corresponding values of other carbons can be calculated by using the equation

$$(R_1{}^{\mathrm{e}})_i = R_1{}^{\mathrm{e}}(\mathrm{f}) + \left(\frac{r_{2x}}{r_{ix}}\right)[(R_1{}^{\mathrm{e}})_2 - R_1{}^{\mathrm{e}}(\mathrm{f})] \qquad (10)$$

The results given in Table IV indicate very good agreement between theory and experimental results. This is especially noteworthy since the competition between indole and $CDCl_3$ for Tempo has been neglected and since the electron nuclear dipole–dipole interaction has been assumed to dominate completely the relaxation in the complex.

Acknowledgment. We thank Dr. Eric Johnston, Dr. D. Dalling, and Mark S. Solum for their valuable discussions and experimental assistance. This work was supported by the Department of Energy, Division of Fossil Energy, under the Grant No. DE-FG22-80PC30226.

Registry No. Pyridine, 110-86-1; pyridazine, 289-80-5; *s*-triazine, 290-87-9; pyrazine, 290-37-9; pyrimidine, 289-95-2; 2,2′-dipyridyl, 366-18-7; quinoline, 91-22-5; isoquinoline, 119-65-3; quinazoline, 253-82-7; 2-picoline, 109-06-8; 3-picoline, 108-99-6; 6-methylquinoline, 91-62-3; 7-methylquinoline, 612-60-2; 8-methylquinoline, 611-32-5; 1,5-diazabicyclo[4.3.0]non-5-ene, 3001-72-7; imidazole, 288-32-4; indole, 120-72-9; naphthalene, 91-20-3; Tempo, 2564-83-2.

Representation of Electron Densities. 1. Sphere Fits to Total Electron Density Surfaces

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Abstract: A method is detailed enabling fits to calculated total electron densities using spheres of adjustable radii centered on the nuclear positions. Best atomic radii are obtained for a series of molecules with use of Hartree–Fock models. Minimal split-valence and polarization basis set results are compared. The dependency of atom size (in molecules) on the electronegativity of attached groups and on steric and strain conditions is examined, and a set of average radii for use in molecular models is proposed. Comparisons between calculated radii and atomic charges obtained from Mulliken population analyses suggest that the latter method generally underestimates the population of hydrogen and overestimates the population of lithium and sodium.

The size and shape of a molecule are defined by the positions of the nuclei and the spatial distribution of the electrons about them. As such, visual representations of electron distributions, i.e., *electron densities*, can be instrumental in helping in the understanding of both the structures of molecular systems and their potential reactivity. Because some electron density may be found even at very large distances from the nuclear positions, examination of the *total electron density* function itself is not revealing. More useful is a representation obtained by constructing an *electron density surface*, defined by a fixed *electron density contour*, within which the volume, surface area, various contact distances, etc., are determined and, given identical contours, may be compared for different molecules.

The determination of electron density surfaces from quantum mechanical wave functions is not yet practical for all systems of interest, e.g., large biomolecules. Still, some idea of the "electronic" size and shape of a particular species may be garnered by constructing space-filling representations with, for example, CPK models.[2] Such representations, while easily manipulated and highly portable, will not be as accurate nor as flexible as direct portrayals of the electron density as calculated from quantum mechanics. Nevertheless, in many instances models of this type may provide significant information.

In order to combine the convenience and portability of CPK-type models with the inherent accuracy and generality of quantum mechanical electron density representations, we have recently developed a technique for fitting calculated electron density surfaces to spheres centered on the nuclei.[3] In addition to the obvious convenience, i.e., portability, brought about by representing calculated electron densities by nuclear-centered spheres, definition of the set of "optimum" radii for atoms in a molecule provides a means for assessing *intramolecular* electronic effects. For example, one would expect to see the effects of substitution by electron-withdrawing and electron-donating groups manifested as the decrease or increase, respectively, of the size, i.e., radius, of the atom to which the substituent is attached. Effects on atom size could be quantified and might be related to (or even used as a measure of) substituent electronegativity. In addition, relationships between the sizes of atoms in molecules and measurable properties such as NMR chemical shifts and coupling constants might be anticipated.

The use of models in which atoms in molecules are represented as interconnecting spheres, while presumably obscuring features such as π clouds and nonbonded lone pairs, is, in fact, not without support. It has previously been noted that electron densities formed by the superposition of calculated atom densities effectively mimic actual surfaces.[4] Models constructed on this basis usually assume that the radius of a particular element is invariant, or that it can be approximated by one of a small set of fixed radii for different molecular environments.[5] The variation, or lack thereof, in atomic size as evaluated by comparing radii from sphere fits can provide some notion of the transferability of this type of data.

The partitioning of the space occupied by a molecule into spherical regions is not an unusual approach. Such schemes have been used to evaluate atomic populations. Radii for these analyses have been established in a variety of ways, e.g., using tabulated van der Waals radii[6] and the radius at which the spherically averaged density is at a minimum.[7] In the SCF-Xα-SW method[8]

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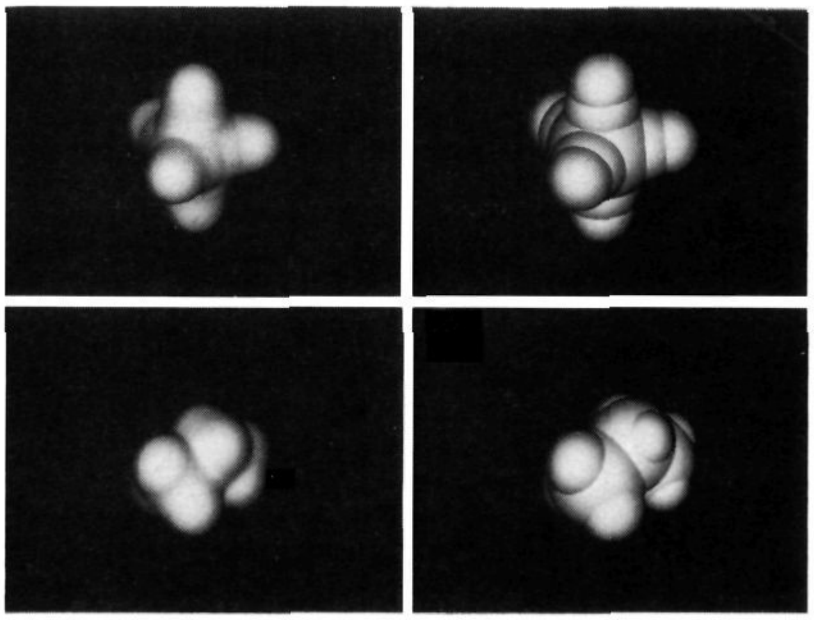
the total potential is evaluated by dividing the space in and near a molecule into three regions, including a spherically bound area centered on each nuclei. The spheres are constrained to touch and the resulting potential to be continuous at the contact points. Gross atomic populations can be determined by using the spheres so determined.[9] Yet another scheme for determining the local electronic charge on an atom is based on fitting a basis of spherical Gaussian functions to charge densities from ab initio calculations.[10] The latter method is especially useful for the comparisons of theoretical data with that from X-ray structure determinations. It is clear that spherical partitioning is a natural procedure, providing an easily interpretable set of parameters.

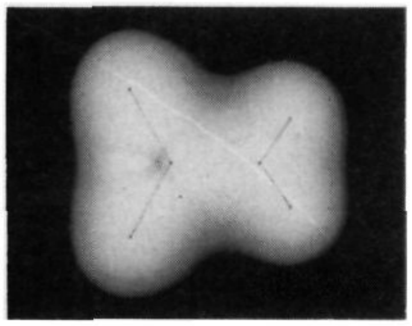
Our goals in this paper are twofold. The first is to systematically examine best (spherical) atom fits to electron densities in molecular systems as a function of theoretical level. Previous work has suggested that properties derived from calculated electron densities, e.g., atomic charges, are quite sensitive to the level of theory employed.[11] While it is desirable that applications be made at a high enough level of theory such that results closely resemble those of limiting quantum mechanical treatments, it is absolutely necessary to know what the magnitudes of errors due to limitations in the particular model will likely be. Our second objective will be to delineate the factors that influence atom size in molecules and to explore correlations between size and electronegativity as well as steric and strain effects. We will also be concerned with the limitations of transferability of atomic sizes from one molecular environment to another and with the possible utility of the theoretical data as a means for formulating portable and accurate space-filling representations.

Calculational Methods

All calculations have been performed by using Hartree–Fock models and the STO-3G,[12] 3-21G[13a,b] (3-21G$^{(*)}$[13c] for molecules incorporating second-row elements), and 6-31G*[14] basis sets. The Gaussian 83 series of computer programs has been employed.[15] Optimized geometries, used throughout in this work, have either been reported elsewhere[13,14,16] or are given in the text.



igure 1. Total electron densities (left) and sphere fits to total electron ensities (right) for iron pentacarbonyl (top, STO-3G//STO-3G) and thylsilane (bottom, 3-21G$^{(*)}$//3-21G$^{(*)}$).



igure 2. Total electron density for $H_2Ti{=}CH_2$. STO-3G//STO-3G.

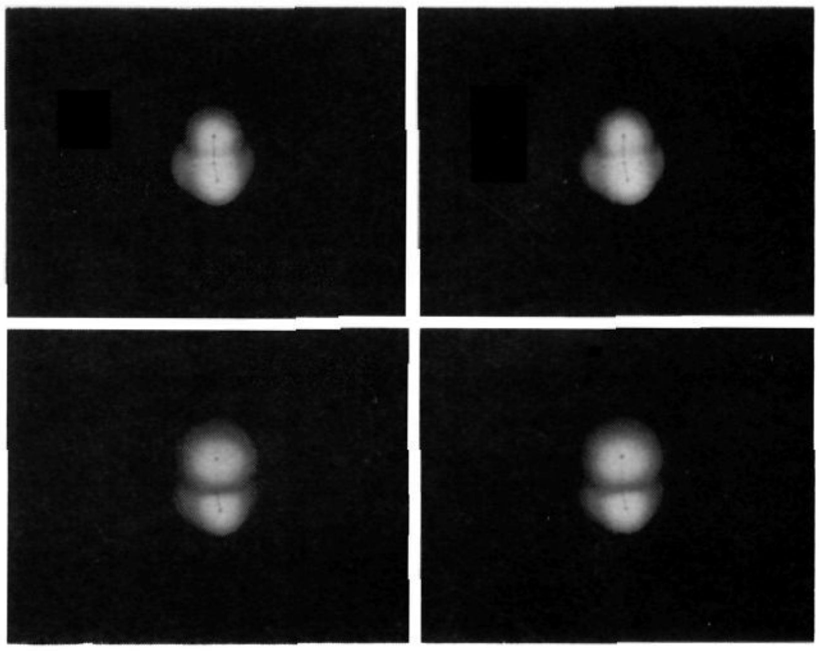


Figure 3. Total electron densities (left) and valence electron densities (right) for methyl fluoride (top, 3-21G//3-21G) and methyl chloride (bottom, 3-21G$^{(*)}$//3-21G$^{(*)}$).

Calculated electron density surfaces correspond to a contour level of ψ^2 equal to 0.002 e$^-$/bohr^3. These enclose approximately 98% of the total electron density and yield best atom radii comparable to average van der Waals distances (see section following on Average Bonding Radii in Molecules). [An alternative procedure would be to define a contour level for each molecule so as to enclose a fixed (high) percentage of the total electron density. Such an approach suffers in that a surface incorporating a fixed percentage of the total density of a molecule containing a large number of electrons is not directly comparable to the surface of equal percentage enclosure for a molecule with a small number of electrons.] The techniques used in constructing and displaying the density surfaces shown below have been described in detail elsewhere.[17]

Atomic radii were determined in the following fashion. For each atom in the molecule an initial guess radius, r, is provided, and a subset of points is selected from a set of 194 points distributed nearly uniformly on a sphere of radius r, such that no point in the subset impinges on the space enclosed by any other sphere. The gradient of the electron density is evaluated at each point in the subset. Following the gradient vector, the point of contact with the fixed surface ($\psi^2 = 0.002$) is determined, relative to the distance from the atomic center. The radius for an atom is taken to be the average of the contact distances for that center. The process is then repeated by using the set of calculated radii as initial guesses until convergence is reached to within a preset tolerance (0.005 Å in this work).

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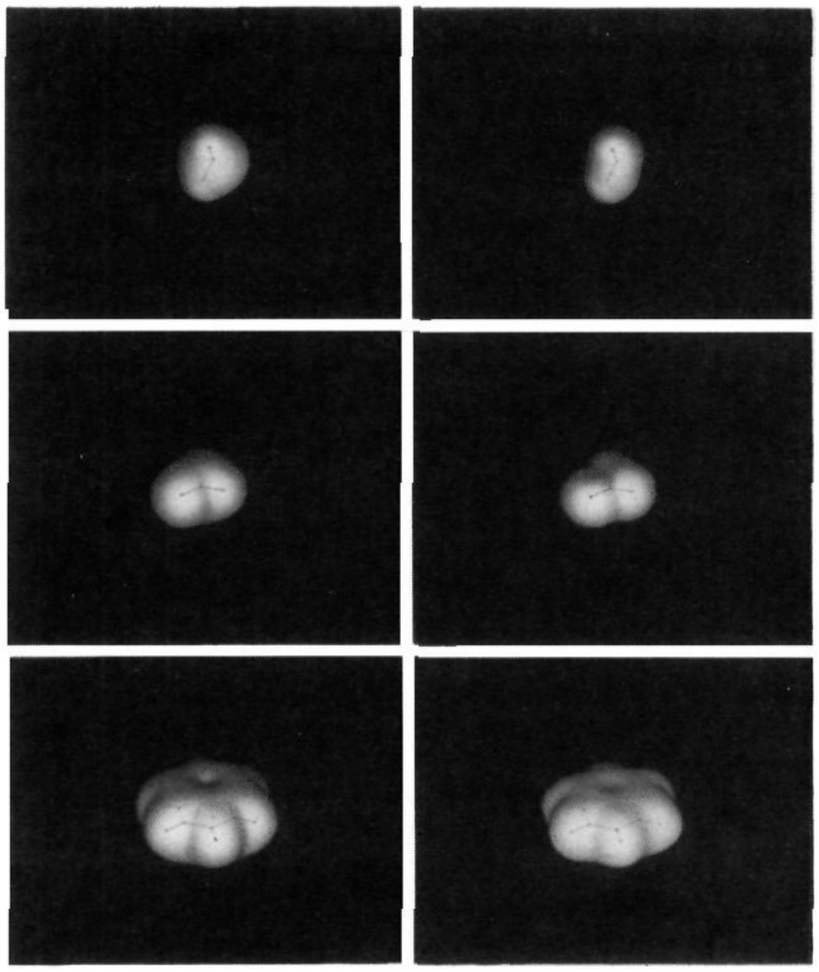

Figure 4. Total electron densities (left) and total electron densities constructed eliminating specific molecular orbitals (right) for ammonia (top, missing nitrogen lone pair), formaldehyde (middle, missing π orbital), and benzene (bottom, missing π system). 3-21G//3-21G.

Discussion

Use of Superposed Spheres as Models. Portrayals of electron density distributions as superposed best-fit spheres are visually nearly identical with the calculated electron density surfaces from which they are derived, e.g., Figure 1. The principal difference between the two representations is the sharper demarcation of atoms in the sphere fit model. We note, however, that nuclear-centered spheres may not always provide accurate representations of actual electron density surfaces. For example, the total electron density surface for $H_2Ti{=}CH_2$, shown in Figure 2, contains a modest depression rather than a bulge directly over titanium. This is due to the fact that the titanium–carbon π bond is made up of a d-type function on the metal and that, unlike a p orbital, this function contains a nodal plane passing through the metal perpendicular to the plane of the molecule.[18]

As is evident from the examples given in Figure 3, electron density surfaces constructed by using only the set of valence molecular orbitals are not noticeably different from those obtained by using both core and valence functions. More significant is the observation that the surfaces appear to change only slightly as a result of removal of "chemically interesting" molecular orbitals from the total density representations. Compare the total electron density surfaces of ammonia, formaldehyde, and benzene with surfaces produced by eliminating the lone pair, π bond, and aromatic π systems, respectively (Figure 4). In effect, spherical models are derived in just this way, either acknowledging the anisometric character of atoms in such systems and establishing an "average" radius or assuming that such features are relatively unimportant in determining the size and shape of a molecule and ignoring them.

Selection of Theoretical Level. Many studies have compared calculated electron density surfaces to those determined experimentally by X-ray diffraction.[19] These comparisons are not without their difficulties; discrepancies may be due not only to failings in the theoretical models but also to uncertainties in the experimental data and to interactions between molecules in the crystal environment, not considered in isolated-molecule calculations. Electron density surfaces derived from near-limiting Hartree–Fock calculations have, in general, been found to be in good agreement with experimentally derived surfaces, and the limited number of studies which have explicitly considered the effects of electron correlation on density distributions suggests their relative unimportance.[20] This is fortunate, as Hartree–Fock models are more widely applicable than schemes that take partial account of electron correlation.

Table I. Sphere Fit Radii of Hydrogen in Compounds HX *(Standard Deviations in Parentheses)*

molecule[a]	radius of hydrogen, Å		
	STO-3G	3-21G (3-21G$^{(*)}$)	6-31G*
H_2	1.182 (0.041)	1.19 (0.07)	1.212 (0.034)
LiH	1.648 (0.219)	1.699 (0.181)	1.714 (0.192)
BeH_2	1.389 (0.096)	1.464 (0.096)	1.409 (0.103)
BH_3	1.298 (0.063)	1.356 (0.063)	1.320 (0.053)
CH_4	1.222 (0.041)	1.192 (0.050)	1.236 (0.043)
NH_3	1.185 (0.043)	1.128 (0.035)	1.161 (0.043)
OH_2	1.167 (0.051)	1.079 (0.042)	1.081 (0.037)
FH	1.148 (0.045)	1.005 (0.041)	1.007 (0.037)
NaH	1.367 (0.107)	1.679 (0.163)[b]	1.693 (0.182)[c]
MgH_2	1.347 (0.092)	1.568 (0.157)[b]	1.569 (0.162)[c]
AlH_3	1.323 (0.072)	1.435 (0.083)[b]	1.421 (0.103)[c]
SiH_4	1.282 (0.050)	1.370 (0.053)[b]	1.316 (0.060)
PH_3	1.265 (0.050)	1.320 (0.053)[b]	1.302 (0.037)
SH_2	1.238 (0.049)	1.241 (0.061)[b]	1.242 (0.037)
ClH	1.179 (0.043)	1.173 (0.033)[b]	1.173 (0.028)

[a] All molecular geometries from ref 11a, unless otherwise noted. [b] Molecular geometry from ref 13c. [c] Molecular geometry from ref 14b.

The minimal STO-3G basis set,[12] presently defined for the first 54 elements of the periodic table, is small enough to be routinely applicable to reasonably large molecules. Much better representations such as the 6-31G* polarization basis set,[14] currently defined for first- and second-row elements, yield properties, e.g., equilibrium geometries and relative energies, that often closely approach Hartree–Fock limiting values. However, basis sets of this size are readily applicable only to relatively small systems comprising four to five heavy atoms at most. The recently developed split-valence 3-21G representation[13a,b] and the related 3-21G$^{(*)}$ supplemented split-valence basis for second-row elements[13c] offer a compromise between the widespread applicability of STO-3G and the high quality of properties derived from the 6-31G* basis set. These basis sets are significantly smaller than 6-31G*, and hence can be applied to a wider variety of systems. The results of 3-21G (3-21G$^{(*)}$) calculations are of a quality comparable to those from the larger, more flexible 6-31G* basis.

We have compared the sphere-fit radii derived from the minimal, split-valence (and supplemented split-valence) and polarized basis sets for selected atoms in three series of molecules, hydrogen in HX, methyl carbon in CH_3X, and both α and β carbons in $CH_2{=}CH(X)$, where X is one of a variety of substituents. The data are given in Tables I–III. Note that in nearly all cases, carbon radii from 3-21G calculations are larger than those obtained from either STO-3G or 6-31G* models. This is consistent with work by Streitwieser,[16] who has recently reported that atomic charges derived from STO-3G electron densities are uniformly smaller than values from 6-31G* calculations, while those obtained from the 4-31G split-valence basis set[22] are generally larger.

The "quality" of the sphere fits, as determined by the standard deviation for each atom, is tabulated with the radii in Tables I–III. Errors in the fits are insensitive to basis set; the mean errors are 0.066, 0.067, and 0.068 Å for STO-3G, 3-21G (3-21G$^{(*)}$), and 6-31G* calculations, respectively. As the standard deviations are

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(18) For a discussion, see ref 17b.

(19) For recent reviews, see: (a) P. Coppens and E. D. Stevens, *Adv. Quantum Chem.*, **10**, 1 (1977); (b) P. Coppens, *Angew. Chem., Int. Ed. Engl.*, **16**, 32 (1977); (c) A. Streitweiser, Jr., *Tetrahedron*, **37**, 345 (1981).

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Table II. Sphere Fit Radii of Methyl Carbon in CH_3X (Standard Deviations in Parentheses)

	radius of methyl carbon, Å		
molecule[a]	STO-3G	3-21G (3-21G$^{(*)}$)	6-31G*
CH_3F	1.758 (0.055)	1.813 (0.052)	1.732 (0.049)
CH_3OH	1.776 (0.049)	1.844 (0.049)	1.763 (0.058)
CH_3NO_2		1.851 (0.059)[b]	
CH_3NH_2	1.809 (0.051)	1.872 (0.050)	1.808 (0.058)
CH_3CN		1.873 (0.051)	1.783 (0.048)
CH_3Cl	1.794 (0.056)	1.877 (0.052)[c]	1.773 (0.042)[d]
CH_4	1.773 (0.044)	1.882 (0.047)	1.802 (0.043)
$CH_3C{\equiv}CH$	1.800 (0.051)	1.883 (0.053)	1.795 (0.049)
CH_3CH_2CN		1.889 (0.047)	
CH_3SH	1.803 (0.051)	1.895 (0.046)[c]	1.822 (0.050)[d]
CH_3CH_2Li		1.896 (0.048)	
CH_3CH_2F		1.897 (0.049)	
$CH_3CH{=}O$	1.802 (0.054)	1.898 (0.051)	
$CH_3CH{=}CH_2$	1.810 (0.059)	1.903 (0.058)	1.829 (0.062)
CH_3CH_3	1.811 (0.052)	1.905 (0.049)	1.883 (0.051)
CH_3SiH_3	1.908 (0.052)	1.922 (0.044)[c]	1.862 (0.048)[d]
$CH_3CH_2CH_3$		1.928 (0.069)	
CH_3Li	1.980 (0.174)	2.028 (0.177)	2.007 (0.109)

[a] All molecular geometries given in ref 16a, unless otherwise noted. [b] CH_3NO_2: CN 1.493, NO_a 1.239, NO_b 1.242, CH_c 1.073, CH_g 1.078 Å, $\angle CNO_a$ 117.7, $\angle CNO_b$ 116.1, $\angle NCH_e$ 107.3, $\angle NCH_gH_{g'}$ 120.6, $\angle H_gCH_{g'}$ 110.4°; subscripts c, g, g′ refer to relative orientations of the CH bond to O_a of 0° and ±60°, respectively. The angle NCH_gH_g' is that between the CN bond and the bisector of the two out-of-plane methyl hydrogens. [c] Molecular geometry from ref 13c. [d] Molecular geometry from ref 14b.

a measure of the nonspherical nature of the atoms, and as they are relatively insensitive to absolute size, this result is not unexpected. The sherical-atom model appears to be least appropriate for atoms attached to highly electropositive elements. Thus, the standard deviation in the carbon radius for CH_3Li at 3-21G is 0.117 Å, while that for CH_3F is only 0.052 Å. Deviations in the radius of hydrogen are also much larger for LiH (0.181 Å) and NaH (0.163 Å) than for FH (0.041 Å) and ClH (0.033 Å). Fitting to nuclear-centered ellipsoids rather than spheres may produce a better model for these systems. Alternatively, allowing the spheres fit to hydrogen atoms to be centered away from the nuclear positions may also improve the fit. Bonding distances to hydrogen derived from X-ray crystallographic data are generally shorter than distances separating the nuclei, suggesting that the center of electron density is shifted away from hydrogen, in the direction of the connecting atom. The center of charge on atoms in highly strained rings may also be significantly shifted away from the nucleus. Again, off-center spheres may be necessary to produce more accurate models. Both of these improvements to the simple spherical-atom model considered in the present paper are currently under investigation in our laboratory.

As the data in Figures 5 and 6 clearly indicate, no good linear relationships exist between hydrogen radii (in HX compounds) obtained from minimal basis set STO-3G calculations and those derived from either the 3-21G or the 6-31G* representations. (Several earlier studies have also indicated the inadequacies of minimal basis sets in describing electron density surfaces.) It is likely that calculated STO-3G density surfaces (or sphere fits to these surfaces, while certainly capable of uncovering gross features, will not provide a reliable source of quantitative data.

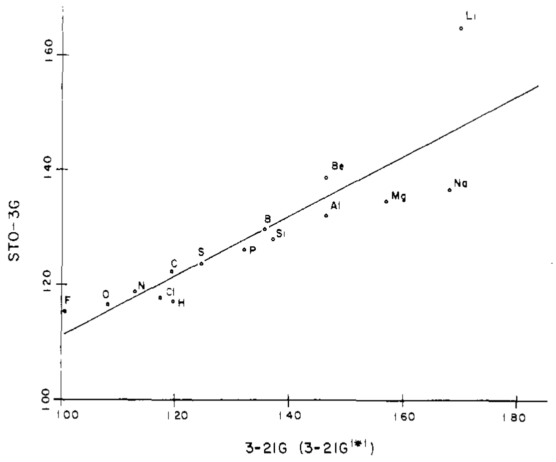

Figure 5. Correlation of STO-3G and 3-21G (3-21G$^{(*)}$) hydrogen radii (angstroms) in compounds HX.

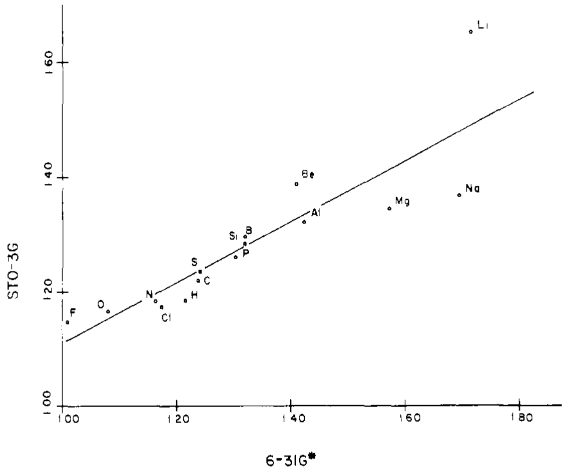

Figure 6. Correlation of STO-3G and 6-31G* hydrogen radii (angstroms) in compounds HX.

On the other hand, hydrogen radii from 3-21G and 6-31G* calculations for the complete set of one-heavy-atom, first- and second-row hydrides are nearly identical (Figure 7); the average absolute deviation between the two sets of data is only 0.02 Å. This is hardly surprising since the descriptions provided hydrogen are also nearly identical for the two basis sets, i.e., polarization functions are not included on hydrogen in the 6-31G* basis set. If polarization functions were to be included on hydrogen atoms, e.g., use of the 6-31G** basis,[14] significant changes in size and perhaps relative size might be expected. The sphere fit radii for hydrogen in a small selection of HX compounds given in Table

Table III. Sphere Fit Radii of α and β Carbons in Compounds $CH_2{=}CHX$ (Standard Deviations in Parentheses)

	radius α-C, Å			radius β-C, Å		
molecule[a]	STO-3G	3-21G	6-31G*	STO-3G	3-21G	6-31G*
$CH_2{=}CHF$	1.698 (0.063)	1.821 (0.059)		1.730 (0.058)	1.866 (0.047)	
$CH_2{=}CH(OH)$		1.823 (0.048)	1.772 (0.051)		1.882 (0.051)	1.840 (0.064)
$CH_2{=}CH(NH_2)$	1.717 (0.063)	1.844 (0.043)		1.743 (0.067)	1.888 (0.052)	
$CH_2{=}CH(CN)$		1.871 (0.044)[b]			1.850 (0.058)[b]	
$CH_2{=}CH_2$	1.726 (0.057)	1.871 (0.055)	1.725 (0.057)	1.726 (0.057)	1.871 (0.055)	1.725 (0.057)
$CH_2{=}CH(CH_3)$		1.888 (0.051)	1.837 (0.057)		1.876 (0.057)	1.821 (0.059)
$CH_2{=}CHLi$	1.889 (0.182)	2.000 (0.115)		1.778 (0.096)	1.884 (0.048)	

[a] All molecular geometries given in ref 16a, unless otherwise noted. [b] $CH_2{=}CH(CN)$: C=C 1.319, C≡N 1.140, C–C 1.427, C_α–H 1.072, C_β–H_{cis} 1.072, C_β–H_{trans} 1.072 Å, $\angle CC_\alpha C_\beta$ 112.8, $\angle C_\alpha C_\beta H_{cis}$ 122.0, $\angle C_\alpha C_\beta H_{trans}$ 120.8, $\angle C_\beta C_\alpha H$ 121.5°. Subscripts cis and trans refer to position of H relative to CN group.

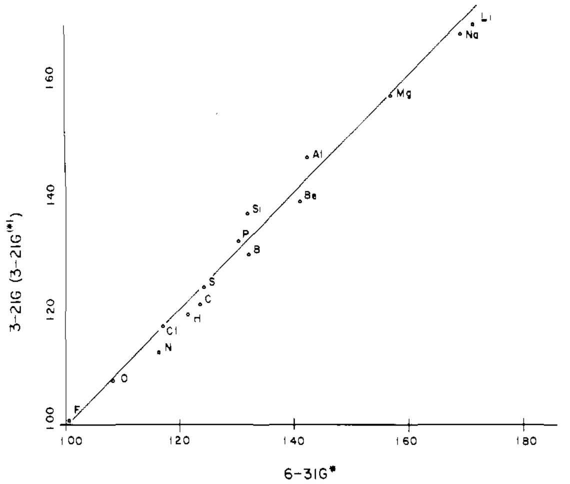

Figure 7. Correlation of 3-21G (3-21G$^{(*)}$) and 6-31G* hydrogen radii (angstroms) in compounds HX.

Table IV. Sphere Fit Radii of Hydrogen in Compounds HX from 6-31G* and Supplemented 6-31G* Basis Sets

	radius of hydrogen, Å	
molecule	6-31G*	supplemented 6-31G*^{a,b}
LiH^c	1.714	1.724
SiH_4	1.316	1.306
H_2S	1.242	1,252
HCl	1.173	1.180
H_2O^c	1.081	1.107
HF^c	1.007	1.026

[a] See text for description of basis set. [b] Optimized 6-31G** structures used. Structures reported in ref 14b unless otherwise noted. [c] Structures reported in ref 17b.

IV, obtained using the 6-31G* basis set supplemented on the hydrogens by single-Gaussian s- and p-type functions (with Gaussian exponent 1.10), are consistently larger than the corresponding 6-31G* values, but only by an average of 0.014 Å. While basis sets that include polarization functions on hydrogen may be necessary for the accurate determination of absolute hydrogen size, the fact that the relative sizes of hydrogen in molecules appear to be faithfully reproduced without such supplementary functions supports the utility of the smaller representations.

Heavy-atom radii are (expectedly) more sensitive to the addition of polarization functions to the heavy-atom representations. Radii from 6-31G* calculations are typically smaller than those obtained from the 3-21G basis. This is consistent with the fact that bond lengths derived from polarized basis sets are nearly always shorter than those obtained from split-valence representations. [It should be mentioned that Hartree–Fock limiting bond lengths are nearly always shorter than experimental equilibrium values. Electron correlation treatments affect mixing of excited-state configurations which generally are more loosely bound than the ground-state structure. For a discussion see ref 33.] In addition, 6-31G* radii are more sensitive to substituent perturbations than values derived from the 3-21G basis set, i.e., they span a broader range. Note, however, that a good linear correlation exists between heavy-atom radii calculated at the two levels of theory. Scaled results from the smaller basis set should accurately mimic those obtained from the larger representations.

We find the 3-21G basis set (3-21G$^{(*)}$ for second-row elements) to be best suited for our purposes, and all applications which follow have been carried out at this level. The failure of STO-3G to produce reasonable quantitative results is unfortunate, since use of a minimal representation would place fewer restrictions on the systems that could be conveniently investigated. Sphere fits to STO-3G electron densities are probably not completely inutile, as the overall structure of the surface appears to be credibly reproduced. The method will certainly be appropriate for such tasks as determining whether or not a molecule will fit in a receptor site.

Table V. Average Sphere Fit Radii from the 3-21G (3-21G$^{(*)}$) Basis Set

atom	radius^a	standard deviation^b	ver der Waals radius^c
H (C-H)	1.190	0.024	1.20
H (N-H)	1.104		
H (O-H)	1.069	0.010	
H (Si-H)	1.365	0.011	
H (P-H)	1.320		
H (S-H)	1.242		
C (sp^3)	1.893	0.050	1.70
C (sp^2)	1.874	0.042	1.70
C (sp)	1.812	0.028	1.78
N (sp^3)	1.734		1.55
N (sp)	1.668		1.60^d
O (sp^3)	1.566	0.002	1.52
O (sp^2)	1.549		1.50^d
F	1.420	0.002	1.40
Si (sp^3)	2.004	0.049	2.1
P (sp^3)	2.051		1.80
S (sp^3)	2.016		1.83
Cl	1.934		1.76

[a] Average radius (angstroms) for all atoms of this type found in all compounds considered in the present paper. [b] Standard deviations (angstroms) are not reported for samples of less than five molecules. [c] Radii (angstroms) taken from ref 23. [d] Average of contact distances for σ and π directions. See ref 23.

Average Radii of Bonded Atoms. The assignment of *average radii* for "bonded" atoms in molecules is not a trivial matter, and gross simplifications are often necessary. Contact distances in molecular and atomic crystals are the most frequent measure of van der Waals radii.[23] Packing densities and the properties of liquids and gases are also often used to derive volume and radii data.[24] The spatial extent of atoms has also been estimated from atomic ionization potentials.[25] All such "experimental" techniques are limited in the molecular environments to which they can be applied. Ionization potentials, a property of the free atom, can never reflect changes in radii as a result of bonding. Contact distances can only be determined for atoms on the "outside" of a molecule, restricting the type of environments that can be investigated. Radii are usually presumed to be unaffected by changes in molecular environment, even though experimental contact distances are often found to differ significantly from one environment to another. The determination of radii from a uniform level of theory transcends these difficulties; a consistent set of atomic radii can be found given only the constraints of the theoretical model.

Radii from 3-21G (3-21G$^{(*)}$) calculations generally agree well with "accepted" values. [As mentioned previously, selection of $\psi^2 = 0.002$ e$^-$/bohr^3 defining the electron density surface was based in part on matching calculated radii to van der Waals distances.] The effective radius of F, for example, is usually taken to be 1.40 Å.[23] Calculated values for HF, CH_3F, $CH_2{=}CH(F)$, and SiH_3F are respectively 1.420, 1.423, 1.419, and 1.355 Å. The average calculated radius of hydrogen attached to carbon in the compounds that we have investigated is 1.19 Å, compared to 1.20 Å, the value usually assumed. Average calculated radii and standard deviations for a number of commonly encountered atoms are reported in Table V. A hydrogen radius for general use has not been provided, since the molecular environments differ so greatly, from lithium hydride, where hydrogen is formally hydride anion, to hydrogen fluoride, where its description approches that of a free proton. Separate radii appropriate for use for bonding to nitrogen, oxygen, silicon, phosphorus, and sulfur (in addition to carbon) have been provided.

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(23) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(24) (a) H. Sackmann, *Z. Phys. Chem.*, **20B**, 235 (1958); (b) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, 1964.

(25) J. D. Morrison, *Rev. Pure Appl. Chem.*, **5**, 46 (1955).

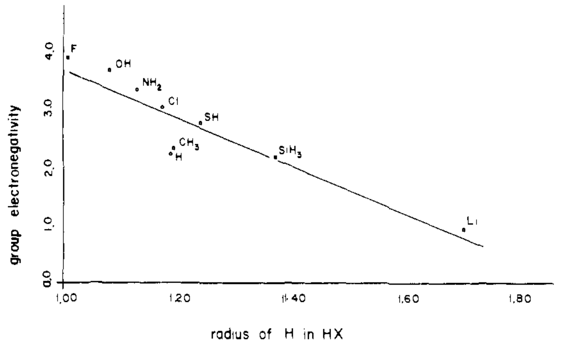

Figure 8. Relationship between the group electronegativity (ref 28a) of X and the radius of hydrogen (angstroms) in compounds HX.

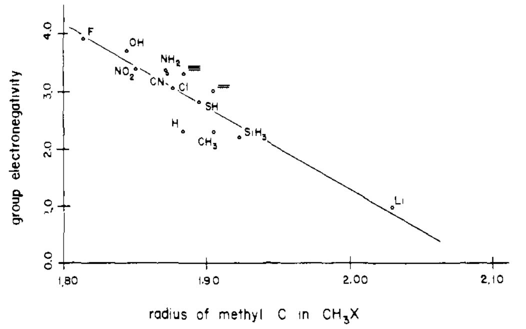

Figure 9. Relationship between the group electronegativity (ref 28a) of X and the radius of the methyl carbon (angstroms) in compounds CH_3X.

The "accepted" van der Waals radii of sp-, sp^2-, and sp^3-hybridized carbon are 1.78, 1.70, and 1.70 Å, respectively.[23] The sphere-fit averages show the opposite ordering, i.e., sp^3, 1.893, sp^2, 1.874, sp, 1.831 Å, in accord with values used in CPK models.[2]

Note the low variance of the data. Standard deviations are on the order of 0.05 Å or less. Transfer of data from one molecule to another should thus be feasible, adding further support to what has tacitly been assumed in the construction or space-filling models from standardized sets of radii.

Relative Sizes of Atoms in Molecules. In addition to selecting normal or average radii for atoms in molecules it is also interesting to explore how the sizes of atoms change with the bonding environment. In doing so, perhaps such chemical notions as electron acceptance and donation, ring strain, and steric crowding can be placed on a more quantitative basis.

Detailed understanding of the factors that govern atomic size is also a prerequisite for the accurate modeling of electron densities. Improved space-filling models could be generated by considering the effects of directly bonded substituents. For example, the radius of methyl carbon in the set of molecules considered in Table II ranges from 2.028 (in CH_3Li) to 1.813 Å (in CH_3F), or a little over 0.2 Å, and parallels the electronegativity of the attached group (vide infra). Effects of ring strain or steric crowding might also be taken into account in order to produce more accurate models. These topics are also considered in the following sections.

Substituent Effects on Atom Size. Correlations with Electronegativity. The "size" of an atom in a molecule should be primarily a function of both its nuclear charge and the number of electrons held in its immediate vicinity. Comparisons of size among the same kind of atom, e.g., carbon, will need to take into account the electron donor or acceptor ability of directly attached substituents. Although neither directly measurable nor uniquely defined, *electronegativity* is by far the most widely used indicator of substituent donor/acceptor ability. (Other attempts to reduce these concepts to a quantitative level have met with considerable success, e.g., linear free energy relationships.) Pauling originally defined electronegativity as "the power of an atom in a molecule to attract electrons to itself".[26] The original Pauling scale, based on bond strengths of diatomic species, has been redefined several times[27] and extended to include values for polyatomic substituents as well as atoms.[28] Chemical intuition, that such measures of "attracting power" should correlate well with measures of electronic size, i.e., atomic radii, is supported by the data in Figures 8 and 9. Here it is seen that the best sphere-fit radius of hydrogen in compounds HX and of methyl carbon in compounds CH_3X, respectively, can be directly related to the electronegativity of the atom or substituent X. (Other systems, e.g., PhX or SiH_3X, would no doubt show similar relationships.) We have already pointed out[29] that it is possible to use calculated radii in systems such as those illustrated above to *determine electronegativity*, especially group electronegativity. The values so obtained form a consistent set and may be extended over a wide range of chemically interesting substituents.

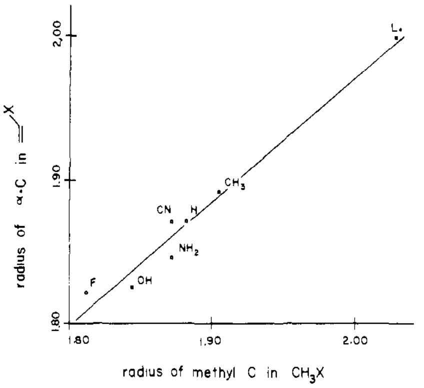

Figure 10. Correlation of the radius of the α carbon (angstroms) in systems $CH_2{=}CHX$ with the radius of the methyl carbon (angstroms) in systems CH_3X.

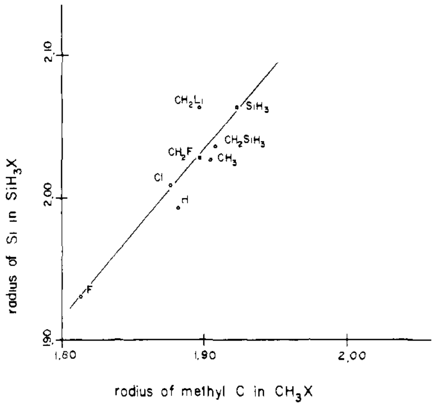

Figure 11. Correlation of the radius of silicon (angstroms) in systems SiH_3X with the radius of the methyl carbon (angstroms) in systems CH_3X.

It is interesting to note that the radius of the β carbon in the vinylic systems considered in Table III is much less sensitive to substitution than that of the corresponding α position, e.g., the radii of the β-methylene carbons in $CH_2{=}CHLi$ and $CH_2{=}CHF$ differ by 0.018 Å, compared to a difference of 0.179 Å for the corresponding α carbons. Even less sensitivity to substitution is seen for the terminal (methyl) carbons in the corresponding saturated systems, CH_3CH_2X. The calculated radius of the methyl carbon in ethyllithium is 1.896 Å, compared to 1.897 Å for the analogous position in ethyl fluoride. Similar observations have been made in a variety of other systems, e.g., substituted benzenes where the substituent affects only the size of the carbon to which

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(26) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, 1939, p 58.

(27) See, for example: (a) R. J. Boyd and G. E. Marcus, *J. Chem. Phys.*, **75**, 5385 (1981); (b) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).

(28) (a) P. R. Wells, *Prog. Phys. Org. Chem.*, **6**, 111 (1968); (b) N. Inamoto and S. Masuda, *Chem. Lett.*, 1003 (1982); (c) J. K. Wilmhurst, *J. Chem. Phys.*, **27**, 1129 (1957).

(29) M. M. Francl and W. J. Hehre, *Tetrahedron Lett.*, submitted.

Table VI. Additivity of Substituent Effects on Carbon Radii in Systems CH_2XY

	radius of methylene carbon, Å	
molecule CH_2XY^b	sphere fit^a	additivity
CH_2F	1.760	1.744
$CH_2(OH)F$	1.802	1.775
$CH_2(OH)_2$	1.829	1.806
$CH_2(CH_3)F$	1.844	1.836
$CH_2(SiH_3)F^d$	1.858	1.853
CH_4	1.882	
$CH_2(CH_3)CN$	1.899	1.896
$CH_2(CH_3)_2$	1.944	1.928
$CH_2(CH_3)SiH_3{}^e$	1.944	1.945
$CH_2(SiH_3)_2{}^f$	1.967	1.962
$CH_2(CH_3)Li$	2.056	2.051
$CH_2(SiH_3)Li^g$	2.061	2.068

[a] 3-21G//3-21G (3-21G$^{(*)}$//3-21G$^{(*)}$). [b] Structures from ref 17a unless otherwise noted. [c] CO 1.397, CF 1.394, OH 0.966, CH_t 1.072, CH_g 1.079 Å, ∠FCO 111.1, ∠HOC 112.1, ∠H_tCO 106.5, ∠H_gCO 112.4, ωFCOH 60.04, ωCOH 178.6, ωH_gCOH 59.81; subscripts t and g refer to relative orientations of CH and OH bonds. 180° and approximately ±60°, respectively. ωABCD are dihedral angles, i.e., between ABC and BCD planes. [d] CSi 1.890, CH 1.083, SiH_t 1.477, CiH_g 1.471, CF 1.430 Å, ∠SiCF 104.6, ∠HHCSi 113.0, ∠HCH 108.3, ∠$H_gH_g{}'SiC$ 123.9, ∠$H_gSiH_g{}'$ 109.7, ∠H_tSiC 109.9°. See footnote *h*. [e] CSi 1.886, CC 1.555, CH 1.088, $C_{Me}H_t$ 1.084, $C_{Me}H_g$ 1.084, SiH_t 1.478, SiH_g 1.478, ∠$C_{Me}CSi$ 113.2, ∠$HHCC_{Me}$ 123.5, ∠HCH 106.4, ∠$H_tC_{Me}C$ 110.7, ∠$H_gH_g{}'C_{Me}C$ 127.5, ∠$H_gC_{Me}H_g{}'$ 108.1°. See footnote *h*. [f] CSi 1.885, CH 1.091, SiH_t 1.477, SiH_g 1.477 Å, ∠SiCSi 115.7, ∠HCH 106.4, ∠H_tSiC 110.8, ∠$H_gH_g{}'SiC$ 126.6, ∠$H_gSiH_g{}'$ 108.2°. See footnote *h*. [g] CSi 1.839, CH 1.094, CLi 2.011, SiH_t 1.492, SiH_g 1.492 Å, ∠SiCLi 110.4, ∠HHCSi 128.8, ∠HCH 108.0, ∠H_tSiC 110.8, ∠$H_gH_g{}'SiC$ 126.6, ∠$H_gSiH_g{}'$ 108.2°. See footnote *h*. [h] Subscripts t, g, and g′ refer to relative orientations of CH or SiH bonds to the CC or SiC bond of 180° and ±60°, respectively. Angle HHCX (X = C, Si) is that between the CX bond and the bisector of the two methylene hydrogens. Angle $H_gH_g{}'XY$ (X, Y = C, Si) is that between the XY bond and the bisector of the two out-of-plane methyl or silyl hydrogens.

it is attached, and it is reasonable to conclude that corrections to atom size due to substitution need only account for directly bonded groups.

Transferability of Substituent Effects. It is important to establish to what extent substituent effects on the size of the atom to which they are directly bonded are transferable. The data in Figure 10 show the correlation between the effect of a substituent X on the size of the methyl carbon in systems CH_3X and its effect on the α carbon in compounds $CH_2{=}CHX$. Figure 11 correlates substituent effects on methyl carbon in systems CH_3X with those on silicon in compounds SiH_3X. In both cases the data are reasonably correlated, and the ordering of substituent effects is maintained. The slope of the least-squares line in Figure 10 is essentially unity; that for Figure 11 is slightly greater than one indicating increased sensitivity of the silicon center (relative to carbon) toward substitution. Further work is necessary to establish the relative sensitivity or insensitivity of a variety of chemically different substrates to substitution.

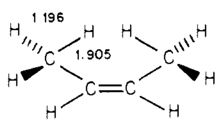
Additivity of Substituent Effects. Our calculations suggest that the effect on atomic size of two substituents attached to the same center is approximately additive. For example, as shown by the data in Table VI, the size of the central (methylene) carbon in disubstituted systems, CH_2XY, is approximately given by the relationship

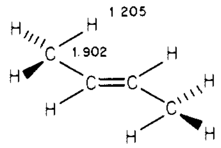
$$r(CH_2XY) \simeq r(CH_4) + [r(CH_3X) - r(CH_4)] + [r(CH_3Y) - r(CH_4)]$$

Largest deviations occur for two strongly electron withdrawing substituents, e.g., X = Y = F or X = F and Y = OH, where the additivity model overestimates the reduction in size of the central carbon. This saturation effect is likely to become more pronounced as more and more groups with similar demands are attached to a single center.

Substituent effects on carbon in other environments, e.g., vinylic carbon, are also likely to be approximately additive as are those for attachment to other elements. Further efforts are needed in order to verify or refute these expectations.

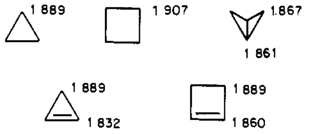
Steric Effects on Atom Sizes. To what extent does steric crowding affect the sizes of molecular charge distributions? Best-fit radii for the in-plane methyl hydrogens in *cis*- and *trans*-2-butene





suggest that the atoms in the more crowded (cis) isomer are smaller than those in the trans compound, but only slightly so. [The structure of *trans*-2-butene is from ref 12a. *cis*-2-Butene: C=C 1.319, C—C 1.510, CH_c 1.080, CH 1.086, CH_{vinyl} 1.076 Å, ∠CCC 127.8, ∠H_cCC 112.6, ∠$CCH_sH_{s'}$ 125.7, ∠$H_sCH_{s'}$ 107.3, ∠$H_{vinyl}C{=}C$ 117.8°. Subscripts c, s, and s′ refer to relative orientations of the (methyl) CH and C=C bonds of 0° and ±60°, respectively. The angle $CCH_sH_{s'}$ is that between the CC single bond and the bisector of the two out-of-plane methyl hydrogens.] Interestingly enough, the methyl carbons in *cis*-2-butene appear to have expanded in size relative to those in the trans form) in partial compensation for the shrinkage of the in-plane hydrogens. While the effects here are very small, i.e., much smaller than errors inherent to representing the actual charge distribution by a superposition of spheres, they do appear to be in the expected direction, i.e., toward shrinkage of atoms in sterically crowded environments. It should be possible, although perhaps not necessary, to introduce corrections to normal (hydrogen) radii to account for severe steric crowding.

Effect of Ring Strain on Atom Size. Best sphere fit radii for carbons in a number of small strained hydrocarbons are shown below.



[The structures of cyclopropane, cyclopropene, and cyclobutene are from ref 17a. Cyclobutane: CC 1.571, CH 1.080 Å, ∠HCH 109.4, point group D_{4h}. Bicyclo[1.1.0]butane: C_1C_3 1.484, C_1C_2 1.513, C_1H 1.061, C_2H_{eq} 1.074, C_2H_{ax} 1.076 Å, ∠$C_1C_2C_3$ 58.73, ∠$C_2C_1C_4$ 96.79, ∠HC_2H 115.2, ∠HC_1C_3 134.7°.] These data, when compared to radii for carbons with roughly equivalent substitution, e.g., 1.944 Å for the central carbon in propane and 1.891 Å for the middle position in propene, suggest significant atom shrinkage upon incorporation into a strained ring. The shrinkage effect does appear to parallel the degree of strain. For example, the carbons in bicyclo[1.1.0]butane, the most strained system considered, are smaller than those in cyclopropane, the next most strained, which in turn are smaller than the carbons in cyclobutane, the least strained. However, the relationship is not linear with CCC bond angle, probably due in part to differing substitution on the ring systems compared.

Atom Sizes and Charges. The charge on an atom in a molecule is widely used as a basis for qualitative discussions of reactivity. Like electronegativity, atomic charge is neither uniquely defined nor subject to experimental measurement. Nevertheless, it is a useful construct, and one which is not likely to be easily given up by chemists. The simplest and most widely employed scheme for partitioning electronic charge into individual atomic contributions is that due to Mulliken.[30] It is also the most widely criticized, and numerous attempts have been made to obtain more realistic descriptions of atomic charges. Among the most notable of recent efforts is work by Bader,[31a] who has proposed a unique definition

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(30) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

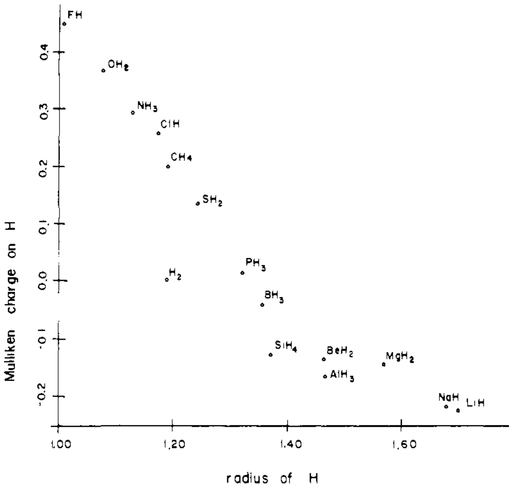

Figure 12. Correlation between the Mulliken charge (electrons) on hydrogen in systems HX and the corresponding hydrogen radius (angstroms).

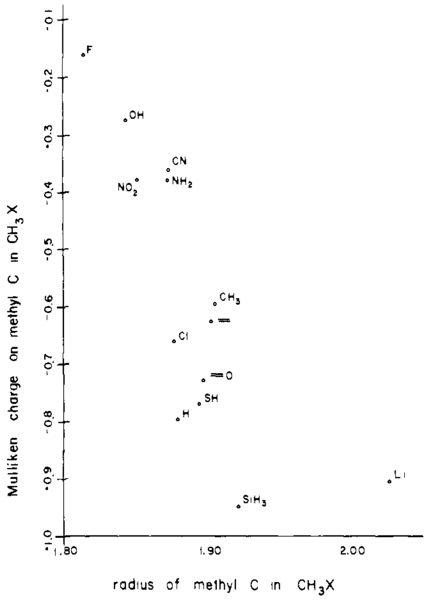

Figure 13. Correlation between the Mulliken charge (electrons) on methyl carbon in systems CH_3X and the corresponding carbon radius (angstroms).

of atomic boundaries in terms of surfaces of minimum electron density between atoms.

As shown by the data in Figures 12 and 13, best radii for hydrogen in molecules HX and for methyl carbon in compounds CH_3X, respectively, only roughly parallel charges obtained from a Mulliken population analysis. In the former case, the majority of the data are inconsistent with the calculated radius for hydrogen in H_2 (net charge of zero), and the Mulliken charges for hydrogen in both LiH and NaH are much too close to zero to account for their large calculated radii. The largest deviation from the best correlation line in Figure 13 is for methane, the central carbon of which is surrounded by four hydrogens instead of three hydrogens and a heavy atom. These apparent problems with the Mulliken analysis are not unanticipated. Here the division of charge between atoms depends on the number of available basis functions. Hydrogen atoms have only 2 basis functions in the 3-21G representation, while the alkali metals lithium and sodium have functions in excess of what is required to accommodate the electron formally associated with those centers.

It is reasonable to anticipate that optimum atom sizes in molecules, as determined by procedures such as that described in this work, will provide a measure of atomic charges.[32] It is also likely that the data so derived will correlate closely to other models which partition the total electronic charge in a more realistic manner than the much used Mulliken procedure. Indeed, the already noted deviation for lithium hydride (Figure 12) suggests that, in fact, the hydrogen atom bears far more negative charge than indicated by the Mulliken analysis. Bader's work is in accord.[31a]

Conclusion

A general method has been described enabling calculated electron densities to be fit to spheres centered at the nuclear positions. Not only does the procedure enable representation of total electron density surfaces in highly portable form but it also yields a measure of atomic size in molecular systems. The following conclusions may be made from the applications of this method to polyatomic systems as described in this paper.

Electron density surfaces obtained from minimal basis set STO-3G calculations are not in good accord with those derived from higher levels of Hartree–Fock theory. Both absolute atom sizes and relative sizes, as a function of molecular environment, are found to be in error. The 3-21G split-valence basis set ($3\text{-}21G^{(*)}$ supplemented split-valence sets for molecules incorporating second-row elements) accurately reproduces both absolute and relative atom sizes obtained from the larger 6-31G* polarization type representation.

Calculated (3-21G level) radii for atoms in molecules are found to correlate well with the electronegativities of directly attached substituents. More remote substitution has little effect on atom size. Substituent effects on size appear to be directly transferable from one substrate to another and to be approximately additive.

Atoms incorporated into small rings are uniformly smaller than those in analogous (equally substituted) acyclic systems. Steric crowding (of hydrogens) also appears to effect some shrinkage in size, although only to a very small degree.

Attempted correlations between atom size and Mulliken atomic charges suggest that the latter method underestimates the electron population on hydrogen bound to heteroatoms and overestimates the population on alkali metal atoms.

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(31) (a) R. F. W. Bader and T. T. Nguyen-Dang, *Adv. Quantum Chem.*, **14**, 63 (1981), and references therein to earlier work. For a recent general review of other approaches, see: (b) D. L. Grier and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **104**, 3556 (1982), and references therein.

(32) Our earlier report[3] demonstrated that the "size" of sulfur in a variety of normal and hypervalent compounds correlated with the formal oxidation state.

(33) D. J. DeFrees, B. A. Levi, S. K. Pollack, W. J. Hehre, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, **101**, 4085 (1979).