Locally Dense Basis Sets for Chemical Shift Calculations

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Calculations of chemical shifts have been carried out using "locally dense" basis sets for the resonant atom of interest, and smaller, attenuated sets on other atoms in the molecule. For carbon, calculations involving a 6-311G(d) triply split valence set with polarization on the resonant atom and 3-21G atomic bases on other heavy atoms result in good agreement with experiment, and are virtually identical to those found employing the larger basis on all atoms. For species such as nitrogen, oxygen, and fluorine where standard balanced basis sets do not agree well with experiment, use of attenuated sets fail as well. The use of locally dense basis sets permits calculations previously impractical, and the successful application to carbon suggests that the chemical shift is most dependent on the *local* basis set, and less so on whether or not a balanced or unbalanced calculation is being carried out.

INTRODUCTION

The NMR chemical shift can now be calculated rather well in the Hartree–Fock approach provided sufficiently large basis sets are employed.[1–17] Generally speaking, basis sets of double-zeta quality are inadequate, and one must use at least a triply split valence set on heavy (non-hydrogen) atoms as well as one or more sets of heavy-atom polarization functions. Because of the size of basis sets required, many calculations currently have been limited to two or three heavy atoms, although Schindler[7] recently has reported a calculation on benzonitrile employing 206 orbitals. Some of the first accurate work was carried out by Höller and Lischka[1] who employed a [7s, 5p, d] basis for first-row atoms, a [5s, p] basis for hydrogen, and a common gauge origin; Schindler and Kutzelnigg,[3–5] employing their IGLO gauge method, have achieved good results using [5s, 4p, d] first-row atom and [3s, p] hydrogen sets, while our own work[8,9,11] involving Ditchfield's GIAO approach[18] has been able to obtain comparable results with the somewhat smaller set made up of [4s, 3p, d] (with six Cartesian d functions) for first-row atoms and [2s] for hydrogen. The results for carbon are especially encouraging while those for other species are less so.

In Schindler's recent calculations on nitrogen chemical shifts,[7] his largest basis set was first row [8s, 6p, d] and hydrogen [4s, 2p], involving 36 orbitals on heavy atoms, and 10 orbitals on each hydrogen. The basis sets required for adequate results on molecules of second-row atoms are even larger. Lazzeretti and Tossell[16] employing a common gauge origin have used a basis as large as [6s, 5p, 4d] for phosphorus involving 45 orbitals per phosphorus atom, while Fleischer, Schindler, and Kutzelnigg[6] in similar calculations involving phosphorus and silicon have used as a "best basis" the set [8s, 7p, 5d] requiring 54 orbitals for each phosphorus or silicon atom. In our own work involving the GIAO approach first-row atoms require 19 orbitals per atom, and we have found that good results for the heavy atoms can be obtained by using a relatively small and nonpolarized [2s] basis for hydrogen.[9,11] These various calculations typically involve a perturbed Hartree–Fock approach; the large basis sets required mean that not only will the Hartree–Fock calculation itself be time and memory consuming, but the perturbation calculation, also iterative in nature, will also be an additional time and space constraint.

The chemical shift is caused by the fact that nuclei in molecules see not only applied external fields but also internal fields due to electron motion in the otherwise rigid (Born–Oppenheimer approximation) nuclear framework. These internally induced fields involve the angular momentum of the electron cur-

rents measured about the nucleus involved multiplied by a r_N^{-3} term, also measured from the nuclear origin. It is clear that a good description of the electronic currents on the atom containing the nuclear center is most desirable, but the question is raised as to whether the description of the electronic structure on neighboring atoms whose shifts are not being calculated need be as good. That is, a large number of atomic basis functions on the atom containing the nuclear center of interest may be necessary, but a smaller number of basis functions on *other* atoms may be satisfactory. Huber and Diehl[19] have found such an approach viable in Hartree–Fock calculations of the electric field gradients and their first and second derivatives with respect to bond length for the deuterium nucleus.

In this article we report the results of calculations where large atomic basis sets are used for the resonant atom in question and smaller, attenuated sets on other atoms whose chemical shifts are not required. Our results show that in those cases where a full, balanced basis yields good agreement with experiment, these "locally dense" and unbalanced basis sets yield chemical shifts in excellent agreement with full, heavy-atom-balanced basis set calculations. Where a full, balanced set does not agree well with experiment, the attenuated sets fail as well. While obviously flawed as a method for determining global properties of molecules, the approach allows the accurate determination of a local quantity such as the chemical shift employing basis sets overall of considerably smaller size and, therefore, calculations of considerably shortened time and memory requirements.

CALCULATIONS

The chemical shift calculations were carried out for a representative set of carbon, nitrogen, oxygen, and fluorine nuclei using Ditchfield's GIAO perturbed Hartree–Fock approach.[18] The set of representative molecules was chosen mainly on the basis of available experimental data and covers many bond types and molecular configurations. Experimental geometries were used in the rigid nuclear framework calculations.[20,21] The basis sets employed in this study were the Pople STO-3G, 3-21G, 4-31G, 6-31G, 6-311G, and

6-311G(d) sets.[22] The d function set consists of the six d Cartesian gaussians, and a fixed hydrogen 31G basis (from the 4-31G set) was employed in all the calculations.

The chemical shift program itself is a slightly modified version of Ditchfield's original program which is based on an early version of the GAUSSIAN series. In order to overcome the relative inefficiency of this version of the Gaussian series relative to current ones, the density matrices were usually first determined by a Gaussian 86 calculation[23] and then read in as the input density matrix to the GIAO calculation.

NOTATION

Any study involving a variety of basis sets, particularly mixed basis, requires that a clear indication of the mixture be exhibited with a minimum of unwieldy notation. A variety of notation of differing degrees of completeness and clarity exists in the literature for denoting basis sets, and it is often useful to employ redundancy to convey a clear description of a particular basis. In the discussion here we will invoke our own description for mixed basis sets, not to necessarily establish new notation but rather to attempt to keep our discussion as clear and free from ambiguity as possible.

Our prior work[9] which focused mainly on first-row atom molecules indicated that the Pople basis 6-311G(d) on heavy atoms and 31G on hydrogen was relatively efficient for calculating the chemical shifts of these molecules. This mixed basis involving only a doubly split valence set for hydrogen but a triply split valence set with polarization for other atoms gives quite good results for carbon but is less successful for nitrogen, oxygen, and fluorine. We refer to this basis as our standard or S basis in the work here.

In the present study we focus on a particular resonant atom R in a molecule and describe it by the standard or locally dense 6-311G(d) set; we use smaller or attenuated atomic basis sets on other heavy atoms in the molecule and in all instances a 31G basis is employed for hydrogen. We describe such mixed basis sets as R:6-311G(d)/X:X-basis/H:31G where the X basis is allowed to vary over the Pople minimum 3G, the split valence 3-21G, the somewhat enhanced split valence 4-31G

and 6-31G, the triply split valence 6-311G, and the 6-311G(d) atomic basis sets. The Pople notation for several of the atomic sets equated to a more conventional notation is shown in Table I along with the definitions of our standard set and a key attenuated molecular basis. This key attenuated basis, here designated as A, is the molecular basis R:6-311G(d)/X:3-21G/H:31G where the standard and locally dense atomic set is used on the resonant atom of interest and the small 3-21G split valence without polarization used on all other heavy atoms. For reasons that are discussed later, another important basis set is what we refer to here as the fully attenuated or FA set corresponding to R:3-21G/X:3-21G/H:31G, where the small split valence set is used on all heavy atoms, and, again, the fixed 31G basis for hydrogen. We note that the fully attenuated or FA molecular basis is not mixed but rather is balanced in the sense of the degree of splitting of the valence shell and the absence of polarization functions on all atoms.

MIXED BASIS SETS STUDY

To determine the dependence of the resonant atom chemical shift on the X-basis employed, calculations were carried out varying the basis set of the other heavy atoms in the molecule over the 3G, 3-21G, 4-31G, 6-31G, 6-311G, and 6-311G(d) sets. We discuss the results in greater detail later but here give an overview of the basic results of this study with illustrations involving carbon, nitrogen, and oxygen as resonant nuclei. Figures 1 through 4 show the calculated shifts both for the designated resonant atom R (that atom with the standard atomic basis set) and the X atom(s) (the other, attenuated atomic basis set atom) as the X-basis is varied.

Figure 1 for ethylene is representative of most results for carbon. Fixing the resonant atom basis at the standard set and the X-atom at the STO-3G level generally is inadequate for predicting the chemical shift. However, once one has reached the 3-21G level on the X-atom the chemical shift of the resonant atom is changed very little thereafter and agrees satisfactorily with experiment. The chemical shift of the X-atom itself is highly dependent on the X-atom atomic basis, and varies widely in value. In some cases such as carbon in ethane (Fig. 2) and in HCN (Fig. 3), an X-atom basis of STO-3G appears to be adequate, but this is more the exception than the rule. Nitrogen in HCN (Fig. 3) and the nitrosyl nitrogen in NNO (not shown) also exhibit this type of behavior, but show that the converged results do not agree with experiment, as indeed the full standard set results also do not. While the chemical shifts for carbon generally converge at the 3-21G level for the X-atom basis, this is not so for other nuclear species. Figure 4 displays the terminal nitrogen and oxygen atoms in NNO; in both cases there is a significant and large change in the calculated shift at the end of this series as one changes the X-atom basis from 6-311G to the standard 6-311G(d) set.

These figures illustrate our conclusions regarding mixed basis sets. In those instances where the chemical shift can be calculated accurately using the standard balanced 6-311G(d) molecular basis it can be calculated just as well by an attenuated basis where nonresonant atoms use the smaller (attenuated) 3-21G atomic basis; in those cases where the chemical shift is not well determined by the full standard basis (nitrogen, oxygen, and fluorine), use of an attenuated molecular basis of the type studied here is likely not useful.

RESULTS

The compilation of our current (and some previous) results is given in Tables II and III. There the calculated isotropic chemical shifts for both our standard unattenuated molecular basis (S) as well as our standard attenuated basis (A) are compared with experiment; columns four and five give the chemical shift for the nonresonant atom (the X atom) of our standard attenuated molecular basis and also the calculated chemical shift for the molecu-

Table I. Basis set notation employed in the present study.

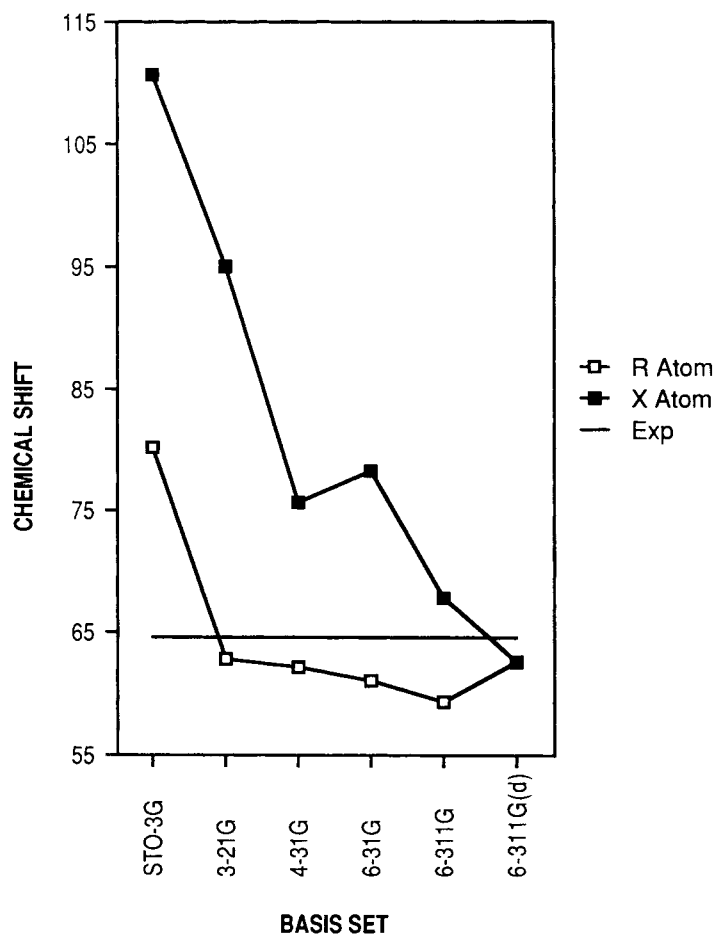| Basis	Description
6-311G(d)	(6311/311/1) = [4s, 3p, d]
3-21G	(321/21) = [3s, 2p]
(H)31G	(31) = [2s]
S	R:6-311G(d)/X:6-311G(d)/H:31G
A	R:6-311G(d)/X:3-21G/H:31G
FA	R:3-21G/X:3-21G/H:31G

Figure 1. The chemical shift for carbon in ethylene for both the R and X atoms as a function of the X-atom basis set. The R-atom basis is fixed at the standard 6-311G(d) atomic set.

lar basis in which all heavy atomic sets are at the 3-21G level (FA). The rms error with experiment is indicated, as are the mean ($\bar{x}$) and standard deviation (σ) of the distribution of errors.

Results for Carbon

Generally speaking, our standard molecular basis gives calculated results which are in reasonably good agreement with experiment. As shown in Table II, the rms error using the standard basis for the 23 carbon nuclei is 7.9 ppm with a similar value for σ, the spread of the errors; the average absolute error is 6.1 ppm. These numbers are significantly enhanced by the large errors for carbon monoxide and methyl fluoride; if these two molecules were dropped from the list the rms error would be reduced to 6.1 ppm and the average absolute error to 5.0 ppm. The adequacy of this relatively efficient basis set in the GIAO approach has been argued be-

fore;[9] we simply wish to point out again that it (and other) calculations of carbon chemical shifts for rigid, equilibrium molecular configurations are reaching the point where careful consideration of the experimental conditions must be given.[25]

The key result here is to note that when one maintains the locally dense or standard atomic set on the resonant carbon atom of interest but uses the smaller 3-21G atomic set on other heavy atoms in the molecule (our molecular basis A), the results, as shown in column 2 of Table II, are virtually identical to the full, standard molecular basis. The rms error between the S and A calculations is only 2.8 ppm; indeed, the A molecular basis has an rms error with experiment of 7.9 ppm, fortuitously the same as the full, standard basis.

Although not tabulated, the principle values of the shift tensor (from which anisotropies are calculated) in the S and A molecular bases also agree very well. The rms error
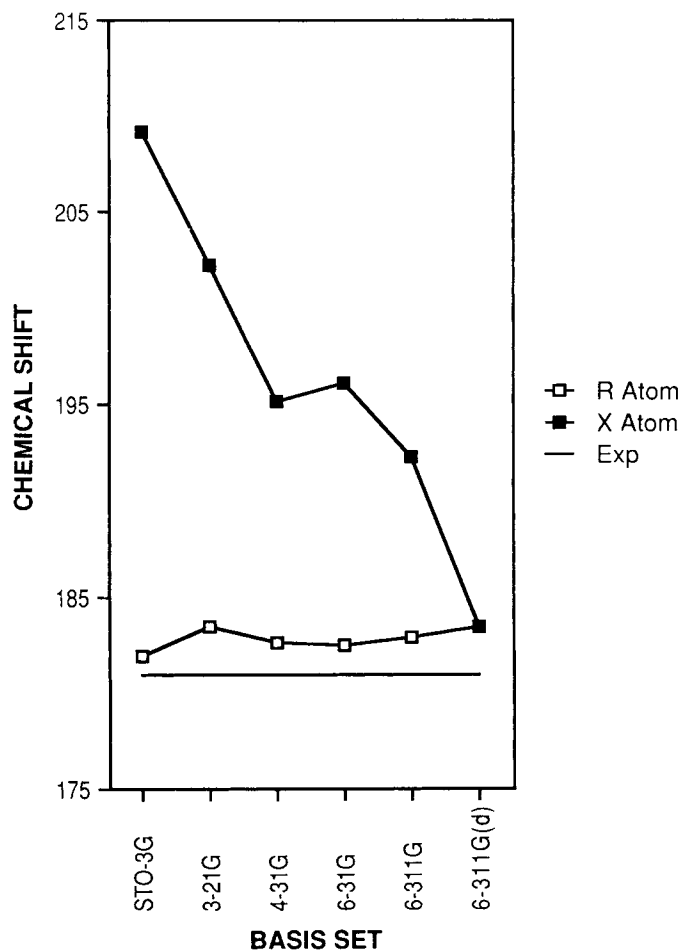
Figure 2. The chemical shift for carbon in ethane for both the R and X atoms as a function of the X-atom basis set. The R-atom basis is fixed at the standard 6-311G(d) atomic set.

of 57 principle values for 22 distinct carbon nuclei is only 4.6 ppm. Differences of 10–20 ppm do occur for the carbonyl carbons in H_2CO, CH_3CHO, HCOOH, and the central carbon in H_2CCCH_2, and are associated with the direction of the multiple bond involved. Removing these four large differences lowers the agreement between the two bases to 1.8 ppm. Thus, the locally dense basis set approach for carbon is reproducing the principle values of the shift tensors (and, therefore, the anisotropies) as well as the isotropic shifts. In Table IV anisotropies are shown not previously determined[9] for the S and A molecular bases along with experimental data; agreement with experiment is quite satisfactory.

The use of the locally dense basis set type of calculation now allows calculations that were previously difficult. For example, butane in the standard molecular basis S would be a 96 orbital calculation; in our standard attenuated set A it becomes a 66 orbital calcula-

tion. Not only can the calculation be done, but the time of the (two) calculations required to obtain the shift for *both* nonequivalent carbons is reduced by a factor of 2.

The results for the isotropic shift of carbon using the balanced 3-21G molecular basis is shown in the fifth column of Table II and yields an rms error of 27.4 ppm, clearly inadequate. Interestingly enough, the chemical shift calculated for the X-atom in the A molecular basis set (shown in column four) agrees rather well with those obtained for the balanced 3-21G calculations. Indeed, these two sets differ from each other by an rms error of only 2.0 ppm. This result, though unexpected, is consistent with our results for the resonant atom (using the locally dense basis set) and its agreement in the A molecular basis with our standard molecular basis, and suggests that the determination of the chemical shift for a particular atom depends mainly on the *local* basis set, and
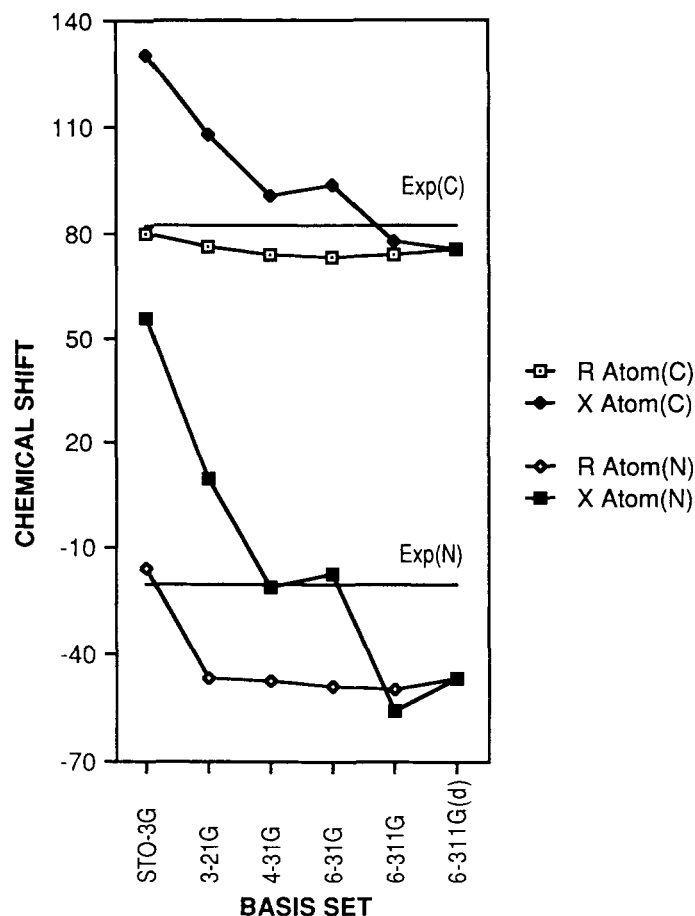
Figure 3. The chemical shifts of carbon and nitrogen in HCN as a function of the X-atom basis set. The R-atom basis in each case is the standard 6-311G(d) set.

less so on whether or not a balanced or unbalanced (mixed) calculation is being performed. A similar conclusion was arrived at by Huber and Diehl in their electric field gradient calculations.[19]

We note finally that while the balanced 3-21G calculation (column five of Table II) has a large rms error when compared to experiment, its relative error (σ, 7.4 ppm) is just as good as the standard molecular basis S on either an absolute or relative basis (7.9, 7.8 ppm). Evidently some kind of uniform error is being made in the 3-21G calculation which allows *differences* of shifts to be reasonably well represented. However, when determining the underlying causes of the chemical shift it will be important to have calculations which agree on an *absolute* scale with experiment.

Results for Nitrogen, Oxygen, and Fluorine

The success of using mixed basis sets in the calculation of carbon chemical shifts is evi-

dently dependent on the fact that a full and balanced basis yields results which are close to experiment. As seen in Table III, full and balanced basis sets for nitrogen, oxygen, and fluorine generally do not agree well with experiment (for our calculations or others), so it is perhaps not particularly surprising that the use of mixed basis sets fails as well.

With the exception of the terminal nitrogen in NNO the attenuated basis A for nitrogen does agree rather well with the standard basis S but, as seen from the rms error and sigma values, not with experiment. Generally, the calculated nitrogen chemical shifts are too low (too large a paramagnetic contribution), and show signs of moving upward toward experimental results as one gets to the larger atomic basis sets. The behavior of nitrogen in HCN (Fig. 3) is fairly typical of most nitrogen shifts calculated in this study. The behavior of the terminal nitrogen in NNO (Fig. 4) shows, however, that there can be significant exceptions to the convergence of the shift with the X-basis set.
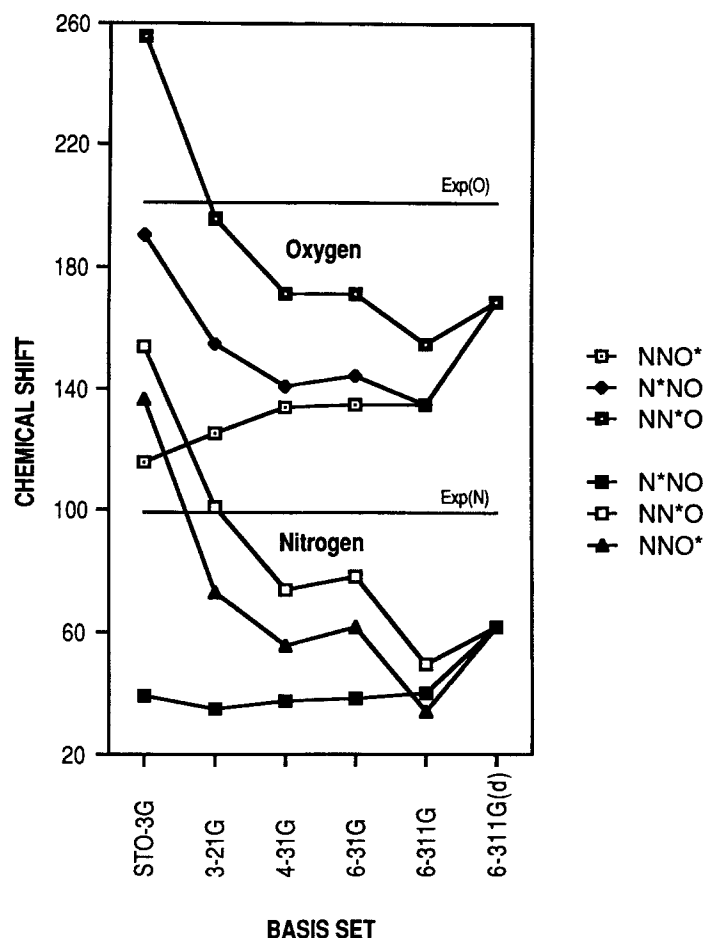
Figure 4. Chemical shifts for the terminal nitrogen and oxygen atoms in NNO as a function of the X-atom basis set. Note here that two atoms in each calculation have an attenuated set; the R-atom (denoted by an *) basis of each calculation is the standard 6-311G(d) basis.

For oxygen the entire situation is not good. Although the range of oxygen shifts studied here is some four times that of the carbon compounds, the rms errors are 10 or 15 times larger. We are simply not able to adequately calculate oxygen chemical shifts yet, and there is a paucity of experimental data. In most of the cases there is a significant increase in the calculated oxygen shift as one moves from the 6-311G X-basis to the fuller standard atomic basis. This change is usually in a positive direction, and in the few cases where experimental data is available seems to be moving toward the experimental result. The situation for oxygen is well illustrated by the data in Figure 4. For both nitrogen and oxygen one sees a significant change in the calculated shift in the mixed basis sets as one approaches the standard atomic basis.

The results for fluorine are similar to nitrogen in that a number of potentially consistent results are obtained (CH_3F, CH_2F_2) only to be offset by several bad examples (OF_2, F_2).

Clearly, before attempting the use of mixed basis sets for calculating nitrogen, oxygen, or fluorine chemical shifts one must determine if there is a better standard basis which in a full and balanced calculation yields significantly better agreement with experiment than is currently available.

Other Effects of Mixed Bases

The use of a mixed or locally dense basis has value for the calculation of locally important observables such as the chemical shift. There are obvious defects, however, with the application of the method in terms of other, global properties of the molecule. The effective symmetry of a system will be destroyed or lowered when, for example, a resonance carbon atom has a larger number of atomic functions centered on it compared to other, equivalent carbons in the molecule. We can illustrate these effects by considering ethane in the A basis in which one carbon (the resonance

Table II. Calculated and observed isotropic chemical shifts for carbon for a variety of mixed and balanced basis sets and for both R- and X-atom centers. The rms errors measure the agreement with experiment while $\bar{x}$ and σ denote the mean and standard distribution of the differences between calculated and experimental data. References to experimental results are given in parentheses.

| Carbon | σ_R | | | σ_X | |
	S	A	Experiment	R:6-311G(d)/X:3-21G/H:31G[a]	R:3-21G/X:3-21G/H:31G
CH_4	194.7	—	195.1 (25)	—	211.1
$(CH_2)_3$	197.6	196.4	189.7 (24)	213.8	214.0
CH_3CN	191.4	189.8	187.7 (25)	207.6 ±0.8	206.8
CH_3CH_3	183.4	183.3	180.9 (25)	202.3	203.3
$CH_3CH_2CH_2CH_3$	173.7	175.5	173.1 (26)	195.7 ±0.4	195.8
$CH_3CH_2CH_3$	178.1	178.0	170.9 (28, 29)	197.8 ±0.4	198.1
$CH_3CH_2CH_3$	176.6	176.9	169.2 (28, 29)	198.1	199.1
$CH_3CH_2CH_2CH_3$	165.1	167.1	159.9 (26)	189.5 ±0.5	189.9
CH_3NH_2	164.3	163.0	158.3 (25)	186.5	185.2
CH_3CHO	167.7	168.9	157.2 (25)	187.1 ±0.9	186.7
CH_3OH	147.1	145.8	136.6 (25)	170.9	169.8
$CHCH$	117.8	118.4	117.2 (25)	146.0	142.4
CH_3F	130.0	129.8	116.8 (25)	154.0	155.1
CH_2CCH_2	114.5	114.5	115.2 (25)	141.3 ±1.8	139.2
HCN	75.2	75.9	82.1 (25)	107.9	101.4
CH_3CN	67.9	68.3	73.8 (25)	98.8 ±2.4	95.4
CH_2CH_2	62.5	62.7	64.5 (25)	95.1	91.9
CO_2	54.6	55.2	58.8 (25)	86.9	84.2
$HCOOH$	28.5	31.8	26.8 (27)	58.6 ±0.6	57.3
CO	−20.6	−16.0	1.0 (25)	8.8	11.9
CH_3CHO	−7.2	−0.4	−6.7 (25)	26.5 ±0.9	25.3
H_2CO	4.4	9.9	−9.3 (30)	37.4	35.4
CH_2CCH_2	−37.0	−32.9	−29.3 (25)	9.5	8.3
rms error	7.9	7.9	—	28.8	27.4
σ	7.8	7.5	—	7.6	7.4
$\bar{x}$	1.8	3.1	—	28.3	26.9

[a]Results with ± figures represent mean and standard deviation for more than one X-atom result.

carbon) has a 6-311G(d) atomic set while the other is described in a 3-21G manner. Because these particular Gaussian sets are optimized to reproduce atomic energies, the R-atom in ethane will tend to have some of its orbital levels lying at lower energies than those of the X-atom; in effect, the R-atom appears more electronegative than the X-atom and, as such, attracts charge to it; thus, a small dipole moment is induced in ethane in the mixed basis. The energy of ethane in the A basis is also higher than that in the S or standard basis, since one has a greater number of degrees of freedom in the standard basis. One can also compare the energies of ethane (or other molecules) in the S, A, and the fully attenuated FA basis. It is found that the energy of the ethane molecule in the A basis lies approximately midway between that of the S and FA calculations. Similar additivity relationships are observed for all the examples studied here including the larger and more complicated molecules and those

containing heteronuclear heavy atoms. For the molecular species investigated in the present work this energy additivity by (local 6-311G(d) and 3-21G) basis is valid to approximately ±2%.

DISCUSSION

We have shown that it is possible to accurately calculate a locally important observable like the chemical shift with a locally dense, mixed basis set where a large number of atomic basis functions are placed on the resonance atom of interest and a smaller, attenuated set of atomic functions used on other heavy atoms in the molecule. Our calculations show that the use of locally dense basis sets is appropriate when the full, standard basis is adequate (carbon), but when the standard balance basis is inadequate (nitrogen, oxygen, and fluorine) the attenuated molecular bases fail as well. We have not yet applied the method to second row

Table III. Calculated and observed isotropic chemical shifts for nitrogen, oxygen, and fluorine for a variety of mixed and balanced basis sets, and for both R- and X-atom centers. The notation is the same as that employed in Table II.

	σ_R			σ_X	
	S	A	Experiment	R:6-311G(d)/X:3-21G/H:31G[a]	R:3-21G/X:3-21G/H:31G
Nitrogen					
NH_3	262.6	—	264.5 (34)	—	278.8
CH_3NH_2	252.3	251.7	250.0 (35)	270.3	271.3
NNO	61.9	34.8	99.5 (36)	86.9 ±14.2	61.5
NNO	−27.8	−30.0	11.3 (36)	14.3 ±1.7	−1.6
CH_3CN	−41.6	−43.9	−9.1 (35)	4.8 ±11.6	−6.7
HCN	−46.4	−46.9	−20.4 (36)	9.4	−10.9
N_2	−109.4	−107.9	−61.6 (36)	−47.2	−87.8
rms error	31.6	40.7	—	17.7	20.9
σ	17.8	20.3	—	13.4	20.4
$\bar{x}$	−26.1	−35.3	—	11.5	−4.2
Oxygen					
H_2O	331.3	—	344.0 (38)	—	349.0
CH_3OH	348.9	351.5	270.9 (31)	363.2	363.3
CO_2	220.0	212.2	243.4 (38)	236.6 ±9.9	224.3
NNO	168.7	125.2	200.5 (38)	175.5 ±20.5	139.6
H(CO)OH	153.7	156.2	—	190.2 ±6.1	189.6
CO	−86.5	−125.1	−42.3 (38,39)	−21.5	−59.5
H(CO)OH	−105.5	−140.0	—	−76.7 ±35.1	−105.5
CH_3CHO	−401.3	−474.3	—	−354.5 ±51.7	−420.0
H_2CO	−422.8	−505.1	−312.1 (38)	−328.4	−449.9
OF_2	−415.3	−368.6	−473.1 (38,40)	−275.7	−255.3
rms error	60.2	106.6	—	90.0	106.5
σ	58.9	101.4	—	78.9	105.9
$\bar{x}$	−12.4	−32.9	—	43.7	11.5
Fluorine					
ClF[b]	696.2	674.9	637.1 (41)	657.4	626.7
CH_3F	491.6	502.3	471.0 (41)	494.2	497.1
HF	416.5	—	410.0 (42)	—	425.3
CH_2F_2	371.3	390.0	339.1 (43)	389.0 ±6.3	398.5
CHF_3	297.5	337.7	274.1 (41)	317.9 ±1.3	339.3
PF_3[b]	272.0	315.6	228.3 (41)	313.6 ±23.2	342.5
OF_2	31.0	38.5	−59.3 (44)	74.3 ±21.8	72.7
F_2	−181.3	−91.2	−232.8 (41)	−157.1	−90.2
rms error	47.7	81.3	—	71.9	86.3
σ	24.7	36.0	—	37.0	53.1
$\bar{x}$	40.8	72.9	—	61.7	68.1

[a]See footnote a of Table II.
[b]McLean-Chandler [$6s, 5p, d$] bases (ref. 45) were used as a standard basis for second row atoms.

elements. The success of the method with carbon was illustrated in Table II where both the A and S basis sets gave rms errors of 7.9 ppm for the isotropic shift. These errors are reduced to about 6 ppm if several of the species with the larger discrepancies are removed. Carbon anisotropies are also well reproduced. The agreement of the A molecular basis calculation of the isotropic shift with experiment is shown graphically in Figure 5

where calculated vs. observed chemical shifts are plotted. We (and others) are now able to calculate carbon shifts rather accurately, and our current work has shown that certain classes of attenuated basis sets are equally as successful as larger, balanced ones.

The advantages and disadvantages of using mixed basis sets are at once evident. The energy is obviously affected but, as mentioned previously, there appears to be a kind of ad-

Table IV. Observed and calculated carbon shift anisotropies (ppm) for the S (R:6-311G(d)/X:6-311G(d)/H:31G) and A (R:6-311G(d)/X:3-21G/H:31G) molecular bases. $\Delta\sigma$ is given by $\Delta\sigma = \sigma_\parallel - \sigma_\perp$, or $\Delta\sigma = \sigma_{33} - 1/2\,(\sigma_{22} + \sigma_{11})$, $\sigma_{33} > \sigma_{22} > \sigma_{11}$. References to experimental results are indicated in parentheses.

	Calculated S	A	Experiment	
$(CH_2)_3$	56.4	54.7	48	(46)
$C\,H_3CN$	12.8	15.0	5	(47)
$CH_3C\,N$	343.0	342.9	311	(47)
$C\,H_3CHO$	44.0	42.3	46, 47.5	(48, 49)
$CH_3C\,HO$	190.0	179.8	168, 174	(48, 49)
$C\,H_2CCH_2$	98.6	98.2	83	(32)
$CH_2C\,CH_2$	72.4	94.6	58	(32)
CO_2	342.9	343.9	335	(32)
$C\,H_3CH_2CH_2CH_3$	22.1	23.3	—	
$CH_3C\,H_2CH_2CH_3$	26.3	27.5	—	
$C\,H_3CH_2CH_3$	23.2	24.2	—	
$CH_3C\,H_2CH_3$	6.4	6.4	—	
HCOOH	108.0	101.4	—	

ditivity of energies between full and mixed basis calculations; this would imply that energy differences may well be relatively unaffected by the use of mixed basis sets. The charge distribution of the molecule is obviously modified since the effective symmetry is destroyed when equivalent atoms have different sets of atomic functions; accordingly, mixed basis set calculations of the type here are likely not useful for global properties such as dipole moments. On the other hand, the chemical shift seems to be dominated by local effects (due to the r_N^{-3} dependence in the theory) which appear to be quite susceptible

to the approach we have employed. The use of mixed basis sets in our method requires two calculations on butane, for example, to obtain the chemical shifts for the two nonequivalent carbon atoms, while a single balanced calculation would suffice. However, as we have pointed out, the reduction of basis set size using an attenuated molecular basis is sufficiently time saving that the two calculations required using a mixed basis can be carried out in less than the time required for a single, balanced, larger basis set calculation. Ideally, one should use in all instances a balanced basis set; ideally, one should do more than
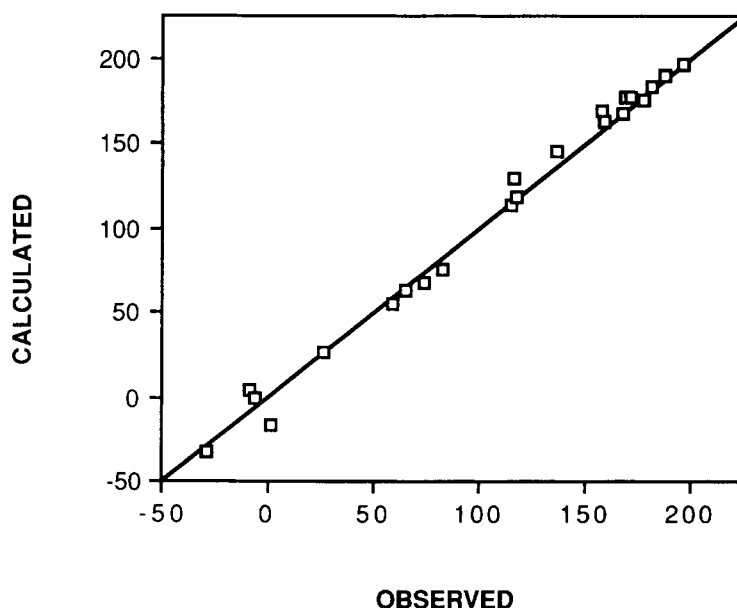

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Figure 5. Calculated versus observed isotropic chemical shifts for the carbon species shown in Table II where the attenuated set A (R:6-311G(d)/X:3-21G/H:31) is used to determine the calculated shift.

Hartree–Fock. However, CI calculations of chemical shifts are currently relatively impractical and one is forced to use simpler approaches. What we have shown here is that the use of locally dense basis sets allows an accurate calculation of a quantity which might otherwise be difficult to obtain. The success of the method is that not only do the locally dense basis set calculations agree with the fuller balanced ones but also they both agree rather well with experiment.

The use of locally dense basis sets in quantum mechanical calculations is much like the "hybrid force field" suggested by Kollman et al.[50] for use in molecular mechanics. In large systems such as proteins and nucleic acids all atom molecular mechanics determinations are extremely time consuming; a united atom approach in which, for example, hydrogens on carbon are considered as part of a single carbon-hydrogen entity are quite useful and successful; they work. A hybrid force field in which one uses an all atom representation at the active site of an enzyme, for example, and a united atom formalism elsewhere would allow one to retain high accuracy at that point of importance (the active site) in the molecule.

The application of mixed basis set calculations to biological systems is pertinent. Using our standard or S molecular basis for the simple amino acid glycine would entail a calculation involving 103 orbitals; calculations involving our attenuated or A basis would require 63. Valine in the S basis would require 172 orbitals, the attenuated basis only 102. Because the time and memory requirements of calculations go as the fourth power as the number of orbitals, the savings in time and computer disk space is obvious. That is, we can now attack important parts of larger systems that the use of an overall balanced and large basis set would otherwise preclude.

For reasons that are still not clear, the chemical shifts for nitrogen, oxygen, and fluorine are relatively inaccurate. Schindler,[7] in his calculation of nitrogen shifts, concludes that correlation effects which are neglected in his and other coupled Hartree–Fock approaches likely play an important role in the calculation of NMR shifts for nitrogen atoms involved in NN multiple bonds. The use of locally dense basis sets will allow us to further investigate this question by using sets of basis functions significantly larger than our so called standard or S set on nitrogen or other such species, and smaller numbers of functions on other atoms in the molecule; that is, local basis sets significantly larger than our current standard one can now be investigated that previously were not possible.

The success of locally dense basis sets is clearly dependent upon the property being calculated. The chemical shift is sensitive to the electron distribution near the resonant nucleus, and therefore requires a good description of that distribution in the vacinity of the resonant nucleus and a lesser description further away. As shown by Huber and Diehl's field gradient work,[19] other properties which have a similar local dependence should be amenable to this approach. In short, it may well be better to treat a small part of a molecule accurately rather than treat the entire system poorly.

References

1. R. Höller and H. Lischka, *Mol. Phys.*, **41**, 1017 (1980); *Mol. Phys.*, **41**, 1041 (1980).
2. T. Weller, W. Meiler, H.-J. Köhler, H. Lischka, and R. Höller, *Chem. Phys. Lett.*, **98**, 541 (1983).
3. M. Schindler and W. Kutzelnigg, *J. Chem. Phys.*, **76**, 1919 (1982).
4. M. Schindler and W. Kutzelnigg, *J. Am. Chem. Soc.*, **105**, 1360 (1983).
5. M. Schindler and W. Kutzelnigg, *Mol. Phys.*, **48**, 781 (1983).
6. A. Fleischer, M. Schindler, and W. Kutzelnigg, *J. Chem. Phys.*, **86**, 6337 (1987).
7. M. Schindler, *J. Am. Chem. Soc.*, **109**, 5950 (1987).
8. D. B. Chesnut and C. K. Foley, *Chem. Phys. Lett.*, **118**, 316 (1985).
9. D. B. Chesnut and C. K. Foley, *J. Chem. Phys.*, **84**, 852 (1986).
10. D. B. Chesnut and C. K. Foley, *J. Chem. Phys.*, **85**, 2814 (1986).
11. D. B. Chesnut, *Chem. Phys.*, **110**, 415 (1986).
12. P. Lazzeretti and R. Zanasi, *J. Chem. Phys.*, **72**, 6768 (1980).
13. J. A. Tossell and P. Lazzeretti, *Chem. Phys. Lett.*, **128**, 420 (1986).
14. J. A. Tossell and P. Lazzeretti, *Chem. Phys. Lett.*, **132**, 464 (1986).
15. J. A. Tossell and P. Lazzeretti, *J. Chem. Phys.*, **84**, 369 (1986).
16. P. Lazzeretti and J. A. Tossell, *J. Phys. Chem.*, **91**, 800 (1987).
17. J. A. Tossell and P. Lazzeretti, *J. Chem. Phys.*, **86**, 4066 (1987).
18. R. Ditchfield, *Mol. Phys.*, **27**, 789 (1974).
19. H. Huber and P. Diehl, *Mol. Phys.*, **54**, 725 (1985).

20. Landolt-Börnstein, *Zahlenwerte and Functionen*, K. H. Hellwege, Ed., Springer, Berlin, 1976.

21. M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwenderman, D. A. Ramsey, F. J. Lovas, W. J. Lafferty, and A. G. Mahi, *J. Phys. Chem. Ref. Date*, **8**, 619 (1979).

22. W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory*, J. Wiley and Sons, New York, 1986.

23. Gaussian 86, Release C, M. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, R. Martin, J. J. P. Stewart, F. Bobrowicz, D. Defrees, R. Seeger, R. Whiteside, D. Fox, E. Fluder, and J. A. Pople, Carnegie Mellon University, 1987.

24. An estimated gas phase result using the liquid phase data of Ref. 27 and the average propane liquid-to-gas correction of Ref. 28.

25. A. K. Jameson and C. J. Jameson, *Chem. Phys. Lett.*, **134**, 461 (1987).

26. I. D. Gay, and J. F. Kriz, *J. Phys. Chem.*, **82**, 319 (1978), using liquid-phase data from Refs. 25 and 27.

27. E. Breitmaier and W. Voelter, *"Carbon-13 NMR Spectroscopy,"* 3rd ed., VCH, Weinheim, Federal Republic of Germany, 1987.

28. K. Jackowski and W. T. Raynes, *Mol. Phys.*, **34**, 465 (1977).

29. L. J. M. van DeVen and J. W. de Haan, *J. Chem. Soc., Chem. Commun.*, **78**, 94 (1978).

30. A liquid phase result estimated in Ref. 31 from the combined data of Refs. 32 and 33.

31. C. J. Jameson, in *Specialist Periodical Report on NMR*, Vol. 16, G. A. Webb, Ed., Royal Society of Chemistry, London, 1987, p. 1.

32. A. J. Beeler, A. M. Orendt, D. M. Grant, P. W. Cutts, J. Michl, K. W. Zilm, J. W. Downing, J. C. Facelli, M. S. Shindler, and W. Kutzelnigg, *J. Am. Chem. Soc.*, **106**, 7672 (1984).

33. D. B. Newmann and J. W. Moskowitz, *J. Chem. Phys.*, **50**, 2216 (1969).

34. S. G. Kukolich, *J. Am. Chem. Soc.*, **97**, 5704 (1975).

35. Calculated in Ref. 31 on data from Refs. 36 and 37.

36. C. J. Jameson, A. K. Jameson, D. Oppusunggu, S. Wille, P. M. Burrell, and J. Mason, *J. Chem. Phys.*, **74**, 81 (1981).

37. M. Alei, Jr., A. E. Florin, W. M. Litchman, and J. F. O'Brien, *J. Phys. Chem.*, **75**, 932 (1971).

38. R. E. Wasylishen, S. Mooibroek, and J. B. Macdonald, *J. Chem. Phys.*, **81**, 1057 (1984).

39. M. A. Frerking and W. D. Langer, *J. Chem. Phys.*, **74**, 6990 (1981).

40. I. J. Solomon, J. N. Keith, A. J. Kacmarek, and R. K. Ramsey, *J. Am. Chem. Soc.*, **90**, 5408 (1968), report a value of −541.

41. C. J. Jameson, A. K. Jameson, and P. M. Burrell, *J. Chem. Phys.*, **73**, 6013 (1980).

42. D. K. Hinderman and C. D. Cornwell, *J. Chem. Phys.*, **48**, 4148 (1968).

43. C. J. Jameson, A. K. Jameson, and J. Honarbakhsh, *J. Chem. Phys.*, **81**, 5266 (1984).

44. J. W. Negben, W. B. Rene, and F. I. Metz, *J. Mol. Spectrosc.*, **20**, 72 (1966), using data from J. R. Holmes, B. B. Stewart, and J. J. MacKenzie, *J. Chem. Phys.*, **37**, 2728 (1962).

45. A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, **72**, 5639 (1980).

46. K. W. Zilm, A. J. Beeler, D. M. Grant, J. Michl, T.-C. Chou, and E. L. Allred, *J. Am. Chem. Soc.*, **103**, 2119 (1981).

47. B. R. Appleman, and B. P. Dailey, *Adv. Magn. Reson.*, **7**, 231 (1974).

48. A. Pines, M. G. Gibby, and J. S. Waugh, *Chem. Phys. Lett.*, **15**, 373 (1972); J. S. Waugh, M. G. Gibby, A. Pines, and S. Kaplan, *Proceedings 17th Colloque Ampére*, Turku, Finland, 1972.

49. K. W. Zilm and D. M. Grant, *J. Am. Chem. Soc.*, **103**, 2913 (1981).

50. S. J. Weiner, P. A. Kollman, D. T. Nguyen, and D. A. Case, *J. Comp. Chem.*, **7**, 230 (1986).