P(z)$ at the lithium atom is almost zero. Quantitatively, it does not exceed 2% of the value at the electronegative atom. Indeed, there is but little polarization of the lone pair toward lithium. In LiF, for example, if we consider a plane at the F nucleus orthogonal to the F—Li bond, 0.93 electron lies behind this plane in the 6-31G* result for each of the degenerate HOMOs (F lone pair) and 1.07 electrons lie between this plane and Li. Consequently lithium p - π orbitals play essentially no role. The charge transfer that does occur in LiX molecules is mediated by σ -type MOs in which polarization is provided mathematically by Li p wavefunctions.

Ionicity versus Covalency

The concepts of ionic and covalent bonds have been embodied in chemistry for many decades.²⁰ In this section we examine archetypal examples of ionic, covalent, and polar covalent bonds, namely, those in LiF, CH₃CH₃, and CH₃F, to observe the characteristics of each type of bond. In Figure 4(a) the projected density $P(z)$ (4-31G) of LiF is examined. The ionic bond is characterized by a high degree of charge transfer and a low value of $P(z)$ at its minimum $P(z_0)$. This is indicative of only a small degree of shared electron character. The comparisons of 6-31* and 4-31 basis sets demonstrate that this conclusion is not sensitive to basis set. The same result is derived for earlier studies of the effect of basis set on the electron density function for LiF.²¹

Conversely, Figure 5(d) shows $P(z)$ for CH₃CH₃. Here there is no charge transfer and $P(z_0)$ is large (0.227 versus 0.084 $e/a.u.$ for LiF; Table II). Finally, Figure 5(a) shows a polar covalent bond (CH₃—F) characterized by charge transfer and large $P(z_0)$.

Using these criteria, we can now attempt to classify the bonds in the other species examined here. The position of the $P(z)$ minimum and its value are summarized in Table II for both series of compounds. The series LiX is examined first [Figs. 4(a)–(g)]. In no case does lithium form a bond with a large value of $P(z_0)$ in the internuclear region. In all cases, however (except, of course, Li₂), a large degree of charge transfer (Table I) occurs

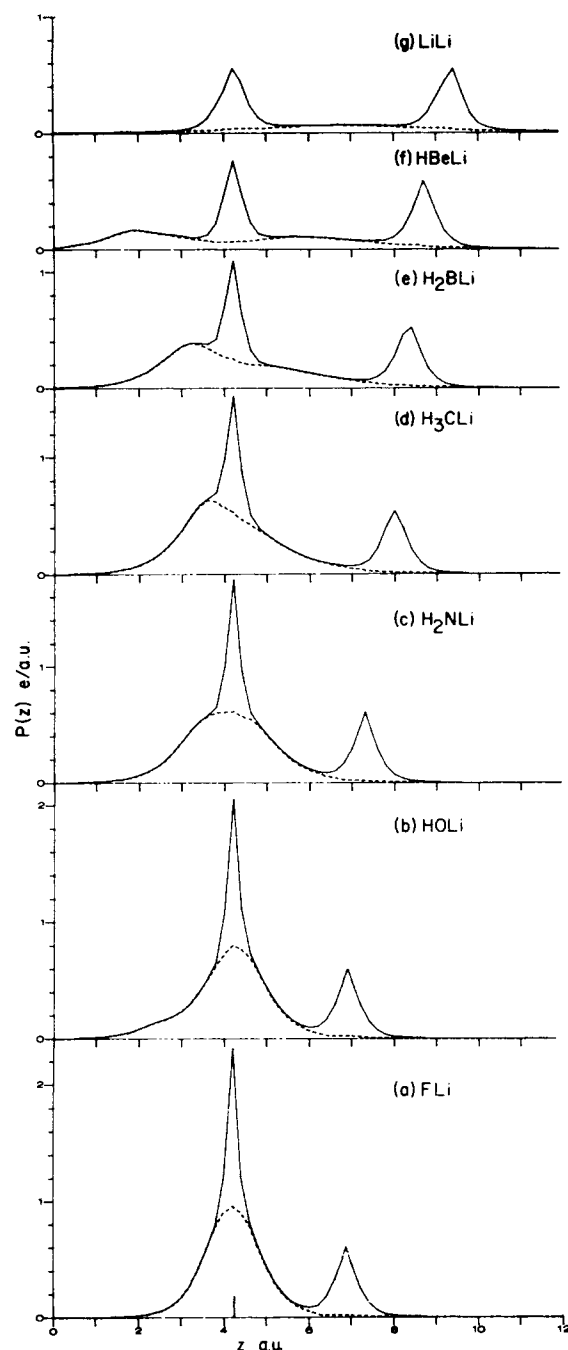


Figure 4. $P(z)$ for LiX: (—) total $P(z)$; (---) $P(z)$ for valence MOs; 4-31G basis set. X = (a) F, (b) OH, (c) NH₂, (d) CH₃, (e) BH₂, (f) BeH, (g) Li.

from lithium to the more electronegative element. Even LiBeH appears to have a strongly ionic bond. The situation for the series CH₃X is more complex [Figs. 5(a)–(f)]. For X = F, OH, NH₂, CH₃, and

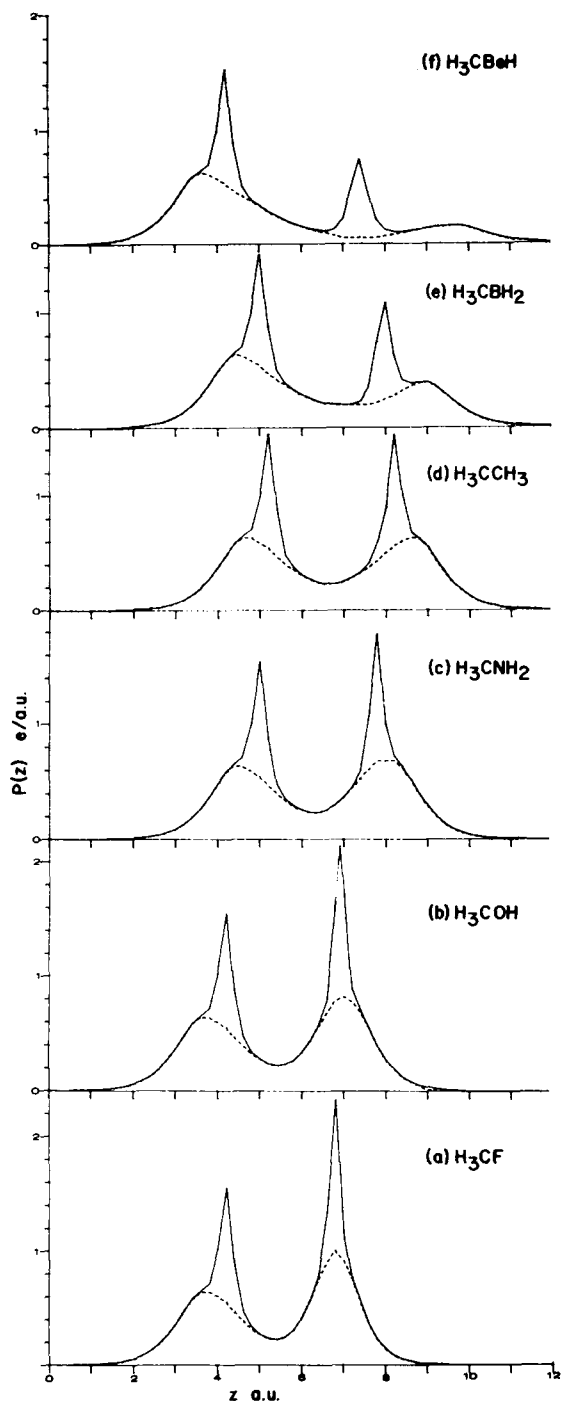


Figure 5. $P(z)$ for CH_3X : (—) total $P(z)$, (---) $P(z)$ for valence MOs; 4-31G basis set. X = (a) F, (b) OH, (c) NH_2 , (d) CH_3 , (e) BH_2 , (f) BeH .

BH_2 , $P(z_0)$ has the characteristics of a covalent bond. Nonetheless, both CH_3F and CH_3BH_2 display charge transfer of ca. 0.5 electron. Conversely, CH_3BeH and CH_3Li have both large charge

transfer (ca. 0.7 electron) and rather low values of $P(z_0)$. In this respect CH_3Li , CH_3BeH , and all the LiX s share the electronic characteristics of the unambiguously ionic LiF , whereas CH_3BH_2 , CH_3NH_2 , and CH_3OH resemble CH_3F . The C—Be bond, however, does show perceptibly more covalent character than any of the bonds to Li.

The covalency of methyl lithium has been examined frequently. In a recent study of electron density patterns Hinchcliffe and Saunders²² concluded that CH_3Li is covalent because the density in the bonding region is shared equally. Our interpretation²³ differs because there is so little density that, although it may be shared equally, it does not meet the essential criterion of significant covalency.

In comparison with other compounds discussed Li_2 is in a class by itself. As a homonuclear diatomic there is no charge transfer, but $P(z_0)$ has low magnitude. Indeed, the valence electrons do not peak at the nuclei and are rather diffuse. The Li—Li bond is long and weak and Li_2 may represent the simplest case of a true metallic bond.

Comparison with Mulliken Populations

Because one aim of this work is to provide a means of assigning electrons to molecular regions, it is useful to compare the results obtained from the projection function with those taken from Mulliken population analysis. Table I shows this comparison for the basis sets studied.

In a comparison of the results it is important to remember that Mulliken populations are basis set populations assigned to the atoms on which they are centered with a defined division of overlap populations. Integrated spatial populations depend on the definition of individual space. For this reason it is convenient to distinguish ionic and other noncovalent bonded systems from those sharing significant electron density. The former group consists of individual regions with so little overlap that assignment of space to individual atoms or groups involves little ambiguity.

The lithium compounds LiX , in which X ranges from BH_2 to F, fall into this ionic category. For all cases direct integration shows substantially more charge transfer than Mulliken analysis. The effect

is especially pronounced in the minimal basis set (STO-3G) but important even in the larger bases. It is probably a result of mathematical functions centered on lithium being required to help define electron-rich adjacent regions but assigned by the procedure to lithium. In LiBeH the Mulliken scheme has BeH donating ca. 0.1 electron to Li, whereas direct integration shows transfer of ca. 0.6 electron in the opposite direction. No reasonable change in spatial assignments will change this gross result. One clear conclusion from this comparison is that Mulliken populations involving Li compounds are wholly unreliable and should not be given serious consideration.

For compounds involving significant covalency the situation is more complex because the integrated populations are now more sensitive to spatial divisions which are not so clear-cut; for example, in polar covalent systems demarcations based on empirical covalent radii are seriously different from demarcations based on *P* minima. Nevertheless, Mulliken populations show qualitative agreement with integrated populations by use of consistent criteria for spatial regions such as minimum *P*, particularly for bonds between carbon and elements to the right of the periodic table.

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