tion for the unstable (*e.g.*, $H_2O \cdots HClO_4$) state. This mechanism is more easily described in terms of the slower reverse reaction. In that reverse, the solvent first reorganizes from the configuration which is in equilibrium with the reactants ($H_2OH^+ \cdots OClO_3^-$) into an intermediate configuration, the proton then transfers to give $H_2O \cdots HOClO_3$, but before the solvent can relax, the proton is transferred back to form reactants. It is this back transfer event which is ultrafast.

In contrast, the $H_2O + H_3O^+$ reaction is not ultrafast. This reaction should have a large F_{sr} and should thus follow the coupled mechanism. In fact, its rate constant (2×10^{11} sec^{-1} at 25° after correction to a per proton basis)[1b] is within a factor of 2 of the reciprocal of the macroscopic dielectric relaxation time for water (1.2×10^{11} sec^{-1}). It would appear that this reaction proceeds as fast as it can *via* the coupled mechanism (*i.e.*, with $k \approx \tau^{-1}$).

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A Comparison of Diborane Molecular Properties from Minimum Basis Set and Extended Slater Orbital Wave Functions

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Abstract: A comparison of extended and optimized minimum STO basis set wave functions for B_2H_6 indicates that boron hydride energies, ionization potentials, diamagnetic susceptibility and shielding constants, and total electron densities may be reliably determined from a minimum basis set calculation. Minimum basis set difference densities and nuclear quadrupole coupling constants are only qualitatively correct. Minimum basis set atomization energies appear to be more accurate than those computed with large basis sets, when the atomic wave functions are determined using the molecular exponents.

The study of diborane (B_2H_6) by self-consistent field (SCF) methods has been the subject of much theoretical work.[1-10] As the prototype boron hydride, B_2H_6 is the simplest stable member of a large class of molecules whose chemical and physical properties have long fascinated chemists. The nature of electron-deficient bonding, the anomalous character of chemical shifts,[11,12] the mechanism of molecular rearrangements,[13] and the interpretation of chemical reactivity[14] have all inspired much theoretical research and speculation.

Most of the previous boron hydride SCF calculations have been done with minimum basis set wave functions. Because a boron hydride minimum basis set provides a favorable ratio (2:1) of basis orbitals to occupied orbitals, it has been hoped that improvement of the wave function would be unnecessary for the investigation of most boron hydride properties. The present study was undertaken in order to test the adequacy of the minimum basis set approximation.

Wave Functions

A discussion of the minimum basis set wave function chosen for purposes of comparison has been given in a previous paper.[5g] The basis consists of a 1s, 2s, 2p (three isotropic components) set of Slater-type orbitals (STO's) on each boron and a 1s STO on each hydrogen. The exponent of each orbital has been optimized with the total SCF energy as the variational criterion.

The expanded basis set reported here consists of 68 STO's, 19 on each boron and 5 on each hydrogen. The basis orbitals for both the minimum and expanded basis sets are given in Table I. For the large basis set, exponents of s and p orbitals on boron are

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taken from best atom values determined by Bagus.[15] The remaining orbital exponents were chain optimized using a BH molecular fragment with an internuclear distance equal to the boron-terminal hydrogen bond length of 2.26 au. Only one optimization of the boron 3d and hydrogen 2p exponents was performed, since the original estimate of these exponents proved nearly optimal. The hydrogen 1s and hydrogen 2s exponents were chain optimized twice because of partial coupling between the two orbitals. The optimizations assured a convergence of each exponent to at least 0.02 au. No attempt was made to differentiate between the terminal hydrogen (H_t) and bridge hydrogen (H_b) basis sets, since we felt the size and composition of the expanded basis would provide adequate flexibility in the electron density near both hydrogens.

Table I. Basis Sets for B_2H_6

	Minimum Slater exponent		Expanded Slater exponent
H_t 1s	1.1473	H 1s	1.1449
H_b 1s	1.2095	H 2s	1.0205
		H 2p	1.952
B 1s	4.68	B 1s	7.338
B 2s	1.4426	B 1s	3.996
B 2p	1.4772	B 2s	1.724
		B 2s	1.110
		B 3s	4.796
		B 2p	4.558
		B 2p	1.753
		B 2p	0.931
		B 3d	1.48967

The geometry of diborane has been determined by several authors using gas-phase electron diffraction techniques.[16] Kuchitsu[17] later refined these results with the use of rotational constants obtained from high-resolution infrared and Raman spectroscopy. Since the minimum Slater set results were obtained using the experimental results of Bartell and Carroll,[16b] we have used this same geometry for the expanded Slater calculation (see Table II).

Table II. Geometry of B_2H_6[a]

	x	y	z
H(1)	−1.9474	0.0	−2.82425
H(2)	−1.9474	0.0	2.82425
H(3)	1.9474	0.0	−2.82425
H(4)	1.9474	0.0	2.82425
H(5)	0.0	−1.89471	0.0
H(6)	0.0	1.89471	0.0
B(1)	0.0	0.0	−1.67715
B(2)	0.0	0.0	1.67715

[a] Coordinates are given in atomic units (1 au of distance = 0.529173 × 10^{-10} cm).

Computer Programs

The SCF wave functions were obtained using computer programs written by Stevens and described elsewhere.[18] Two-electron integrals were calculated to an accuracy of 10^{-5} au. Time for the large basis set calculation was slightly more than 10.25 hr on an IBM 360-65 computer. Of this time 9 hr were spent evaluating approximately 650,000 atomic orbital two-electron integrals, while 1 hr was required to transform these integrals to a symmetry orbital basis. Details of the minimum basis set SCF calculation have been given previously.[5g] Expectation values of one-electron operators were computed for both wave functions using a program written by Laws and described in another paper.[19]

Comparison of Results

A comparison of results from the minimum and extended Slater basis set calculations is given in Table III,[20] along with results of several earlier calculations. As expected, our large Slater basis yields the lowest total energy, almost 0.06 au below the best previous results. However, even wave function A is within 1% of the experimental energy. Hence the total energy is not a particularly sensitive function of the quality of the SCF wave function in B_2H_6.

Some controversy has surrounded the use of Mulliken charges and overlap populations[21] as a means of theoretical analysis.[22] A comparison of Mulliken charges computed from wave functions A and F (see Table III) suggests that gross atomic populations are much too basis set dependent to be of practical use in characterizing charge distributions. Overlap populations depend more on molecular geometry than atomic charges and exhibit much less wave function dependence (see Table III). The presence of polarization functions in the expanded Slater set F is undoubtedly responsible for much of the increase in both B–B and B–H overlap populations relative to minimum Slater set calculations A and B. The reduction in B–B overlap population on introduction of anisotropy in the minimum Slater basis p orbitals is particularly curious in view of the difference densities previously obtained[5g] (see Figure 1) which suggest an increase in B–B bonding with the anisotropic p orbital set. An explanation lies in the fact that Mulliken overlap populations consider only two-center contributions to the overlap operator.[21a,22a] The boron p_z orbital is more contracted in the anisotropic wave function (see ref 5g, Table III), and the resulting decrease in p_z–p_z and p_z–2s overlap is sufficient to lower the total B–B overlap population. The total electron density, however, is a sum of contributions from one- and two-center charge distributions and depends on the detailed shape of the component orbitals. In this case at least, these additional factors are sufficient to produce a net positive change in electron density along the B–B axis (Figure 1), despite the lowered overlap population.

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Table III. Comparison of B_2H_6 Calculations[a]

	Minimum Slater		Gaussian			Extended Slater	
	A	B	C	D	E	F	Exptl[a]
Total energy	−52.7183	−52.7204	−52.753	−52.7551	−52.7558	−52.8331	−53.269
Kinetic energy	52.6275	52.7039				52.7446	
Nuclear attraction	−183.9028	−183.9604				−184.2149	
$-E/T$	1.00173	1.0003		0.99882		1.00168	1.0
Charges H_t	−0.067	−0.065	0.045			0.023	
H_b	0.010	0.011	−0.002			0.099	
B	0.125	0.118	−0.088			−0.145	
Overlap populations B–B	0.312	0.298	0.064			0.338	
B–H_t	0.820	0.822	0.880			0.886	
B–H_b	0.394	0.397	0.345			0.420	
Electron densities Center of symmetry	0.096	0.096		0.092		0.109	
H_t	0.463	0.457		0.453		0.462	
H_b	0.489	0.486		0.493		0.467	
Atomization energy	−0.931					−0.775	−0.963
Orbital energies $1a_g$	−7.6209	−7.6223	−7.6416	−7.6484		−7.6219	
$1b_{1u}$	−7.6206	−7.6220	−7.6410	−7.6479		−7.6213	
$2a_g$	−0.8768	−0.8777	−0.8979	−0.8734	−0.8926	−0.8796	−0.788
$2b_{1u}$	−0.6323	−0.6346	−0.6457	−0.6427	−0.6403	−0.6411	−0.5913
$1b_{2u}$	−0.5574	−0.5577	−0.5558	−0.5493	−0.5523	−0.5564	−0.541
$1b_{3u}$	−0.5375	−0.5386	−0.5446	−0.5285	−0.5363	−0.5343	−0.512
$3a_g$	−0.5162	−0.5195	−0.5174	−0.5205	−0.5163	−0.5223	−0.490
$1b_{2g}$	−0.4673	−0.4681	−0.4737	−0.4744	−0.4642	−0.4691	−0.4348
$1b_{3g}$	0.2058	0.1961	0.1084			0.1123	
$4a_g$	0.4507	0.4562	0.1992			0.1901	

[a] The experimental quantities are taken from ref 20 and the vertical ionization potentials of ref 10. Electron densities are given in e/(au)^3. All energy terms are given in Rydbergs (1 Rydberg = 10,9678 cm^{-1}). The labeling of the irreducible representation for the point group D_{2h} here follows the recommendations of the Joint Commission for Spectroscopy of the International Astronomical Union and the International Union of Pure and Applied Physics, *J. Chem. Phys.*, **23**, 1997 (1955). The above assignments correspond to placing terminal hydrogens in the *XZ* plane and bridge hydrogens in the *YZ* plane.

Since the Mulliken charges and B–B overlap population reported in calculation C differ so much from the three Slater set results, we feel some comments are in order concerning this discrepancy. Karplus and Kern[22b] have earlier pointed out that wave functions which yield nearly equal total energies may differ significantly in their estimation of atomic charges. The basis orbital exponents in both minimum Slater calculations discussed here were thoroughly optimized, and the expanded Slater basis was chosen with considerable care. In calculation C, Burnell and Kaufman use a hydrogen basis set determined optimal for the hydrogen atom. They have made no attempt to scale or otherwise optimize the orbital exponents, as was done in both calculations D and E.[23] Their boron atom basis set is taken from an optimal carbon atom basis[24] and scaled according to a procedure used previously by Csizmadia and Harrison.[25] While this technique of basis selection may be adequate for purposes of computing total and orbital energies, we feel the more sensitive Mulliken charges and overlap populations cannot be computed reliably from such a wave function.[22a] Hence the comparison of our Slater basis calculations should provide a more realistic picture of the reliability with which such numbers may be determined when the basis set is carefully chosen.

Boron hydride atomization energies computed from minimum Slater set molecular wave functions have been found remarkably accurate when the atomic wave functions are determined from basis sets employing optimized molecular exponents.[14c] The surprising cancellation of errors due to correlation effects, orbital contraction, and minimum basis set inadequacies apparently does not carry over to a significant extent in the expanded basis set calculation (see Table III). The improvement in atomic energies computed using the extended basis more than offset the corresponding reduction in molecular energy. Thus the earlier "prescription" for obtaining atomization energies[14c] from minimum basis set calculations appears to give results in better agreement with experimental data.

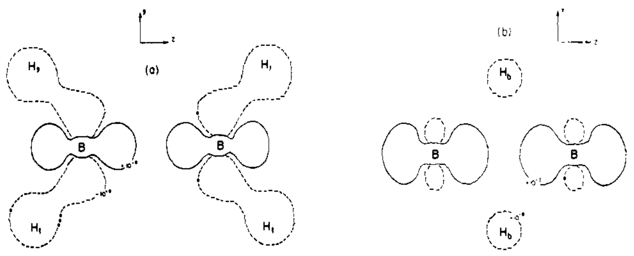

Figure 1. Difference density (wave function B density minus wave function A density) in e/au^3. (a) Terminal hydrogen plane (*xz*). (b) Bridge hydrogen plane (*yz*).

Orbital energies for each of the calculations A–F are given in Table III, and the Koopmans' theorem[26]

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(23) Variation of linear expansion coefficients does allow for first-order changes in the hydrogen exponents of ref 8. Though Burnelle and Kaufman refer to a study by Moskowitz and Harrison [J. W. Moskowitz and M. C. Harrison, *J. Chem. Phys.*, 42, 1726 (1965)] as justification for their procedure, the latter paper bases its conclusions almost totally on energetic considerations, devoting a total of five sentences to a discussion of population analysis.

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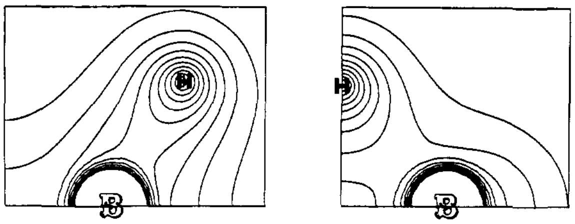

Figure 2. Total electron density in B_2H_6 using wave function A. (a, left) Terminal hydrogen plane (*xz*) showing B(2) and H(4). (b, right) Bridge hydrogen plane (*yz*) showing B(2) and H(6). In both Figure 2a and 2b the center of molecular symmetry is at the lower left hand corner of the map. The contour intervals are successive multiples of 0.04 e/au^3, except for the single contour around the center of symmetry in Figure 2b, which corresponds to 0.100 e/au^3.

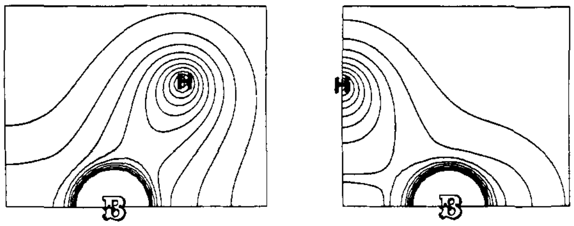

Figure 3. Total electron density analogous to that of Figure 2, but using wave function F. Contours are identical with those of Figure 2, except for the single contour around the center of symmetry in Figure 3b, which corresponds to a density of 0.115 e/au^3.

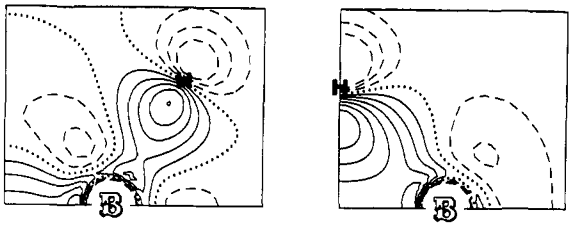

Figure 4. Difference density obtained by subtracting Figure 2 density from Figure 3 density. Contour intervals are 0.004 e/au^3. Solid lines indicate positive density, dotted lines zero density, and dashed lines negative density.

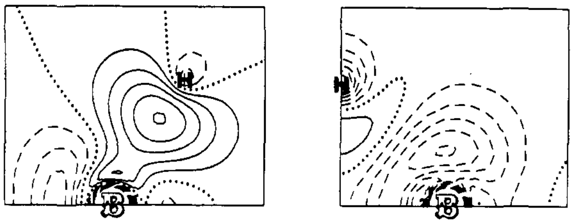

Figure 5. Difference density (molecular density minus sum of spherical atom densities) computed from wave function A. Contour intervals are 0.01 e/au^3.

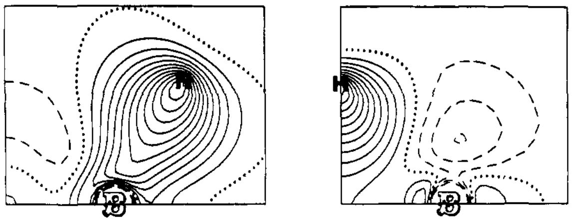

Figure 6. Difference density computed from wave function F. Contour intervals are 0.01 e/au^3.

ionization potentials are compared to the experimental results of Brundle, *et al.*[10] The ordering of eigenvalues is identical in all calculations. The discrepancies in orbital energies computed from wave functions A and F are relatively small compared to the differences between experimental and calculated ionization potentials. Hence the minimum basis set would seem as reliable as any of the others for computing such numbers. However, the discrepancies in virtual orbital eigenvalues suggest the minimum basis would be unsuitable for computing transition energies.

The use of electron density maps has previously been suggested as a consistently reliable method of comparing charge distributions obtained from different wave functions.[22b] A comparison of several point densities in Table III shows reasonable agreement between minimum Slater, Gaussian, and expanded Slater densities. A comparison of electron density contour maps obtained from wave functions A and F (Figures 2 and 3) shows gross features of the charge distribution to be similar. Both maps indicate a concentration of charge in the $B-H_4$ and $B-H_6$ bonding regions, with relatively little density along the B–B axis. Figure 4 shows the difference in electron density between calculations F and A. The effect of sp hybridization on the hydrogen atoms is particularly clear in this figure. An increase in charge within $B-H_t$, $B-H_b$, and B–B units is evident, but the change in density between $B-H_t$ and $B-H_b$ atoms is significantly greater than along the B–B axis. Thus the expanded basis set density maps reinforce an earlier interpretation[5g] that the two $B(H_t)_2$ units are joined primarily through hydrogen bridge bonds rather than by direct B–B linkage.

A useful picture of chemical bonding can usually be obtained from the difference between the molecular density and sum of spherical atom densities. In Figures 5 and 6 we show these difference densities obtained from wave functions A and F. In each case the atomic wave functions were composed of basis orbitals used in the corresponding molecular SCF calculation. Wave functions for the boron and hydrogen atoms correspond to the ground state of each atom. The concentration of electron density in $B-H_t$ and $B-H_b$ units is particularly dramatic in the extended basis set results of Figure 6. There is relatively little density change along the B–B axis. In Figure 5 the small size of the basis set and lack of polarization functions on hydrogen produce a more diffuse concentration of charge in the $B-H_t$ bond and only a small positive density in the hydrogen bridge bonds. The use of anisotropic p orbitals on boron (see Figure 1) would shift charge from the $B-H_t$ bonds into the region between $B(H_t)_2$ units, producing a more balanced difference density. Figures 5 and 6 and the results of additional work on difference density maps[27] strongly suggest that minimum basis set difference densities do not in general provide a quantitatively accurate picture of bonding effects on molecular charge distributions.

Calculation of one-electron operator expectation values can provide a sensitive test of wave function quality over a large region of space. Though the correlation error affects such properties only to second order when the exact Hartree–Fock wave function is

(27) E. A. Laws, unpublished results.

Table IV. B_2H_6 One-Electron Operator Expectation Values[a]

	H(1)		H(5)		B(1)	
Basis set	A	F	A	F	A	F
$1/r$	5.4721	5.4700	6.2701	6.2838	14.9474	14.9767
p_2^2/r	4.4279	4.4282	−4.9581	−5.0261	1.0949	1.1287
p_2^1/r	3.4253	3.4460	0	0	0	0
p_2^0/r	0.7856	0.7956	0.5702	0.5402	1.4869	1.5140
p_1^1/r^2	1.0247	1.0755	0	0	0	0
p_1^{-1}/r^2	0	0	1.2685	1.3804	0	0
p_1^0/r^2	0.7983	0.8380	0	0	0.4692	0.5333
p_2^2/r^3	0.8000	0.8084	−0.8248	−0.8856	0.7450	0.8012
p_2^1/r^3	0.5020	0.5132	0	0	0	0
p_2^0/r^3	0.004884	0.005683	0.07697	0.06424	0.1239	0.1501
			Center of Symmetry			
r^2		121.8328 (A)			121.7098 (F)	
$p_2^2r^2$		30.0956 (A)			29.7725 (F)	
$p_2^0r^2$		51.1925 (A)			50.5716 (F)	

[a] All quantities are reported in atomic units.

Table V. B_2H_6 One-Electron Properties[a]

	A	F
F_x(H(1))	−0.0439	0.00688
F_z(H(1))	−0.0319	0.00779
F_y(H(5))	−0.0966	0.0153
F_z(B(1))	−0.0599	0.00431
$eQ_{D(1)}q_a/h$	−224.3	−221.2
$eQ_{D(1)}q_y/h$	180.2	183.5
$eQ_{D(1)}Q_b/h$	44.1	37.8
θ	24.0	22.9
$eQ_{D(5)}q_x/h$	217.0	228.6
$eQ_{D(5)}q_y/h$	−153.9	−182.3
$eQ_{D(5)}q_z/h$	−63.1	−46.3
$eQ_{B(1)}q_x/h$	−1626	−1641
$eQ_{B(1)}q_y/h$	3035	3488
$eQ_{B(1)}q_z/h$	−1409	−1847
χ^d	−96.488	−96.391
χ_{xx}^d	−110.801	−110.522
χ_{yy}^d	−122.719	−122.311
χ_{zz}^d	−55.945	−56.340
σ^d(H(1))	97.129	97.091
σ^d(H(5))	111.292	111.536
σ^d(B(1))	265.312	265.833
σ_{xx}^d(H(1))	84.452	84.503
σ_{xx}^d(H(5))	138.355	138.633
σ_{xx}^d(B(1))	273.650	274.261
σ_{yy}^d(H(1))	123.749	123.802
σ_{yy}^d(H(5))	94.352	94.027
σ_{yy}^d(B(1))	283.367	284.278
σ_{zz}^d(H(1))	83.184	82.969
σ_{zz}^d(H(5))	101.171	101.947
σ_{zz}^d(B(1))	238.919	238.959

[a] Quadrupole coupling constants are reported in kilocycles per second. Susceptibility and shielding constants are given in parts per million. Forces (F) are reported in atomic units (1 au of force = 8.2378×10^{-3} dyn). θ is given in degrees (see Figure 7). The nuclear quadrupole moment of the deuteron and ^{11}B nucleus were taken to be 0.002796 barns [H. Narumi and T. Watanabe, *Progr. Theor. Phys.*, **35**, 1154 (1966)] and 0.0355 barns [G. Wessel, *Phys. Rev.*, **92**, 1581 (1953)]. The coupling constants of the terminal deuteron have been referred to the principal axes of the quadrupole coupling tensor (see Figure 7). θ is given in degrees.

used, this condition is not generally satisfied by a finite basis set expansion. We refer to other papers for a thorough discussion of this point[28] and concentrate here on examining the basis set dependence of one-electron properties as determined from wave functions A and F. The range of angular and radial dependence of the one-electron properties chosen for comparison (see Table IV) is sufficiently broad to allow a reasonably thorough probe of wave function quality. Because some of these operators depend strongly on electron density in regions of space which have little effect on the SCF energy, examination of these properties allows a particularly sensitive test of basis set convergence.

In Tables IV and V we give the computed expectation values of the operators and properties listed in Table VI. Angular independent operators such as $1/r$ and r^2, which measure only averaged radial features of the charge distribution, are nearly identical in calculations A and F. The operator p_2/r^3 is particularly sensitive to electron sensity near the nucleus and shows considerable dependence on wave function quality in this comparison.

Table VI. One-Electron Operators and Associated Molecular Properties

Operator	Property
$1/r$, p_2/r	Average diamagnetic shielding σ^d and tensor components
r^2, p_2r^2	Average diamagnetic susceptibility χ^d and tensor components
p_1r	Dipole moment, gauge dependence of χ^d
p_1/r^2	Hellmann-Feynman forces F gauge dependence of σ^d
p_2/r^3	Nuclear quadrupole coupling constant eqQ/h and tensor components

A qualitative judgment about the electron density in the region of a nucleus can be made from examination of Hellmann-Feynman forces.[29] The symmetry of B_2H_6 is such as to preclude a net Hellmann-Feynman force on the molecule, even for a finite basis set wave function. Although the experimental geometry used in these calculations is almost certainly not identical with the equilibrium Hartree-Fock geometry, the difference between the two should be sufficiently small that Hellmann-Feynman forces will be very nearly zero in the limit of an exact Hartree-Fock solution. The nuclear forces computed from wave functions A and F are given in Table V. The extended Slater basis is seen to reduce the force on each boron by more than an order

(28) (a) R. E. Stanton, *J. Chem. Phys.*, **36**, 1298 (1962); (b) D. Tuan, *ibid.*, **52**, 5247 (1970); (c) J. Goodisman, *ibid.*, **38**, 304 (1963).

(29) (a) H. Hellmann, "Einfuhrung in die Quantenchemie," F. Deuticke, Ed., Leipzig, 1937, p 285; (b) R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939).

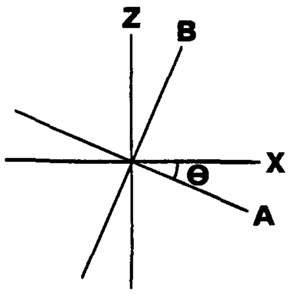

Figure 7. Orientation of the principal axes of the D(1) quadrupole coupling tensor in the *XZ* plane.

of magnitude and the forces on each hydrogen by roughly a factor of 5. It is particularly interesting to note that the direction of all forces has been reversed. The direction of the minimum basis set forces is such as to force the nuclei further apart. This condition probably arises from a lack of polarization functions. Consequently the electron density in the internuclear regions is insufficient to shield the nuclei from each other. The extended basis set wave function seems to have crowded too much charge between the nuclei, possibly due to the inadequate representation of correlation effects.

Nuclear quadrupole coupling constants (electric field gradients) provide another sensitive probe of electron density near the nucleus. The variation in computed p_2/r^3 expectation values (see Table IV) is indicative of the wave function sensitivity of this property. In Table V we list the computed quadrupole coupling constants for the molecule $B_2{}^{11}D_6$ (Figure 7). The discrepancy between the bridge deuteron coupling constants probably arises from the inability of the minimum basis set H_{1s} orbital to adequately describe the bridge bond density (see Figure 4b). The similarity between the magnitude of the D(1) and D(5) quadrupole coupling constants found using wave function F indicates that there is greater similarity in the electron density near D(1) and D(5) than the minimum basis set would suggest.

The average diamagnetic susceptibility and its tensor components show considerably less dependence upon the basis sets. The numbers reported in Table V were computed with the gauge at the center of mass. The discrepancy between values computed from wave functions A and F is less than 1% in all cases. This invariance is probably due in part to the not insignificant role played by molecular geometry in determining these numbers.[30] The results of this study and previous work on other molecules[19,31] suggest that diamagnetic susceptibilities may be accurately computed to within only a few per cent uncertainty by a minimum basis calculation. Since paramagnetic susceptibilities can be obtained directly from the experimental rotational magnetic moments,[31] a complete determination of boron hydride susceptibilities should be possible without recourse to a large basis set perturbation calculation.[32]

Calculations of paramagnetic shielding terms by SCF coupled Hartree-Fock techniques have been reported for a number of diatomic molecules and several small polyatomics.[33-35] However, extension of this method to molecules as large as most of the boron hydrides seems economically unfeasible at this time, and more approximate techniques appear incapable of giving sufficiently accurate results.[36] However, diamagnetic shielding constants may be computed straightforwardly from only the ground state wave function.[37] The results of such calculations for B_2H_6 are given in Table V. In each case the gauge has been taken at the position of the shielded nucleus. The agreement between the two calculations is remarkable and strongly suggests that minimum basis set wave functions can be trusted to give diamagnetic shielding constants to within a few per cent uncertainty.

The proton shielding constants reported here are in remarkable agreement with earlier results obtained by Kern and Lipscomb (KL).[38] Using Yamazaki's relatively crude SCF wave function[7] and the approximate results of Saika and Slichter,[39] KL found $\sigma^d = 112.69$ ppm for H_b and 96.05 ppm for H_t. These results are within a few parts per million of our more rigorous numbers. Taking the absolute shielding constants of H_b and H_t to be 33.3 and 29.0 ppm, respectively,[40] the paramagnetic shielding constants are computed to be −78.2 ppm for H_b and −68.1 ppm for H_t.[41] However, we emphasize again the gauge dependence of these individual terms. At an appropriate choice of origin the diamagnetic term will vanish altogether, while at another gauge it will equal the total chemical shift.

A revealing comparison can be made between our computed Mulliken charges and the diamagnetic shielding constants. Although the hydrogen charges suggest that H_b is more positive than H_t, the shielding constants imply that more electron density is concentrated near H_b. An examination of our total density maps (Figures 2 and 3) reveals that the bridge hydrogen is in fact surrounded by greater electron density. These observations are indicative of Mulliken charges' strong dependence on basis set composition. Hence they reveal little about total electron density, since the same wave function can be expressed by an infinite number of basis set expansions. In B_2H_6 the total density near H_b is augmented by valence shell electrons from both boron atoms, while the H_t density is affected by only one boron valence shell. Thus more charge surrounds

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(30) If we assume that one electron is localized on each hydrogen nucleus and five electrons on each boron, the computed χ^d is 68% of the values in Table V. A similar calculation for benzene gives $\chi_{zz}{}^d$ within 6% of the SCF value (see ref 33).

(31) R. M. Stevens, E. Switkes, E. A. Laws, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **93**, 2603 (1971).

(32) (a) To our knowledge, however, boron hydride rotational magnetic moments have not yet been measured; (b) for a discussion of such calculations on CH_4, see R. Hegstrom and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 4538 (1967).

(33) E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *ibid.*, **54**, 4269 (1971), and references cited therein.

(34) G. P. Arrighini, M. Maestro, and R. Moccia, *ibid.*, **52**, 6411 (1970).

(35) R. Ditchfield, D. P. Miller, and J. A. Pople, *ibid.*, **54**, 4186 (1971).

(36) (a) D. Tuan, S. T. Epstein, and J. O. Hirschfelder, *ibid.*, 44, 431 (1966); (b) J. O. Hirschfelder, "Perturbation Theory and Its Applications in Quantum Mechanics," C. H. Wilcox, Ed., Wiley, New York, N. Y., 1966; (c) D. Tuan and K. Wu, *J. Chem. Phys.*, **53**, 620 (1970); (d) D. Tuan, *Chem. Phys. Lett.*, 7, 115 (1970).

(37) For a promising approximate method for computing diamagnetic shielding constants that does not require a molecular SCF wave function, see W. H. Flygare and J. Goodisman, *J. Chem. Phys.*, **49**, 3122 (1968).

(38) C. W. Kern and W. N. Lipscomb, *ibid.*, 37, 275 (1962).

(39) A. Saika and C. P. Slichter, *ibid.*, 24, 1111 (1956).

(40) Calculated from the combined measurements of R. A. Ogg, Technical Report, Stanford University, 1955, and H. S. Gutowsky and C. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951).

(41) We have taken σ^d values from our large Slater set results.

the bridge hydrogen nucleus, but partitioning of this distribution to compute atomic populations requires that H_b surrender charge to both boron atoms, resulting in an H_b population lower than that of H_t. Although partitioning of the electron density has taken more charge from H_b, the total density near H_b is greater because of its proximity to both boron atoms.

Discussion of Results

A thorough comparison of extended and optimized minimum STO basis sets for B_2H_6 has suggested the following conclusions. Boron hydride energies, ionization potentials, diamagnetic susceptibility and shielding constants, and total electron densities may be reliably computed from minimum basis set wave functions. Minimum basis set difference densities and quadrupole coupling constants are only qualitatively correct. The "prescription"[14c] for computing atomization energies appears more accurate when a small, rather than large, basis set is used.

From the results of this work and other studies,[22] we are inclined to feel that Mulliken overlap and atomic populations provide an easily misinterpreted characterization of electron density. Mulliken overlap populations neglect the effect of one-center charge distributions on molecular binding, while Mulliken charges reveal little about total electron density. Thus a comparison of B–B overlap populations from wave functions A and B (see Table III) suggests that direct B–B bonding is reduced in the latter wave function, when in fact just the opposite is true (see Figure 1). Similarly, the Mulliken charges on H_b and H_t seem to imply greater electron density near H_t, but our diamagnetic shielding calculations and electron density maps belie this implication. An alternative method of partitioning electron density has recently been suggested by Bader, Beddall, and Cade (BBC).[42] Although BBC feel their scheme allows a "natural partitioning" of the charge distribution, the technique is clearly more cumbersome than Mulliken's and the applicability to general polyatomics is not yet tested. In lieu of a better partitioning scheme, we are inclined to feel that electron density contour maps are the most reliable and practical means of characterizing charge distributions.

The accuracy of our minimum basis diamagnetic shielding constants suggests that wave functions previously obtained for larger boron hydrides may be used to compute reliable diamagnetic chemical shifts and thus provide a useful comparison with numbers obtained by more approximate ring current calculations.[12] Since the absolute proton chemical shifts in B_2H_6 are known,[40] a determination of both diamagnetic and paramagnetic proton shielding constants in other boron hydrides should be possible when the chemical shifts relative to B_2H_6 protons are known.[11,31b] A report of such calculations is planned for future publication.

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A Self-Consistent Field Study of Decarborane(14)

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Abstract: A self-consistent field wave function for decaborane(14), $B_{10}H_{14}$, has been obtained from a minimum basis set of Slater-type orbitals. Electron density and difference density maps are used to discuss molecular bonding properties and possible valence structures. Static reactivity indices are found to correlate well with the experimental order of electrophilic and nucleophilic substitutions. The atomization energy and ionization potential are found in good agreement with experimental numbers, but the dipole moment is too large by roughly 40%. Theoretical values for the diamagnetic susceptibility and shielding constants are reported and the implications of these numbers discussed.

The chemical and physical properties of decaborane(14), $B_{10}H_{14}$, have been more extensively studied than those of any other boron hydride. The geometry is accurately known from the neutron diffraction study of Tippe and Hamilton,[1] and the nuclear magnetic resonance (nmr) spectra of both ^{11}B and ^1H have been completely analyzed.[2,3] The ionization potential,[4] heat of formation,[5] dipole moment,[6] and magnetic susceptibility[6] have all been determined, and voluminous literature exists on the molecule's reactivity, particularly in regard to addition and substitution reactions.[7]

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