

Molecular Orbital Theory of the Properties of Inorganic and Organometallic Compounds 4. Extended Basis Sets for Third- and Fourth-Row, Main-Group Elements*

K. D. Dobbs and W. J. Hehre*

Department of Chemistry, University of California, Irvine, California 92717

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Two new series of efficient basis sets for third- and fourth-row, main-group elements have been developed. Split-valence 3-21G basis sets have been formulated from the minimal expansions by Huzinaga, in which each atomic orbital has been represented by a sum of three Gaussians. The original expansions for *s*- and *p*-type orbitals (except those for 1*s*) have been replaced by new combinations in which the two sets of orbitals (of the same *n* quantum number) share Gaussian exponents. The Huzinaga expansions for 1*s*, 3*d* and 4*d* (fourth-row elements only) have been employed without further alteration. The valence atomic functions 4*s*, 4*p* for third-row elements; 5*s*, 5*p* for fourth-row elements) have been split into two and one Gaussian parts. Supplemented 3-21G^(*) representations have been formed from the 3-21G basis sets by the addition of a set of single *d*-type Gaussian functions.

The performance of 3-21G and 3-21G^(*) basis sets is examined with regard to the calculation of equilibrium geometries, normal mode vibrational frequencies, reaction energies, and electric dipole moments involving a variety of normal and hypervalent compounds containing third- and fourth-row, main-group elements. The supplementary functions incorporated into the 3-21G^(*) basis sets are generally found to be important, especially for the proper description of equilibrium bond lengths and electric dipole moments. 3-21G^(*) representations are recommended for general use in lieu of the unsupplemented 3-21G basis sets.

INTRODUCTION

Single-determinant Hartree-Fock molecular orbital theory has proven remarkably successful in the calculation of equilibrium geometries, vibrational frequencies, and relative energies of molecules containing first- and second-row elements.¹ Even minimal basis sets, such as the now widely employed STO-3G representation,² are capable of reproducing a wide variety of experimental equilibrium structures to a reasonable degree of accuracy. More flexible split-valence basis sets, such as the 3-21G representation,³ fare even better in the task of structure determination. In addition, theoretical treatments at this level are moderately successful in describing molecular vibrational frequencies, as well as relative isomer energies and electric dipole moments, properties which generally are not well handled at the minimal basis set level. Note, however, that molecules incor-

porating second-row elements with expanded valence octets, i.e., hypervalent molecules, do not appear to be properly described using either minimal or split-valence representations. Only when the basis sets for these elements are supplemented by *d*-type functions are their performances generally acceptable. Supplemented STO-3G and 3-21G basis sets for second-row atoms have appeared in the literature.^{4,5}

Larger atomic orbital representations, such as the 6-31G* full polarization basis set,⁶ generally lead to further improvements in all calculated properties for both normal and hypervalent molecules. In addition, they appear to be among the simplest representations suitable for calculations beyond the single-determinant (Hartree-Fock) framework.^{7,8}

Given present computer and computer program technology, minimal basis sets such as STO-3G are routinely applicable to molecules containing up to 10–20 first- and/or second-row atoms. Split-valence basis sets comprise more atomic functions than minimal repre-

*Dedicated to John Pople on the occasion of his 60th birthday.

sentations, and their range of application is necessarily more limited. In practice, however, the 3-21G split-valence basis set, which comprises the same number of primitive Gaussian functions as STO-3G (although a significantly greater number of basis functions), is not much more costly computationally than the minimal STO-3G set, at least for applications which are bounded by integral evaluation steps, i.e., derivative evaluation as is required for structure optimization and vibrational frequency calculation, rather than by the SCF procedure. Molecules comprising 10–15 heavy (non-hydrogen) atoms are easily in the range of application of the 3-21G basis set. Larger basis sets, which include polarization (*d*-type) functions on some or all heavy atoms, are somewhat more costly to apply. The supplemented 3-21G basis set for second-row elements, termed 3-21G^(*),⁵ is only slightly more expensive than its unsupplemented parent for molecules incorporating only one or two second-row elements; application of the 6-31G* basis set is in practice limited to molecules comprising at most 5–10 first- and/or second-row atoms.

Far less information is available regarding the performance of simple molecular orbital methods for molecules containing heavier elements. STO-3G minimal basis sets have been proposed for the third- and fourth-row, main-group elements,^{9,10} and for first- and second-row transition metals.¹¹ Equilibrium geometries calculated at this level for a wide variety of compounds containing both third- and fourth-row, main-group elements are generally in reasonable accord with the available experimental structural data;^{9,10} the geometries of simple transition metal complexes also seem to be relatively well described at the minimal basis STO-3G level, although significant exceptions to this general rule have already been noted.¹¹

Experience with molecules containing first- and second-row elements makes it quite clear that STO-3G minimal basis sets will not fare as well in describing the relative thermochemical stabilities and normal mode vibrational frequencies of molecules containing third- and fourth-row, main-group elements as they did in obtaining equilibrium structures. It will, more than likely, be necessary to turn to split-valence and higher repre-

sentations in order to obtain reasonable descriptions of these properties. A number of larger than minimal basis sets have been proposed for the third- and fourth-row, both main-group elements and transition metals alike.¹² Unfortunately, none of these basis sets have as yet been applied to a large series of diverse molecules, in order that their overall utility be assessed. In fact, only a very limited number of studies involving the calculation of equilibrium structures and/or vibrational frequencies of molecules containing third- and fourth-row elements have been carried out to date. Little is known, therefore, about the ability of any of these basis sets to reproduce experimental equilibrium structures, relative energies, and vibrational frequencies. Also of concern, is the fact that none of these representations have been constructed to permit integral evaluation steps to proceed in as highly efficient a manner as possible. In particular, considerable computational savings could have been achieved if the exponents of the individual Gaussian functions which go to make up all atomic orbitals of given *n* quantum number, e.g., 2s, 2p_x, 2p_y, 2p_z, had been constrained to be identical.¹³ Although such exponent restrictions somewhat limit the overall flexibility of the atomic orbital representations, basis sets already constructed in this manner, e.g., STO-3G, 3-21G, have proven to be highly successful theoretical tools for the study of molecular structure and energetics.¹

We report here the development of efficient split-valence, 3-21G and supplemented split-valence, 3-21G^(*), basis sets for third- and fourth-row, main-group elements. (Future papers in this series will address the formulation of even larger basis sets for these elements, as well as the corresponding basis sets for first- and second-row transition metals). Our present work is both an extension of previous efforts with lighter elements,^{3,5} and of the work of Huzinaga^{12d,12e,14} directed at the construction of uniform Gaussian minimal basis sets for the entire Periodic Table. It should allow for continued exploration, by theoretical means, of the properties of molecules containing heavy, main-group elements. As in previous work, we stress primarily equilibrium structures, normal mode vibrational frequencies, relative energies, and electric dipole moments (the latter

as an indicator of molecular charge distributions) in our assessment of the performance of these new basis sets.

CONSTRUCTION OF 3-21G SPLIT-VALENCE BASIS SETS FOR THIRD- AND FOURTH-ROW, MAIN-GROUP ELEMENTS

Development of 3-21G split-valence basis set for third- and fourth-row, main-group elements proceeds along similar lines to the previous development of the corresponding basis sets for first- and second-row elements.³ In particular, functions that comprise the valence shell are split into two (inner and outer) parts, while inner shell atomic orbitals are each represented by a single basis function. Basis sets for third-row, main-group elements are then written as follows:

K to Kr: 1s

$$\begin{aligned} &2s, 2p_x, 2p_y, 2p_z \\ &3s, 3p_x, 3p_y, 3p_z, 3d_{xx}, 3d_{yy}, 3d_{zz}, \\ &\quad 3d_{xy}, 3d_{xz}, 3d_{yz} \\ &4s', 4p'_x, 4p'_y, 4p'_z \\ &4s'', 4p''_x, 4p''_y, 4p''_z \end{aligned}$$

Even though valence *p*-type functions are formally unoccupied in the ground states of potassium and calcium, experience with first- and second-row alkali and alkaline earth metals suggests their involvement in the bonding in molecules. Note, that a set of six second-order functions is employed to represent the 3*d* shell, in lieu of the usual complement of five *d* functions. The latter set may be formed as linear combinations of the six second-order functions, with a 3*s*-type function ($3d_{xx} + 3d_{yy} + 3d_{zz}$) remaining.

Basis sets for fourth-row, main-group elements are written in a similar manner:

Rb to Xe: 1s

$$\begin{aligned} &2s, 2p_x, 2p_y, 2p_z \\ &3s, 3p_x, 3p_y, 3p_z, 3d_{xx}, 3d_{yy}, 3d_{zz}, \\ &\quad 3d_{xy}, 3d_{xz}, 3d_{yz} \\ &4s, 4p_x, 4p_y, 4p_z, 4d_{xx}, 4d_{yy}, 4d_{zz}, \\ &\quad 4d_{xy}, 4d_{xz}, 4d_{yz} \\ &5s', 5p'_x, 5p'_y, 5p'_z \\ &5s'', 5p''_x, 5p''_y, 5p''_z \end{aligned}$$

Here again, *p*-type functions are included in the valence description of the alkali and alkaline earth elements.

Each of the inner shell atomic basis functions is represented by three Gaussian functions (termed primitives); inner and outer parts of valence basis functions are in terms of two and one Gaussians, respectively, i.e.,

$$\begin{aligned} \phi_{1s}(r) &= \sum_{k=1}^3 d_{1s,k} g_s(\alpha_{1,k}, r) \\ \phi_{2s}(r) &= \sum_{k=1}^3 d_{2s,k} g_s(\alpha_{2,k}, r) \\ \phi_{2p}(r) &= \sum_{k=1}^3 d_{2p,k} g_p(\alpha_{2,k}, r) \\ \phi_{3s}(r) &= \sum_{k=1}^3 d_{3s,k} g_s(\alpha_{3s,k}, r) \\ \phi_{3p}(r) &= \sum_{k=1}^3 d_{3p,k} g_p(\alpha_{3p,k}, r) \\ \phi_{3d}(r) &= \sum_{k=1}^3 d_{3d,k} g_d(\alpha_{3d,k}, r) \\ \phi_{4s}(r) &= \sum_{k=1}^3 d_{4s,k} g_s(\alpha_{4s,k}, r) \\ \phi_{4p}(r) &= \sum_{k=1}^3 d_{4p,k} g_p(\alpha_{4p,k}, r) \\ \phi_{4d}(r) &= \sum_{k=1}^3 g_{4d,k} g_d(\alpha_{4d,k}, r) \\ \phi'_{4s}(r) &= \sum_{k=1}^2 d'_{4s,k} g_s(\alpha'_{4,k}, r) \\ \phi'_{4p}(r) &= \sum_{k=1}^2 d'_{4p,k} g_p(\alpha'_{4,k}, r) \\ \phi''_{4s} &= g_s(\alpha''_4, r) \\ \phi''_{4p} &= g_p(\alpha''_4, r) \\ \phi'_{5s} &= \sum_{k=1}^2 d'_{5s,k} g_s(\alpha'_{5,k}, r) \\ \phi'_{5p} &= \sum_{k=1}^2 d'_{5p,k} g_p(\alpha'_{5,k}, r) \\ \phi''_{5s} &= g_s(\alpha''_5, r) \\ \phi''_{5p} &= g_p(\alpha''_5, r) \end{aligned} \quad (1)$$

The parameters α and d in eqs. (1) are Gaussian exponents and linear expansion coefficients, respectively. g_s , g_p , and g_d are normalized Gaussian functions, e.g.,

$$\begin{aligned} g_s(\alpha, r) &= (2\alpha/\pi)^{3/4} \exp(-\alpha r^2) \\ g_x(\alpha, r) &= (128\alpha^5/\pi^3)^{1/4} x \exp(-\alpha r^2) \\ g_{xx}(\alpha, r) &= (2048\alpha^7/9\pi^3)^{1/4} x^2 \exp(-\alpha r^2) \end{aligned} \quad (2)$$

with similar expressions for the remaining p and d components. Note from eqs. (1) that, for a given n quantum number, the Gaussians that comprise s - and p -type atomic orbitals are constrained to have the same exponents. As indicated in the introduction, this leads to significant computational advantages. The d -type atomic orbitals are treated independently. While computational savings would also accrue from exponent constraints here, the radial extensions of $3d$ and $4d$ orbitals in main-group compounds are sufficiently different than those of the associated s - and p -type functions to warrant their treatment in a completely independent manner.

In our previous work on first- and second-row elements,³ Gaussian exponents and linear expansion coefficients were determined as to minimize unrestricted Hartree-Fock energies for atoms in their ground-state electronic configurations. Here we take an alternative approach, and instead develop 3-21G representations around the uniform series of minimal basis sets recently published by Huzinaga for the first 86 elements of the Periodic Table.¹⁴ In these representations, each atomic orbital is described by a sum of three Gaussians, the individual Gaussian exponents and linear expansion coefficients being first determined as least-squares fits to atomic (ground state) Hartree-Fock functions, and then further refined by total (atomic) energy minimization. Full details of the numerical procedures involved have already been provided by Huzinaga.¹⁴ Expansions representing $1s$, $3d$, and (for the elements In to Xe) $4d$ atomic orbitals are taken as is.

Expansions describing $2s$, $2p$, $3s$, $3p$, $4s$ and $4p$ (for elements except potassium and calcium), and $5s$ and $5p$ (for fourth-row elements except rubidium and strontium) atomic orbitals are modified from those provided by Huzinaga. Specifically, all functions of given n quantum number, e.g., $2s$, $2p_x$, $2p_y$, $2p_z$, are constrained to be made up of Gaussian primitives sharing a common set of exponents. This involves simultaneous least-squares fitting of the Huzinaga s - and p -type functions (of given n quantum number) to expansions in which the Gaussian exponents are held in common. Following the fitting procedure, the three Gaussian expansions describing the valence $4s$ and $4p$ atomic orbitals for gallium to kryp-

ton, and the $5s$ and $5p$ orbitals for indium to xenon are split into two and one Gaussian expansions, and the resulting functions renormalized. This is the procedure recommended by Huzinaga for development of split basis sets from the minimal representations.¹⁴

$4s$ and $4p$ atomic orbitals of potassium and calcium as well as $5s$ and $5p$ atomic orbitals of rubidium and strontium are handled in a similar manner. In particular, the Huzinaga three-Gaussian expansions for $4s$,¹⁴ as well as the single-Gaussian $4p$ orbital recommended by Huzinaga for use as polarization functions¹⁴ are simultaneously fit to three-Gaussian expansions for which the exponents of the individual s and p functions are held in common. This same method is also applied to the $5s$ and $5p$ orbitals of rubidium and strontium. These new functions are later split into two-Gaussian and one-Gaussian parts, and renormalized.

Final constrained basis functions for third-row, main-group elements are given in Table I; those for the corresponding fourth-row elements are provided in Table II. The remaining functions may be found in Huzinaga's published tabulation.¹⁴

EVALUATION OF 3-21G BASIS SETS

The performance of 3-21G basis sets for third- and fourth-row, main-group elements will be assessed in four areas: equilibrium geometries, normal mode vibrational frequencies, reaction energies, and electric dipole moments.

Equilibrium Geometries

Equilibrium geometries for one-heavy-atom hydrides obtained at the 3-21G level are compared with experimental structures (available for all systems except CaH_2 , GaH_3 , SrH_2 , and InH_3) in Table III. STO-3G data, where available, are also included for comparison. The 3-21G calculations offer a generally improved description of equilibrium bond lengths over STO-3G, especially for hydrides comprising elements on the left-hand-side of the periodic table. Here the minimal basis set calculations generally yield distances that are shorter than experimental values; on the

Table I. Constrained Gaussian basis functions for third-row, main-group elements.

K						
Shell	α	d_s	d_p	α	d_s	d_p
2sp	7.155720(+1)	-1.093429(-1)	1.339654(-1)	8.039744(+1)	-1.093028(-1)	1.354332(-1)
	1.543894(+1)	1.130640(-1)	5.302673(-1)	1.733075(+1)	1.088996(-1)	5.372215(-1)
	4.474551	9.462575(-1)	5.117992(-1)	5.083624	9.492768(-1)	5.018044(-1)
3sp	4.121275	-2.699730(-1)	1.994922(-2)	4.782229	-2.816074(-1)	1.900928(-2)
	1.188621	3.646323(-1)	4.340213(-1)	1.462558	3.410510(-1)	4.360377(-1)
	3.756738(-1)	8.107533(-1)	6.453226(-1)	4.792230(-1)	8.381044(-1)	6.386709(-1)
4sp'	2.445766(-1)	-2.688250(-1)	3.081035(-4)	4.396824(-1)	-2.697049(-1)	3.081105(-4)
	3.897175(-2)	1.128983	9.998787(-1)	5.913040(-2)	1.113293	9.998964(-1)
4sp''	1.606255(-2)	1.0	1.0	2.389701(-2)	1.0	1.0
Ga						
Shell	α	d_s	d_p	α	d_s	d_p
2sp	2.095834(+2)	-1.115162(-1)	1.442658(-1)	2.244360(+2)	-1.115150(-1)	1.446395(-1)
	4.569171(+1)	9.269636(-2)	5.731775(-1)	4.895543(+1)	9.120021(-2)	5.753796(-1)
	1.413297(+1)	9.622870(-1)	4.490858(-1)	1.518370(+1)	9.634491(-1)	4.459949(-1)
3sp	1.459954(+1)	2.910292(-1)	2.656186(-2)	1.591257(+1)	-2.895652(-1)	2.297302(-2)
	4.860842	-3.231876(-1)	4.833137(-1)	5.441437	2.938828(-1)	4.732446(-1)
	1.549111	-8.643910(-1)	5.924304(-1)	1.742603	8.891993(-1)	6.032779(-1)
4sp'	1.267943	-2.851306(-1)	3.018346(-2)	1.466538	-3.967339(-1)	2.789294(-2)
	1.883995(-1)	1.128022	9.884658(-1)	2.630934(-1)	1.190670	9.874901(-1)
4sp''	5.723676(-2)	1.0	1.0	8.482072(-2)	1.0	1.0
As						
Shell	α	d_s	d_p	α	d_s	d_p
2sp	2.377783(+2)	-1.128384(-1)	1.496798(-1)	2.550164(+2)	-1.119076(-1)	1.461488(-1)
	5.425662(+1)	8.722744(-2)	5.623223(-1)	5.557654(+1)	9.099936(-2)	5.813714(-1)
	1.632803(+1)	9.681883(-1)	4.593235(-1)	1.735661(+1)	9.636682(-1)	4.374597(-1)
3sp	1.710185(+1)	-2.914537(-1)	2.568559(-2)	1.844568(+1)	-2.917925(-1)	2.442141(-2)
	5.805144	2.969619(-1)	4.833968(-1)	6.328759	2.846212(-1)	4.833648(-1)
	1.902084	8.865791(-1)	5.887854(-1)	2.096758	8.973052(-1)	5.879038(-1)
4sp'	1.675404	-5.057610(-1)	2.528246(-2)	1.872633	-5.677639(-1)	2.825548(-2)
	3.416557(-1)	1.251764	9.874328(-1)	4.174736(-1)	1.294127	9.849060(-1)
4sp''	1.136303(-1)	1.0	1.0	1.370907(-1)	1.0	1.0
Br						
Shell	α	d_s	d_p	α	d_s	d_p
2sp	2.706015(+2)	-1.121487(-1)	1.477514(-1)	2.876446(+2)	-1.120607(-1)	1.475279(-1)
	5.825357(+1)	9.314451(-2)	6.010557(-1)	6.262009(+1)	9.013913(-2)	5.868918(-1)
	1.846933(+1)	9.616794(-1)	4.128704(-1)	1.969174(+1)	9.643301(-1)	4.295068(-1)
3sp	1.976142(+1)	-2.938704(-1)	2.500708(-2)	2.112321(+1)	-2.958173(-1)	2.606955(-2)
	6.821752	2.802663(-1)	4.866098(-1)	7.303286	2.792167(-1)	4.922498(-1)
	2.291629	9.020357(-1)	5.824234(-1)	2.488850	9.037303(-1)	5.742737(-1)
4sp'	2.131206	-6.518031(-1)	2.870833(-2)	2.361374	-7.202454(-1)	2.877518(-2)
	4.993537(-1)	1.336012	9.840695(-1)	5.860160(-1)	1.376846	9.833391(-1)
4sp''	1.647637(-1)	1.0	1.0	1.944473(-1)	1.0	1.0
Kr						
Shell	α	d_s	d_p	α	d_s	d_p

other hand, 3-21G bond lengths are longer than experimental distances. For example, the STO-3G bond distance in germane is 0.095 Å shorter than the experimental value, whereas the 3-21G length is 0.013 Å longer. Similarly, the STO-3G bond length in stannane is too short by 0.081 Å while the 3-21G

distance is longer than the experimental value by 0.026 Å. Overall, the mean absolute deviation of 3-21G from experimental bond is 0.040 Å, compared with an error of 0.067 Å for STO-3G.

The 3-21G bond angles are consistently larger than both experimental and STO-3G

Table II. Constrained Gaussian basis functions for fourth-row main-group elements

Rb						
Shell	α	d_s	d_p	α	d_s	d_p
2sp	3.041283(+2)	-1.123296(-1)	1.484409(-1)	-3.221246(+2)	-1.122353(-1)	1.488368(-1)
	6.626058(+1)	9.075080(-2)	5.891247(-1)	7.009046(+1)	8.954360(-2)	5.919466(-1)
	2.091945(+1)	9.639410(-1)	4.258251(-1)	2.217641(+1)	9.648135(-1)	4.221715(-1)
3sp	2.246533(+1)	-3.004850(-1)	2.445410(-2)	2.392763(+1)	-3.024718(-1)	2.483697(-2)
	7.877468	2.783566(-1)	4.944538(-1)	8.475114	2.700841(-1)	4.934775(-1)
	2.705271	9.076099(-1)	5.718567(-1)	2.942934	9.159200(-1)	5.709829(-1)
4sp	2.692116	-3.311623(-1)	1.190051(-2)	2.940966	-3.519846(-1)	9.723336(-3)
	7.230563(-1)	5.096991(-1)	4.951731(-1)	8.523559(-1)	4.972546(-1)	4.983220(-1)
	2.598383(-1)	6.982461(-1)	5.737244(-1)	3.215375(-1)	7.238598(-1)	5.650561(-1)
5sp'	1.897140(-1)	-2.711927(-1)	3.081009(-4)	3.480419(-1)	-2.851468(-1)	3.081096(-4)
	3.399726(-2)	1.141550	9.998654(-1)	4.817715(-2)	1.120939	9.998935(-1)
5sp''	1.471231(-2)	1.0	1.0	2.180335(-2)	1.0	1.0
Sn						
Shell	α	d_s	d_p	α	d_s	d_p
2sp	5.504423(+2)	-1.127094(-1)	1.523703(-1)	5.742875(+2)	-1.127462(-1)	1.525798(-1)
	1.197744(+2)	8.344350(-2)	6.096508(-1)	1.249537(+2)	8.286347(-2)	6.110106(-1)
	3.866927(+1)	9.696880(-1)	3.970249(-1)	4.039576(+1)	9.701505(-1)	3.951549(-1)
3sp	4.702931(+1)	-2.758954(-1)	-1.408485(-1)	4.880662(+1)	-2.824534(-1)	-1.509628(-1)
	2.249642(+1)	5.977348(-2)	5.290867(-1)	2.383588(+1)	6.605595(-2)	5.399677(-1)
	6.697117	1.082148	6.620681(-1)	7.048296	1.081987	6.604823(-1)
4sp	6.572360	4.284831(-1)	1.091305(-2)	6.973378	4.340356(-1)	1.195130(-2)
	2.502158	-4.633644(-1)	5.036759(-1)	2.693040	-4.610286(-1)	5.067195(-1)
	9.420246(-1)	-8.219679(-1)	5.581809(-1)	1.025958	-8.285579(-1)	5.529106(-1)
5sp	1.001221	-4.364172(-1)	-2.316334(-2)	1.131463	5.252085(-1)	-2.107053(-2)
	1.659704(-1)	1.189893	-9.903309(-1)	2.034092(-1)	-1.229226	-9.905914(-1)
5sp''	5.433974(-2)	1.0	1.0	7.056383(-2)	1.0	1.0
Sb						
Shell	α	d_s	d_p	α	d_s	d_p
2sp	5.988890(+2)	-1.127201(-1)	1.530671(-1)	6.232631(+2)	-1.128200(-1)	1.534195(-1)
	1.300386(+2)	8.264433(-2)	6.135972(-1)	1.353600(+2)	8.225243(-2)	6.148996(-1)
	4.213286(+1)	9.702579(-1)	3.916990(-1)	4.400048(+1)	9.706007(-1)	3.895162(-1)
3sp	5.151333(+1)	-2.770433(-1)	-1.378699(-1)	5.419078(+1)	-2.744120(-1)	-1.433312(-1)
	2.443595(+1)	5.750323(-2)	5.363550(-1)	2.582039(+1)	5.182968(-2)	5.391881(-1)
	7.420931	1.084703	6.508676(-1)	7.809583	1.087622	6.522851(-1)
4sp	7.314235	4.403812(-1)	1.530518(-2)	7.764217	4.467306(-1)	1.274620(-2)
	2.844053	-4.737341(-1)	5.160832(-1)	3.043932	-4.694704(-1)	5.221231(-1)
	1.105855	-8.221350(-1)	5.387570(-1)	1.199253	-8.298105(-1)	5.326614(-1)
5sp'	1.278637	6.016951(-1)	-2.225276(-2)	1.340364	5.904699(-1)	-2.558834(-2)
	2.412321(-1)	-1.258692	-9.896434(-1)	2.780884(-1)	-1.281968	-9.871016(-1)
5sp''	8.662967(-2)	1.0	1.0	9.672607(-2)	1.0	1.0
Te						
Shell	α	d_s	d_p	α	d_s	d_p
2sp	6.481887(+2)	-1.128507(-1)	1.541145(-1)	6.736611(+2)	-1.129128(-1)	1.544275(-1)
	1.403064(+2)	8.322834(-2)	6.194618(-1)	1.458491(+2)	8.290529(-2)	6.206174(-1)
	4.569880(+1)	9.697516(-1)	3.837583(-1)	4.757708(+1)	9.700289(-1)	3.820041(-1)
3sp	5.669469(+1)	-2.736965(-1)	-1.523217(-1)	5.916752(+1)	-2.739774(-1)	-1.518572(-1)
	2.748875(+1)	4.649968(-2)	5.437686(-1)	2.861159(+1)	4.553006(-2)	5.471507(-1)
	8.209096	1.091576	6.561679(-1)	8.596596	1.092528	6.519540(-1)
4sp	8.191679	4.508277(-1)	1.186988(-2)	8.638676	4.558408(-1)	9.585056(-3)
	3.244596	-4.632094(-1)	5.265246(-1)	3.462818	-4.617355(-1)	5.298193(-1)
	1.300489	-8.386360(-1)	5.266076(-1)	1.401040	-8.442883(-1)	5.235985(-1)
5sp'	1.451380	6.658515(-1)	-2.754131(-2)	1.578474	7.277718(-1)	-2.807244(-2)
	3.281033(-1)	-1.328584	-9.851368(-1)	3.750814(-1)	-1.362797	-9.842642(-1)
5sp''	1.150759(-1)	1.0	1.0	1.331790(-1)	1.0	1.0
I						
Shell	α	d_s	d_p	α	d_s	d_p
2sp	6.481887(+2)	-1.128507(-1)	1.541145(-1)	6.736611(+2)	-1.129128(-1)	1.544275(-1)
	1.403064(+2)	8.322834(-2)	6.194618(-1)	1.458491(+2)	8.290529(-2)	6.206174(-1)
	4.569880(+1)	9.697516(-1)	3.837583(-1)	4.757708(+1)	9.700289(-1)	3.820041(-1)
3sp	5.669469(+1)	-2.736965(-1)	-1.523217(-1)	5.916752(+1)	-2.739774(-1)	-1.518572(-1)
	2.748875(+1)	4.649968(-2)	5.437686(-1)	2.861159(+1)	4.553006(-2)	5.471507(-1)
	8.209096	1.091576	6.561679(-1)	8.596596	1.092528	6.519540(-1)
4sp	8.191679	4.508277(-1)	1.186988(-2)	8.638676	4.558408(-1)	9.585056(-3)
	3.244596	-4.632094(-1)	5.265246(-1)	3.462818	-4.617355(-1)	5.298193(-1)
	1.300489	-8.386360(-1)	5.266076(-1)	1.401040	-8.442883(-1)	5.235985(-1)
5sp'	1.451380	6.658515(-1)	-2.754131(-2)	1.578474	7.277718(-1)	-2.807244(-2)
	3.281033(-1)	-1.328584	-9.851368(-1)	3.750814(-1)	-1.362797	-9.842642(-1)
5sp''	1.150759(-1)	1.0	1.0	1.331790(-1)	1.0	1.0
Xe						
Shell	α	d_s	d_p	α	d_s	d_p
2sp	6.481887(+2)	-1.128507(-1)	1.541145(-1)	6.736611(+2)	-1.129128(-1)	1.544275(-1)
	1.403064(+2)	8.322834(-2)	6.194618(-1)	1.458491(+2)	8.290529(-2)	6.206174(-1)
	4.569880(+1)	9.697516(-1)	3.837583(-1)	4.757708(+1)	9.700289(-1)	3.820041(-1)
3sp	5.669469(+1)	-2.736965(-1)	-1.523217(-1)	5.916752(+1)	-2.739774(-1)	-1.518572(-1)
	2.748875(+1)	4.649968(-2)	5.437686(-1)	2.861159(+1)	4.553006(-2)	5.471507(-1)
	8.209096	1.091576	6.561679(-1)	8.596596	1.092528	6.519540(-1)
4sp	8.191679	4.508277(-1)	1.186988(-2)	8.638676	4.558408(-1)	9.585056(-3)
	3.244596	-4.632094(-1)	5.265246(-1)	3.462818	-4.617355(-1)	5.298193(-1)
	1.300489	-8.386360(-1)	5.266076(-1)	1.401040	-8.442883(-1)	5.235985(-1)
5sp'	1.451380	6.658515(-1)	-2.754131(-2)	1.578474	7.277718(-1)	-2.807244(-2)
	3.281033(-1)	-1.328584	-9.851368(-1)	3.750814(-1)	-1.362797	-9.842642(-1)
5sp''	1.150759(-1)	1.0	1.0	1.331790(-1)	1.0	1.0

Table III. Calculated and experimental equilibrium geometries of one-heavy-atom third- and fourth-row, main-group hydrides.

Hydride	Point Group	Geometrical Parameter	STO-3G	3-21G	3-21G ^(*)	Expt.
KH	C _{∞v}	r(KH)	2.081	2.361	2.353	2.242 ^a
CaH ₂	D _{∞h}	r(CaH)	2.017	2.148	2.157	—
GaH	C _{∞v}	r(GaH)		1.689	1.695	1.663 ^a
GaH ₃	D _{3h}	r(GaH)	1.316	1.581	1.592	—
GeH ₄	T _d	r(GeH)	1.430	1.538	1.546	1.525 ^b
AsH ₃	C _{3v}	r(AsH)	1.456	1.521	1.522	1.511 ^b
		<(HAsH)	93.9	95.1	93.3	92.1
H ₂ Se	C _{2v}	r(SeH)	1.439	1.471	1.464	1.460 ^b
		<(HSeH)	92.4	93.4	92.1	90.6
HBr	C _{∞v}	r(HBr)	1.414	1.432	1.417	1.415 ^a
RbH	C _{∞v}	r(RbH)	2.211	2.528	2.490	2.367 ^a
SrH ₂	D _{∞h}	r(SrH)	2.151	2.328	2.327	—
InH	C _{∞v}	r(InH)		1.867	1.877	1.838 ^a
InH ₃	D _{3h}	r(InH)	1.582	1.772	1.781	—
SnH ₄	T _d	r(SnH)	1.630	1.737	1.744	1.711 ^c
SbH ₃	C _{3v}	r(SbH)	1.644	1.726	1.727	1.704 ^b
		<(HSbH)	94.4	93.8	93.6	91.6
TeH ₂	C _{2v}	r(TeH)	1.624	1.678	1.675	1.658 ^d
		<(HTeH)	92.4	92.0	91.8	90.3
HI	C _{∞v}	r(HI)	1.599	1.638	1.631	1.609 ^a

^aK. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules*, Van Nostrand, Reinhold, New York, 1979.

^bJ. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote, *Structure Data on Free Polyatomic Molecules*, Landolt-Bornstein, New Series, Group II, Springer-Verlag, Berlin, 1976, Vol. 7.

^cH. W. Kattenberg and A. Oskam, *J. Mol. Spectrosc.*, **51**, 377 (1974).

^dN. K. Moncur, P. D. Willson, and T. H. Edwards, *J. Mol. Spectrosc.*, **52**, 380 (1974).

values, consistent with previous experience with lighter elements.³

A comparison of calculated and experimental equilibrium geometries for a selection of two-heavy-atom hydrides for which gas-phase data exist is provided in Table IV. Again STO-3G data are included (where available) for comparison. Where one or two right-hand (electronegative), main-group elements are involved, 3-21G bond distances between heavy (non-hydrogen) atoms are generally longer than experimental values, sometimes significantly so, e.g., by 0.125 Å in Br₂ and 0.183 Å in I₂. As commented in the introduction, this was also a feature of 3-21G representations for second-row elements, e.g., the calculated bond length in Cl₂ was 0.205 Å longer than the experimental value, and it has generally been concluded that the 3-21G level is not suitable for determining equilibrium geometries for molecules of this type. The method does far better for bonds between

carbon and a third- or fourth-row element, although significant errors are found in some systems, e.g., 0.062 Å in CH₃I. Overall, the mean absolute deviation between 3-21G and experimental bond distances connecting heavy atoms is 0.104 Å. This is actually considerably larger than the mean absolute error (of 0.041 Å) associated with the STO-3G calculations for the comparisons of heavy-atom bond distances provided in Table IV.

Calculated bond angles are generally in reasonable accord with the experimental data, although the systems dealt with here are too small to permit comparisons of skeletal bond angles, i.e., those involving the heavy-atom skeleton.

The performance of the 3-21G basis set in describing the geometries of hypervalent species containing third- and fourth-row, main-group elements may be assessed by the data in Table V. The results for single bonds closely parallel those for the corresponding

Table IV. Calculated and experimental equilibrium geometries for two-heavy-atom third- and fourth-row, main-group hydrides.

Molecule	Point Group	Geometrical Parameter	STO-3G	3-21G	3-21G(*)	Expt.
KOH	C _{∞v}	r(KO)	2.158	2.230	2.170	2.212 ^a
		r(OH)	0.988	0.971	0.969	0.912
KF	C _{∞v}	r(KF)		2.218	2.138	2.171 ^b
KCl	C _{∞v}	r(KCl)		2.829	2.787	2.667 ^b
KBr	C _{∞v}	r(KBr)		3.004	2.885	2.821 ^b
KI	C _{∞v}	r(KI)	3.014	3.283	3.194	3.048 ^b
GaF	C _{∞v}	r(GaF)		1.703	1.748	1.774 ^b
GaCl	C _{∞v}	r(GaCl)		2.309	2.258	2.202 ^b
GaBr	C _{∞v}	r(GaBr)		2.447	2.360	2.352 ^b
GaI	C _{∞v}	r(GaI)		2.742	2.636	2.575 ^b
GeH ₃ CH ₃	C _{3v}	r(GeC)	1.910	1.963	1.979	1.945 ^a
		r(GeH)	1.433	1.544	1.551	1.529
		r(CH)	1.082	1.084	1.084	1.083
		<(HGeH)	109.3	108.6	108.6	109.3
		<(HCH)	107.4	108.0	108.8	108.4
$\overline{\text{Ge}} \equiv \overset{+}{\text{O}}$	C _{∞v}	r(GeO)		1.602	1.619	1.625 ^b
GeH ₃ F	C _{3v}	r(GeF)	1.706	1.699	1.725	1.732 ^a
		r(GeH)	1.435	1.533	1.543	1.522
		<(HGeH)	110.8	110.7	112.0	113.0
GeH ₃ SiH ₃	C _{3v}	r(GeSi)		2.425	2.399	2.357 ^c
		r(GeH)		1.539	1.550	1.529
		r(SiH)		1.488	1.477	1.483
		<(HGeH)		109.1	108.6	109.3
		<(HSiH)		108.9	108.7	108.3
$\overline{\text{Ge}} \equiv \overset{+}{\text{S}}$	C _{∞v}	r(GeS)		2.070	2.004	2.012 ^b
GeH ₃ Cl	C _{3v}	r(GeCl)	2.160	2.247	2.178	2.150 ^a
		r(GeH)	1.434	1.526	1.539	1.537
		<(HGeH)	112.1	112.5	112.0	111.0
Ge ₂ H ₆	D _{3d}	r(GeGe)	2.358	2.471	2.447	2.403 ^a
		r(GeH)	1.428	1.539	1.549	1.541
		<(HGeH)	108.5	109.0	108.6	106.4
$\overline{\text{Ge}} \equiv \overset{+}{\text{Se}}$	C _{∞v}	r(GeSe)		2.187	2.121	2.135 ^b
GeH ₃ Br	C _{3v}	r(GeBr)	2.280	2.396	2.301	2.297 ^a
		r(GeH)	1.433	1.528	1.540	1.535
		<(HGeH)	110.8	111.6	111.4	106.9
GeTe ₂	C _{∞v}	r(GeTe)		2.412	2.351	2.340 ^b
$\overline{\text{C}} \equiv \overset{+}{\text{Se}}$	C _{∞v}	r(CSe)		1.697	1.674	1.676 ^b
CH ₃ SeH	C _s	r(CSe)		1.985	1.966	1.959 ^a
		r(CH ₃)		1.078	1.080	1.088
		r(CH ₂)		1.078	1.080	1.088
		r(SeH)		1.473	1.465	1.473
		<(H ₃ CSe)		107.3	107.6	
		<(H ₂ CH ₂ CSe) ^d		120.5	120.4	
		<(H ₂ CH ₂ Se)		109.0	109.2	
		<(HSeC)		95.5	94.9	95.5
SiSe	C _{∞v}	r(SiSe)		2.117	2.033	2.058 ^b
SnSe	C _{∞v}	r(SnSe)		2.386	2.320	2.326 ^b
LiBr	C _{∞v}	r(LiBr)	2.047	2.241	2.178	2.170 ^b
CH ₃ Br	C _{3v}	r(CBr)	1.918	2.000	1.953	1.933 ^a
		r(CH)	1.086	1.075	1.077	1.086
		<(HCH)	109.2	111.6	111.0	111.2
BrF	C _{∞v}	r(BrF)	1.771	1.775	1.757	1.756 ^b
NaBr	C _{∞v}	r(NaBr)		2.571	2.463	2.502 ^b
SiH ₃ Br	C _{3v}	r(SiBr)	2.205	2.347	2.201	2.210 ^e
		r(SiH)	1.422	1.476	1.468	1.451
		<(HSiH)	109.9	111.0	110.1	111.0

Table IV. (continued)

BrCl	C _{∞v}	r(BrCl)		2.317	2.138	2.136 ^b
Br ₂	D _{∞h}	r(BrBr)	2.291	2.448	2.273	2.283 ^b
IBr	C _{∞v}	r(IBr)	2.497	2.654	2.486	2.485 ^b
RbOH	C _{∞v}	r(RbO)	2.308	2.372	2.270	2.301 ^b
		r(OH)	1.000	0.974	0.970	0.957
RbF	C _{∞v}	r(RbF)	2.365	2.351	2.238	2.270 ^b
RbCl	C _{∞v}	r(RbCl)	2.810	2.988	2.927	2.787 ^b
RbBr	C _{∞v}	r(RbBr)	2.920	3.199	3.038	2.945 ^b
RbI	C _{∞v}	r(RbI)	3.170	3.463	3.333	3.177 ^b
InF	C _{∞v}	r(InF)		1.931	1.943	1.985 ^b
InCl	C _{∞v}	r(InCl)		2.504	2.470	2.401 ^b
InBr	C _{∞v}	r(InBr)		2.645	2.562	2.543 ^b
InI	C _{∞v}	r(InI)		2.901	2.821	2.754 ^b
SnO	C _{∞v}	r(SnO)	1.712	1.813	1.821	1.833 ^b
SnS	C _{∞v}	r(SnS)		2.272	2.221	2.209 ^b
SnH ₃ Br	C _{3v}	r(SnBr)	2.460	2.578	2.492	2.469 ^a
		r(SnH)	1.630	1.728	1.738	1.767
		<(HSnH)	111.7	111.8	111.7	112.8
SnTe	C _{∞v}	r(SnTe)		2.609	2.558	2.523 ^b
LiI	C _{∞v}	r(LiI)	2.281	2.487	2.453	2.392 ^b
CH ₃ I	C _{3v}	r(CI)	2.110	2.194	2.179	2.132 ^a
		r(CH)	1.084	1.076	1.077	1.084
		<(HCH)	108.9	111.3	111.1	111.2
IF	C _{∞v}	r(IF)	1.962	1.930	1.911	1.910 ^b
NaI	C _{∞v}	r(NaI)	2.561	2.829	2.736	2.711 ^b
SiH ₃ I	C _{3v}	r(SiI)	2.438	2.599	2.467	2.437 ^a
		r(SiH)	1.423	1.476	1.468	1.457
		<(HSiH)	109.9	111.8	110.3	110.5
ICl	C _{∞v}	r(ICl)	2.367	2.491	2.360	2.321 ^b
I ₂	D _{∞h}	r(II)	2.703	2.849	2.692	2.666 ^b

^aSee footnote b of Table III.^bSee footnote a of Table III.^cM. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendeman, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, and A. G. Maki, *J. Phys. Chem. Ref. Data*, **8**, 619 (1979).^dAngle between the bisector of the plane made by H₂CH₂, and the CSe bond.^eM. W. Chase, J. L. Curnutt, J. R. Downey, R. A. McDonald, A. N. Syverud, and E. A. Valenzuela, *J. Phys. Chem. Ref. Data*, **11**, 695 (1982).

hypervalent species incorporating second-row elements.^{3b} The description of single bonds between fluorine and a hypervalent third- or fourth-row element is generally satisfactory (the mean absolute error for 16 comparisons of this type is only 0.015 Å, and the largest single deviation is only 0.032 Å). The method yields an SeCl bond length in Cl₂SeO which is 0.178 Å longer than the experimental value, consistent with the poor performance of 3-21G in describing bond distances between right-hand elements in normal valent compounds (*vide supra*). Of greater concern is the performance of the model in describing multiple bonds in hyper-

valent compounds. While the calculated SeO double bond lengths in SeO₂, F₂SeO, and Cl₂SeO are within 0.037 Å of their respective experimental values (the S = O linkages in SO₂ and SOF₂ were in error by 0.1 Å at the 3-21G level^{3b}), the lengths of formal double bonds between xenon and oxygen in the compounds examined show much larger errors. The double bond in XeOF₄ is nearly 0.2 Å longer than the experimental value, while the linkages in XeO₃ and XeO₄ exceed the experimental lengths by more than 1 Å! Errors of this magnitude were also uncovered in application of 3-21G basis sets to second-row hypervalent compounds,^{3b} e.g., the ClO bond

Table V. Calculated and experimental equilibrium geometries for hypervalent molecules involving third- and fourth-row, main-group elements.

Molecule	Point Group	Geometrical Parameter	3-21G	3-21G(*)	Expt.
AsF ₅	D _{3h}	r(AsF _{ax})	1.682	1.694	1.711 ^a
		r(AsF _{eq})	1.659	1.672	1.656
SeO ₂	C _{2v}	r(SeO)	1.617	1.599	1.608 ^b
		<(OSeO)	112.3	114.4	113.8
F ₂ SeO	C _s	r(SeO)	1.613	1.589	1.576 ^a
		r(SeF)	1.706	1.710	1.730
		<(OSeF)	104.7	104.8	104.8
		<(FSeF)	94.8	95.5	92.2
SeF ₄	C _{2v}	r(SeF _{ax})	1.739	1.742	1.771 ^b
		r(SeF _{eq})	1.688	1.687	1.682
		<(F _{ax} SeF _{ax})	158.5	166.1	169.2
		<(F _{eq} SeF _{eq})	107.2	101.0	100.6
SeF ₆	O _h	r(SeF)	1.678	1.676	1.685 ^c
Cl ₂ SeO	C _s	r(SeO)	1.622	1.606	1.592 ^d
		r(SeCl)	2.361	2.175	2.183
		<(OSeCl)	106.8	105.7	104.0
		<(ClSeCl)	101.2	101.3	96.4
BrF ₃	C _{2v}	r(BrF _{ax})	1.807	1.778	1.810 ^e
		r(BrF _{eq})	1.738	1.721	1.721
		<(F _{ax} BrF _{eq})	82.2	84.4	86.2
BrF ₅	C _{4v}	r(BrF _{ax})	1.713	1.704	1.689 ^e
		r(BrF _{eq})	1.757	1.733	1.774
		<(F _{ax} BrF _{eq})	82.3	83.3	84.8
KrF ₂	D _{∞h}	r(KrF)	1.888	1.826	1.875 ^a
IF ₅	C _{4v}	r(IF _{ax})	1.836	1.845	1.844 ^f
		r(IF _{eq})	1.871	1.872	1.869
		<(F _{ax} IF _{eq})	79.6	81.3	81.9
		<(OXeO)	112.1	107.7	103.0
XeO ₃	C _{3v}	r(XeO)	2.876	1.865	1.76 ^g
XeO ₄	T _d	r(XeO)	2.876	1.817	1.736 ^h
XeOF ₄	C _{4v}	r(XeO)	1.895	1.806	1.703 ⁱ
		r(XeF)	1.923	1.886	1.900
		<(OXeF)	89.4	89.8	91.8
XeF ₂	D _{∞h}	r(XeF)	1.991	1.948	1.977 ^j
XeF ₄	D _{4h}	r(XeF)	1.960	1.917	1.953 ^k

^aSee footnote b of Table III.^bSee footnote c of Table IV.^cL. S. Bartell and A. Jin, *J. Mol. Struct.*, **118**, 47 (1984).^d*Spectroscopic Properties of Inorganic and Organometallic Compounds*, Royal Society of Chemistry, Spottiswoode Ballantyne Ltd., Colchester and London, 1980, Vol. 14.^eD. R. Stull and J. Prophet, *JANAF Thermochemical Tables*, 2nd ed., NSRDS-NBS 37, National Bureau of Standards, Washington, D.C., 1971.^fN. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1984, p. 975.^gD. H. Templeton, A. Zalkin, J. D. Forrester, and S. M. Williamson, *J. Am. Chem. Soc.*, **85**, 817 (1963).^hG. Gunderson, K. Hedberg, and J. L. Huston, *J. Chem. Phys.*, **52**, 812 (1970).ⁱJ. F. Martins and E. B. Wilson, *J. Mol. Struct.*, **26**, 410 (1968).^jS. Reichman and F. Schreiner, *J. Chem. Phys.*, **51**, 2355 (1969).^kJ. H. Burns, P. A. Agron, and H. A. Levy, *Science*, **139**, 1208 (1963).

length in FClO₃ calculated at the 3-21G level is 0.9 Å longer than the experimental value, and it was previously concluded that *d*-type functions on the hypervalent center were required for adequate (and reliable) description of equilibrium geometry. This also appears to be the case for the treatment of hypervalent

molecules incorporating third- and fourth-row, main-group elements.

Normal Mode Vibrational Frequencies

Normal mode vibrational frequencies for the one-heavy-atom hydrides of third- and

Table VI. Calculated and experimental normal mode vibrational frequencies for one-heavy-atom third- and fourth-row, main-group hydrides.

Hydride	Symmetry of mode	Description of mode	3-21G ^a	3-21G ^{(*)a}	Expt.
KH			965 (0.98)	986 (1.00)	984 ^b
GeH ₄	a ₁	sym. stretch	2232 (1.06)	2259 (1.07)	2106 ^c
	e	deg. deform.	953 (1.02)	992 (1.07)	931
	t ₂	deg. stretch	2142 (0.97)	2219 (1.00)	2214
	t ₂	deg. deform.	911 (1.11)	906 (1.11)	819
AsH ₃	a ₁	sym. stretch	2191 (1.04)	2353 (1.11)	2116 ^c
	a ₁	sym. deform.	991 (1.09)	1017 (1.12)	906
	e	deg. stretch	2175 (1.02)	2354 (1.11)	2123
	e	deg. deform.	1086 (1.08)	1122 (1.12)	1003
H ₂ Se	a ₁	sym. stretch	2352 (1.00)	2591 (1.10)	2345 ^c
	a ₁	bend	1166 (1.13)	1192 (1.15)	1034
	b ₁	antisym. stretch	2354 (1.00)	2600 (1.10)	2358
HBr			2473 (0.93)	2802 (1.06)	2649 ^d
RbH			897 (0.96)	947 (1.01)	937 ^b
SnH ₄	a ₁	sym. stretch	2061 (1.08)	1948 (1.02)	1908 ^e
	e	deg. deform.	785 (1.04)	808 (1.07)	753
	t ₂	deg. stretch	1987 (1.04)	1991 (1.04)	1905
	t ₂	deg. deform.	756 (1.11)	764 (1.12)	681
SbH ₃	a ₁	sym. stretch	2038 (1.08)	2066 (1.09)	1891 ^c
	a ₁	sym. stretch	873 (1.12)	879 (1.12)	782
	e	deg. stretch	2015 (1.06)	2072 (1.09)	1894
	e	deg. deform.	915 (1.10)	907 (1.09)	831
H ₂ Te	a ₁	sym. stretch	2167	2246	
	a ₁	bend	971	968	
	b ₁	antisym. stretch	2170	2254	
HI			2269 (0.98)	2400 (1.04)	2309 ^b

^aNumbers of parentheses correspond to the ratios of calculated to experimental frequencies.^bSee footnote a of Table III.^cT. Shimanouchi, *Tables of Molecular Vibrational Frequencies*, consolidated, NSRDS-NBS 39, National Bureau of Standards, Washington, D.C., 1972, Vol. I.^dSee footnote d of Table V.^eSee footnote c of Table III.

fourth-row, main-group elements obtained at the 3-21G level are compared with experimental values in Table VI. In line with previous experience with analogous first- and second-row hydrides,³ the calculated frequencies are (generally) larger than experimental values, although not always so. The range of errors in the calculated frequencies, from 7% below the experimental value in HBr to 13% above for the bending mode in H₂Se, is probably too large to encourage widespread use of theory at this level for frequency assignments. This conclusion has also been reached in the assessment of the 3-21G basis set for second-row elements,^{3b} although the performance of the simple model appears to be satisfactory for molecules incorporating first-row elements alone.^{3a,15}

Reaction Energies

Aside from geometrical structure, the most important property which a theory might be called on to describe is reaction energy. Previous experience clearly indicates the difficulties involved in the accurate description of absolute bond dissociation energies; this may only be accomplished with methods which go beyond the single-determinant (Hartree-Fock) level, and which utilize much larger basis sets than discussed in this paper. A simpler goal, to which we set ourselves at present, is in the description of reaction energies in which the number of bonded electron pairs is maintained. Because the molecules of interest in the present study are small and because experimental thermochemical data

is generally scarce, relatively few reaction sequences are available for examination. We focus on the comparison of calculated and experimental energies (enthalpies) of complete hydrogenation, whereby a molecule comprising two-heavy-atoms is related to the set of one-heavy-atom hydrides.

Total energies for the complete set of molecules dealt with in this study are provided in Table VII. Experimental enthalpies of formation (at 298 K) and zero-point energies are supplied wherever available.

Energies of complete hydrogenation for normal valent compounds are compared with experimental enthalpies in Table VIII. Hydrogenation energies for saturated compounds are remarkably well described at the 3-21G level. The mean absolute error (comparisons are to experimental data which have

not been corrected for zero-point energy) is only 5 kcal mol⁻¹. The situation is entirely different for hydrogenation energies of multiply-bonded systems. Of the seven systems for which experimental data are available, all but one are in error by 13 kcal mol⁻¹ or more; the mean absolute deviation calculated from experimental hydrogenation energies is 17 kcal mol⁻¹.

Hydrogenation energies for hypervalent systems (Table IX) are also poorly described at the 3-21G level. Only five comparisons are available; the mean absolute error is 32 kcal mol⁻¹! While some of the discrepancy no doubt lies in uncertainties in the experimental data, it is clear that theory at this level does not provide a satisfactory description of hydrogenation energies in these systems.

Table VII. Calculated total energies and experimental heats of formation and zero-point energies for molecules containing third- and fourth-row, main-group elements.

Atom (State) or Molecule	Energy (hartrees)		ΔH_f° (298 K)	kcal mol ⁻¹	
	3-21G	3-21G(*)		ΔH_f° (0 K)	E (zero point)
K (² S)	-596.15298	-596.15324			
Ca (¹ S)	-673.40624	-673.41851			
Ga (² P)	-1913.81569	-1913.97931			
Ge (³ P)	-2065.31137	-2065.47536			
As (⁴ S)	-2223.45070	-2223.62226			
Se (³ P)	-2388.48153	-2388.66559			
Br (² P)	-2560.04062	-2560.24462			
Kr (¹ S)	-2739.19757	-2739.41275			
Rb (² S)	-2924.71350	-2924.72143			
Sr (¹ S)	-3117.09618	-3117.10513			
In (² P)	-5715.07850	-5715.15342			
Sn (³ P)	-5996.67301	-5996.74041			
Sb (⁴ S)	-6286.14474	-6286.20738			
Te (³ P)	-6583.20096	-6583.26327			
I (² P)	-6887.84046	-6887.90188			
Xe (¹ S)	-7200.75272	-7200.81102			
KH	-596.66832	-596.67373			
CaH ₂	-674.49511	-674.51655			
GaH ^a	-1914.38814	-1914.55027	52.7	53.0	
GaH ₃	-1915.54858	-1915.70519			
GeH ₄ ^{a,b}	-2067.63800	-2067.81435	21.7	19.1	18.2
AsH ₃ ^{a,b}	-2225.14396	-2225.34712	15.9	17.7	13.2
H ₂ Se ^{a,b}	-2389.62171	-2389.83430	7.1	8.0	8.2
HBr ^c	-2560.62078	-2560.84279	-8.7	-6.8	3.8
RbH	-2925.22397	-2925.24051			
SrH ₂	-3118.17326	-3118.19682			
InH ^a	-5715.64149	-5715.71769	51.5	52.0	
InH ₃	-5716.77424	-5716.85200			
SnH ₄ ^a	-5998.95316	-5999.03572	38.9	41.8	
SbH ₃	-6287.81328	-6287.89889			
H ₂ Te ^a	-6584.32039	-6584.40102	23.8		
HI ^c	-6888.40655	-6888.47885	6.3	6.8	3.3
KOH	-671.13803	-671.17676			
KF	-695.03194	-695.07789			
KCl	-1053.54160	-1053.64036			
KBr	-3156.28573	-3156.51011			
KI	-7484.08217	-7484.15134			

Table VII. (continued)

GaF ^a	-2012.82006	-2012.98450	-60.2	-60.0	
GaCl ^a	-2371.22872	-2371.48548	-19.1	-19.0	
GaBr ^a	-4473.97226	-4474.36816	-11.9	-10.0	
GaI ^a	-8801.75258	-8801.98813	6.9	7.4	
GeH ₃ CH ₃	-2106.48076	-2106.64922			
GeO	-2139.80015	-2139.96923			
GeH ₃ F	-2166.02063	-2166.20072			
GeH ₃ SiH ₃	-2356.19754	-2356.47046			
GeS ^a	-2460.95173	-2461.22744	22.0	22.0	
GeH ₃ Cl	-2524.41686	-2524.69804			
Ge ₂ H ₆ ^a	-4134.15201	-4134.51331	38.8		
GeSe ^a	-4453.86836	-4454.25783	22.8	23.0	
GeH ₃ Br	-4627.16536	-4627.57235			
GeTe ^a	-8648.56585	-8648.82670	42.0	42.2	
CSe	-2426.03322	-2426.24382			
CH ₃ SeH	-2428.45188	-2428.65700			
SiSe ^a	-2675.89676	-2676.18958	23.8	23.0	
SnSe ^a	-8385.21545	-8385.50750	30.8		
LiBr ^c	-2567.53832	-2567.75410	-36.8	-35.0	0.8
CH ₃ Br ^{a,b}	-2599.44917	-2599.66366	-8.4	-4.7	22.5
BrF ^c	-2658.88546	-2659.10664	-14.0	-12.1	1.0
NaBr	-2720.98954	-2721.21228			
SiH ₃ Br ^d	-2849.20614	-2849.53855	-18.7	-14.8	15.9
BrCl ^c	-3017.31928	-3017.64570	3.5	5.3	0.6
Br ₂ ^c	-5120.08881	-5120.53021	7.4	10.9	0.5
IBr ^c	-9447.88823	-9448.18611	9.8	11.9	0.4
RbOH	-2999.68802	-2999.74033			
RbF	-3023.58250	-3023.64491			
RbCl	-3382.10086	-3382.21014			
RbBr	-5484.84404	-5485.07744			
RbI	-9812.64238	-9812.72104			
InF ^a	-5814.04397	-5814.13918	-48.6	-48.2	
InCl ^a	-6172.48177	-6172.65477	-18.0		
InBr ^a	-8275.22698	-8275.52852	-13.6	-11.5	
InI ^a	-12603.01180	-12603.16162	1.8	2.5	
SnO	-6071.09418	-6071.18574			
SnS ^a	-6392.29438	-6392.46880	28.5		
SnH ₃ Br	-8558.49189	-8558.80557			
SnTe ^a	-12579.92250	-12580.08454	38.4		
LiI ^c	-6895.32447	-6895.38785	-21.8	-21.3	0.7
CH ₃ I ^{a,b}	-6927.23687	-6927.30377	3.1	5.4	22.1
IF ^c	-6986.68984	-6986.77642	-22.6	-22.2	0.9
NaI	-7048.78103	-7048.85038			
SiH ₃ I ^d	-7176.98766	-7177.16341	-0.5	2.0	15.6
ICl ^c	-7345.12491	-7345.30282	4.2	4.6	0.5
I ₂ ^c	-13775.68529	-13775.83610	14.9	15.7	0.3
AsF ₅	-2718.04616	-2718.29478			
SeO ₂ ^a	-2537.21962	-2537.47335	-53.9		
F ₂ SeO	-2660.63121	-2660.89711			
SeF ₄	-2783.99576	-2784.27807			
SeF ₆ ^a	-2981.74764	-2982.09566	-267.0	-264.1	
Cl ₂ SeO ^a	-3377.41843	-3377.88996	-6.0		
BrF ₃ ^c	-2856.49165	-2856.78298	-61.1	-58.4	4.0
BrF ₅ ^c	-3054.10014	-3054.47771	-102.5	-98.8	7.7
KrF ₂	-2936.69050	-2936.97224			
IF ₅ ^a	-7382.06553	-7382.32588	-196.6	-194.3	
XeO ₃	-7423.55848	-7423.65562			
XeO ₄	-7497.82603	-7497.98031			
XeOF ₄	-7670.10166	-7670.41184			
XeF ₂	-7398.29239	-7398.44804			
XeF ₄	-7595.81867	-7596.08280			

^aD. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Selected Values of Chemical Thermodynamic Properties*, NBS Technical Note 270-3, National Bureau of Standards, Washington, D.C., 1968.

^bSee footnote b of Table VI.

^cSee footnote d of Table V.

^dSee footnote d of Table IV.

Table VIII. Calculated and experimental complete hydrogenation energies (enthalpies) for normal valent compounds (kcal mol⁻¹).

Hydrogenation Reaction	3-21G	Energy (Enthalpy) 3-21G*	Expt. ^a
KOH + H ₂ → KH + H ₂ O	4	25	
KF + H ₂ → KH + HF	16	42	
KCl + H ₂ → KH + HCl	80	68	
KBr + H ₂ → KH + HBr	75	73	
KI + H ₂ → KH + HI	82	76	
GaF + H ₂ → GaH + HF	59	61	(48)
GaCl + H ₂ → GaH + HCl	59	48	(50)
GaBr + H ₂ → GaH + HBr	54	55	(56)
GaI + H ₂ → GaH + HI	51	51	(52)
GeH ₃ CH ₃ + H ₂ → GeH ₄ + CH ₄	-7	-12	
GeH ₃ F + H ₂ → GeH ₄ + HF	28	31	
GeH ₃ SiH ₃ + H ₂ → GeH ₄ + SiH ₄	-3	-3	
GeH ₃ Cl + H ₂ → GeH ₄ + HCl	20	16	
Ge ₂ H ₆ + H ₂ → 2GeH ₄	-1	5	(5)
GeH ₃ Br + H ₂ → GeH ₄ + HBr	18	24	
CH ₃ SeH + H ₂ → CH ₄ + H ₂ Se	-15	-20	
LiBr + H ₂ → LiH + HBr	69	66	63 (62)
CH ₃ Br + H ₂ → CH ₄ + HBr	-16	-21	-20 (-18)
BrF + H ₂ → HBr + HF	-46	-46	-62 (-60)
NaBr + H ₂ → NaH + HBr	69	68	
SiH ₃ Br + H ₂ → SiH ₄ + HBr	13	22	17 (17)
BrCl + H ₂ → HBr + HCl	-30	-35	-35 (-34)
Br ₂ + H ₂ → 2HBr	-19	-20	-25 (-25)
IBr + H ₂ → HI + HBr	-10	-8	-12 (-12)
RbOH + H ₂ → RbH + H ₂ O	1	23	
RbF + H ₂ → RbH + HF	13	42	
RbCl + H ₂ → RbH + HCl	82	70	
RbBr + H ₂ → RbH + HBr	77	73	
RbI + H ₂ → RbH + HI	84	78	
InF + H ₂ → InH + HF	41	53	(35)
InCl + H ₂ → InH + HCl	59	49	(47)
InBr + H ₂ → InH + HBr	55	57	(56)
InI + H ₂ → InH + HI	54	55	(56)
SnH ₃ Br + H ₂ → SnH ₄ + HBr	26	31	
LiI + H ₂ → LiH + HI	70	64	64 (62)
CH ₃ I + H ₂ → CH ₄ + HI	-15	-18	-17 (-15)
IF + H ₂ → HI + HF	-34	-25	-38 (-36)
NaI + H ₂ → NaH + HI	73	70	
SiH ₃ I + H ₂ → SiH ₄ + HI	11	15	14 (14)
ICl + H ₂ → HI + HCl	-18	-22	-20 (-20)
I ₂ + H ₂ → 2HI	-3	1	-2 (-2)
GeO + 3H ₂ → GeH ₄ + H ₂ O	-34	-39	
GeS + 3H ₂ → GeH ₄ + H ₂ S	-14	-24	(-1)
GeSe + 3H ₂ → GeH ₄ + H ₂ Se	-14	-14	(10)
GeTe + 3H ₂ → GeH ₄ + H ₂ Te	-15	-12	(8)
CSe + 3H ₂ → CH ₄ + H ₂ Se	-123	-124	
SiSe + 3H ₂ → SnH ₄ + H ₂ Se	-27	-38	(-5)
SnSe + 3H ₂ → SnH ₄ + H ₂ Se	6	4	(19)
SnO + 3H ₂ → SnH ₄ + H ₂ O	-48	-42	
SnS + 3H ₂ → SnH ₄ + H ₂ S	3	-11	(10)
SnTe + 3H ₂ → SnH ₄ + H ₂ Te	11	10	(28)

^aBased on experimental data given in Table VII. Corrected for 0 K and for zero-point vibrational energy. Values in parentheses corrected for 0 K only. Temperature correction based on translational and rotational contributions only: 7/2 kT (2.1 kcal mol⁻¹ at 298 K) for linear molecules, 4 kT (2.4 kcal mol⁻¹) for nonlinear molecules.

Electric Dipole Moments

Electric dipole moments calculated at the 3-21G level for compounds incorporating third- and fourth-row, main-group elements

are compared with experimental values (where available) in Table X. For most of the systems considered, the simple model overestimates the magnitude of the dipole mo-

Table IX. Calculated and experimental complete hydrogenation energies (enthalpies) of hypervalent compounds

Hydrogenation Reaction	3-21G	Energy (Enthalpy) 3-21G ^(*)	Expt. ^a
AsF ₅ + 4H ₂ → AsH ₃ + 5HF	58	87	
SeO ₂ + 3H ₂ → H ₂ Se + 2H ₂ O	-129	-103	
F ₂ SeO + 3H ₂ → H ₂ Se + H ₂ O + 2HF	-80	-47	
Cl ₂ SeO + 3H ₂ → H ₂ O + 2HCl	-100	-78	(-87)
SeF ₄ + 3H ₂ → H ₂ Se + 4HF	-61	-18	
SeF ₆ + 4H ₂ → H ₂ Se + 6HF	-90	-5	(-119)
BrF ₃ + 2H ₂ → HBr + 3HF	-166	-122	-148 (-144)
BrF ₅ + 3H ₂ → HBr + 5HF	-284	-186	-239 (-234)
KrF ₂ + H ₂ → Kr + 2HF	-191	-149	
IF ₅ + 3H ₂ → HI + 5HF	-171	-53	(-125)
XeO ₃ + 3H ₂ → Xe + 3H ₂ O	-366	-342	
XeO ₄ + 4H ₂ → Xe + 4H ₂ O	-489	-428	
XeOF ₄ + 3H ₂ → Xe + H ₂ O + 4HF	-445	-287	
XeF ₂ + H ₂ → Xe + 2HF	-162	-101	
XeF ₄ + 2H ₂ → Xe + 4HF	-332	-203	

^aSee footnote a in Table VIII.**Table X.** Calculated and experimental electric dipole moments containing third- and fourth-row, main-group elements.

Molecule	Electric Dipole Moment (debyes)		
	3-21G	3-21G ^(*)	Expt.
KH	9.2	9.1	
GaH	0.4	0.3	
AsH ₃	0.7	0.6	0.2 ^a
H ₂ Se	1.2	1.0	
HBr	1.3	1.1	0.8 ^b
RbH	9.9	9.3	
InH	0.2	0.0	
SbH ₃	0.1	0.0	0.1 ^a
H ₂ Te	0.7	0.4	
HI	0.9	0.6	0.4 ^a
KOH	7.5	6.8	
KF	9.3	8.5	8.6 ^b
KCl	12.6	11.7	10.3 ^b
KBr	12.6	11.1	10.6 ^b
KI	13.7	12.2	10.8 ^b
GaF	1.3	1.6	2.5 ^b
GaCl	4.0	2.8	
GaBr	3.4	1.9	
GaI	4.5	2.5	
GeH ₃ CH ₃	0.6	0.7	0.6 ^a
GeO	3.2	3.5	3.3 ^b
GeH ₃ F	2.1	2.2	2.3 ^c
GeH ₃ SiH ₃	0.2	0.1	
GeS	4.0	2.7	2.0 ^b
GeH ₃ Cl	3.9	2.6	2.1 ^a
GeSe	2.9	1.8	1.7 ^b
GeH ₃ Br	3.1	1.9	
GeTe	2.7	1.6	1.1 ^b
CSe	1.4	1.7	2.0 ^b
CH ₃ SeH	1.5	1.5	1.3 ^d
SiSe	2.3	1.6	
SnSe	4.1	3.3	2.8 ^b
LiBr	7.6	7.0	7.3 ^a
CH ₃ Br	2.2	2.0	1.8 ^a
BrF	1.9	1.7	1.3 ^a
NaBr	9.7	8.8	9.1 ^b
SiH ₃ Br	2.8	1.4	1.3 ^a
BrCl	1.3	0.8	0.6 ^a
IBr	1.1	0.8	

Table X. (continued)

RbOH	8.3	6.4	
RbF	9.9	8.1	8.6 ^b
RbCl	13.5	12.0	10.5 ^b
RbBr	13.7	11.6	10.9 ^b
RbI	14.8	12.7	11.5 ^b
InF	1.9	2.2	3.4 ^b
InCl	4.8	3.8	3.8 ^b
InBr	4.1	2.7	
InI	5.1	3.2	
SnO	3.8	4.4	4.3 ^b
SnS	5.2	4.2	3.2 ^b
SnH ₃ Br	3.4	2.2	
SnTe	4.1	3.0	2.2 ^b
LiI	8.1	7.6	7.4 ^a
CH ₃ I	2.0	1.9	1.6 ^a
IF	2.5	2.2	
NaI	10.5	9.5	9.2 ^b
SiH ₃ I	2.8	1.6	
ICl	2.5	1.8	1.2 ^b
SeO ₂	3.9	3.3	2.7 ^e
F ₂ SeO	4.0	3.3	2.8 ^f
SeF ₄	3.2	2.3	1.8 ^g
Cl ₂ SeO	3.8	2.8	
BrF ₃	2.5	1.8	1.1 ^a
BrF ₅	3.1	2.0	1.5 ^a
IF ₅	4.8	3.1	2.2 ^h
XeOF ₄	3.5	3.2	0.7 ⁱ

^aR. D. Nelson, D. R. Lide, and A. A. Maryott, *Selected Values of Electric Dipole Moments for Molecules in the Gas Phase*, NSRDS-NBS 10, National Bureau of Standards, Washington, D.C., 1967.^bSee footnote a of Table III.^cL. C. Krisher, J. A. Morrison, and W. A. Watson, *J. Chem. Phys.*, **57**, 1357 (1972).^dC. H. Thomas, *J. Chem. Phys.*, **59**, 70 (1973).^eH. Takeo, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, **34**, 370 (1970).^fI. C. Bowater, R. D. Brown, and F. R. Burden, *J. Mol. Spectrosc.*, **28**, 461 (1968).^gI. C. Bowater, R. D. Brown, and F. R. Burden, *J. Mol. Spectrosc.*, **28**, 454 (1968).^hSee footnote i of Table V.ⁱSee footnote k of Table V.

ment, sometimes significantly so. Particularly poorly described are the moments in alkali-metal compounds. For example, the moments in KI and RbI are overestimated by 2.9 and 3.3 debyes, respectively. These deviations parallel the overestimation of the bond lengths in these systems (by 0.235 Å and 0.286 Å, respectively). Also the small experimental dipole moments in hypervalent systems are not properly reproduced at the 3-21G level, e.g., the dipole moment in IF_5 is overestimated by 2.6 debyes, and that in XeOF_4 by 2.7 debyes. The directions of the errors here are consistent with the incorrect description of these systems in terms of zwitterions, the same conclusion reached in applications of 3-21G basis sets to hypervalent compounds of second-row elements.^{3b} Overall the mean absolute error in 3-21G dipole moments is 1.3 debyes.

3-21G(*) Supplemented Split Valence Basis Sets

The 3-21G basis sets for the third- and fourth-row, main-group elements K-Kr and Rb-Xe do not incorporate valence d -type functions. It is to be anticipated, therefore, that these basis sets will not perform well in their description of bonding in molecules containing third- or fourth-row, main-group elements with expanded valence shells, i.e., hypervalent molecules. Experience with the corresponding second-row basis sets supports such a contention, and clearly shows that only when supplementary valence (d -type) functions are added are the representations able to properly account for properties of hypervalent species. It has also been found that the supplementary functions can play a strong role in the description of normal-valent compounds, in many cases leading to greatly improved agreement between calculated and observed properties. For example, the equilibrium bond length in chlorine molecule, which is 0.205 Å longer than the experimental value at the 3-21G level, is brought to within 0.008 Å upon addition of d functions to the valence description. Other properties, e.g., normal mode vibrational frequencies, reaction energies, and dipole moments, for both normal and hypervalent compounds incorporating second-row elements, have also

been shown to systematically improve upon addition of supplemental d -type functions to the 3-21G basis. It has already been pointed out (*vide supra*) that similar problems, leading to errors of similar magnitude exist for compounds incorporating third- and fourth-row, main-group elements.

The 3-21G(*) basis sets for third- and fourth-row, main-group elements have been constructed directly from the corresponding 3-21G representations. For both the third- and fourth-row, main-group elements, a complete set of six second-order Gaussian primitives is added. Gaussian exponents, describing the average radial distribution of the supplementary functions, are taken directly from the work of Huzinaga¹⁴ for the elements Ga-Kr and for In-Xe. Exponent values of 0.100 and 0.110 have been selected for K and Ca and for Rb and Sr, respectively. Because these representations are intended to be used in conjunction with unsupplemented (3-21G) descriptions for hydrogen, helium, and all first-row atoms, and with 3-21G(*) basis sets for second-row elements, they should not be viewed as full polarized basis sets. Rather, they are best seen as representations which, in as simple a manner as possible, account for the participation of d -symmetry functions in main-group elements.

EVALUATION OF 3-21G(*) BASIS SETS

We use the same criteria (equilibrium geometries, vibrational frequencies, reaction energies, and dipole moments) to evaluate the performance of 3-21G(*) representations for third- and fourth-row, main-group elements as previously employed for the corresponding 3-21G basis sets.

Equilibrium Geometries

All bond lengths calculated at the 3-21G(*) level for hydrides AH_n where A is on the left-hand-side of the Periodic Table (Table III) are longer than the corresponding quantities obtained from the 3-21G basis set, sometimes significantly so. Although the 3-21G(*) bond distances for KH and RbH are in better agreement with experiment than those obtained at 3-21G, they are still too long. The bond

lengths in germane and stannane are given better at the 3-21G level, although here the differences are not great. It would appear that 3-21G^(*) basis sets for left-hand elements are improperly balanced. On the other hand, 3-21G^(*) bond lengths for hydrides incorporating right-hand elements are (slightly) shorter than 3-21G values, and generally in better agreement with the experimental data. Overall, the mean absolute deviation of 3-21G^(*) from experimental bond distances in these compounds is 0.036 Å; this is reduced to only 0.020 Å if KH and RbH are removed from the comparison. This is to be compared with a mean absolute error of 0.040 Å from the 3-21G calculations (0.020 Å if the alkali metal systems are removed from the comparison). Clearly, the supplementary functions have little effect in these systems. 3-21G^(*) HAH bond angles are consistently smaller than 3-21G values, and closer to experimental angles.

Equilibrium geometries for two-heavy-atom hydrides (Table IV) provide clearer indication of differences in the performance of 3-21G and 3-21G^(*) basis sets. Addition of *d*-type (polarization) functions to third- and fourth-row elements (second-row elements as well) leads to improvement in calculated bond lengths in all but a very few systems. In a large number of cases, the improvements are significant, and closely parallel changes noted in previous comparisons of 3-21G and 3-21G^(*) basis sets for second-row elements.⁵ For example, the bond lengths in Br₂ and in I₂ shorten by 0.175 Å and 0.183 Å, respectively (to bring them within 0.010 Å and 0.026 Å of their respective experimental values). Similar effects are noted for the central bond lengths (connecting heavy atoms) in other molecules. Bond lengthening in response to addition of polarization functions on the 3-21G basis occurs only in a few systems, and the effects are quite modest, e.g., the central bond length in methylgermane is lengthened by 0.015 Å. Overall, the mean absolute deviation of 3-21G^(*) from experimental bond lengths (connecting heavy atoms) in the set of two-heavy-atom hydrides is 0.039 Å, less than half the error associated with calculations at the 3-21G level (0.104 Å).

Bond lengths in the highly ionic alkali metal compounds improve somewhat due to

the addition of *d*-type functions to the basis, although the residual errors are still large in some instances, e.g., 0.120 Å in KCl, 0.140 Å in RbCl, compared with errors of 0.162 Å and 0.201 Å for the two compounds, respectively, at 3-21G. Small improvements also occur for bond distances involving other left-hand, main-group elements in most (but not all) compounds considered.

The 3-21G^(*) representations provide a more satisfactory and uniform account of the equilibrium structures of hypervalent compounds than afforded by the unsupplemented 3-21G basis sets. The calculations still overestimate the multiple bond lengths in XeO₃, XeO₄, and XeOF₄, although the largest errors are now an order of magnitude less than those noted for the 3-21G calculations. Single-bond lengths are generally well reproduced at the 3-21G^(*) level; the mean absolute deviation of 3-21G^(*) from experimental single bond lengths in these systems is 0.018 Å, nearly identical to the error of 0.024 Å from the 3-21G calculations. The most notable improvement here is for the SeCl bond in Cl₂SeO, which is now within 0.01 Å of the experimental value, compared with an error of 0.18 Å at 3-21G. This parallels the previously noted improvements for single bonds lengths in normal valent compounds.

3-21G^(*) appears to us to be the method of choice for the calculation of equilibrium geometries for molecules incorporating third- and fourth-row, main-group elements, with the possible exception of alkali and alkaline-earth compounds. While it is somewhat more costly to apply than 3-21G, it affords a more uniform description of equilibrium structure over a broad range of normal and hypervalent compounds than available from the unsupplemented basis sets.

Normal Mode Vibrational Frequencies

Frequencies for one-heavy-atom hydrides obtained at the 3-21G^(*) level are displayed alongside 3-21G and experimental values in Table VI. The calculated frequencies are all larger than the experimental quantities, typically by 9%–12%. The range of errors is clearly smaller than observed in the 3-21G calculations. The experience here closely parallels that for analogous systems incorpo-

rating second-row elements.⁵ We view calculations at this level as more likely to provide reasonable frequency assignments than applications of the unsupplemented 3-21G basis sets.

Reaction Energies

The 3-21G^(*) basis set does not offer significantly improved description of hydrogenation energies. The mean absolute error for saturated normal valent compounds (Table VIII) is 4 kcal mol⁻¹, nearly identical to that recorded at the 3-21G level. The performance of the model in dealing with the complete hydrogenation of multiply-bonded systems (Table VIII) is even poorer here (mean absolute deviation of 22 kcal mol⁻¹) than at the 3-21G level (deviation of 17 kcal mol⁻¹). This is also the case for the description of the hydrogenation of hypervalent compounds (Table IX). While we emphasize that some of the experimental data employed here are of questionable value, it is evident that comparisons of this nature are too difficult to handle reliably at the theoretical levels developed in this paper.

Electric Dipole Moments

The 3-21G^(*) basis set offers a much improved description of electric dipole moments for both normal and hypervalent compounds than available from the unsupplemented 3-21G representation. The mean absolute error has been reduced to 0.5 debyes (from 1.3 debyes at 3-21G). The moderately-sized dipole moments in hypervalent compounds are

generally well reproduced at this level, in contrast to the performance of the 3-21G basis set. Significant errors are still recorded for some of the alkali-metal halides, e.g., 1.5 debyes in RbCl, again paralleling the overestimation of bond lengths, by 0.140 Å at 3-21G^(*).

FURTHER BASIS SET IMPROVEMENTS AND ELECTRON CORRELATION EFFECTS

Full polarization basis sets for third- and fourth-row, main-group elements, e.g., analogous to 6-31G* representations for first- and second-row atoms,⁶ have yet to be developed, and the effects which these extensions (over the 3-21G^(*) basis sets discussed here) will have on calculated properties awaits further research. Parallels with data on second-row systems, e.g., as provided in Tables XI and XII, suggest that the effects of further basis set extension, i.e., to 6-31G*, on equilibrium geometries, hydrogenation energies, and electric dipole moments will be small. These data also anticipate that treatment of electron correlation (at the MP2/6-31G* level) will be of little consequence, at least for the saturated systems provided in the examples. Further research is needed to fully assess these factors.

CONCLUSIONS

3-21G split valence and 3-21G^(*) supplemented split valence basis sets have been formulated for third- and fourth-row, main-group elements, based on the series of mini-

Table XI. Comparison of properties of CH₃Cl, CH₃Br, and CH₃I.

Molecule CH ₃ X	Level	CX bond length (Å)	Hydrogenation Energy (kcal mol ⁻¹) ^a	Dipole Moment (debyes)
CH ₃ Cl ^b	3-21G ^(*)	1.806	-25	2.2
	6-31G*	1.785	-22	2.2
	MP2/6-31G*	1.778	-16	—
	Expt.	1.781	-22	1.9
CH ₃ Br	3-21G ^(*)	1.953	-21	2.0
	Expt.	1.933	-20	1.8
CH ₃ I	3-21G ^(*)	2.179	-18	1.9
	Expt.	2.132	-17	1.6

^aEnergy (enthalpy) of reaction: CH₃X + H₂ → CH₄ + HX.

^bData from ref. 1.

Table XII. Comparison of properties for Cl₂, Br₂, and I₂.

Molecule X ₂	Level	XX bond length (Å)	Hydrogenation Energy (kcal mol ⁻¹) ^a
Cl ₂ ^b	3-21G ^(*)	1.996	-51
	6-31G*	1.990	-50
	MP2/6-31G*	2.015	-43
	Expt.	1.988	-41
Br ₂	3-21G ^(*)	2.273	-20
	Expt.	2.283	-25
I ₂	3-21G ^(*)	2.692	1
	Expt.	2.666	-2

^aEnergy (enthalpy) of reaction: X₂ + H₂ → 2HX.^bData from ref. 1.

mal representations proposed by Huzinaga,¹⁴ and modified to take advantage of efficient integral evaluation algorithms.¹³ Applications to the calculation of equilibrium geometries, normal mode vibrational frequencies, hydrogenation energies, and electric dipole moments for a variety of normal and hypervalent compounds is presented. The simpler representation does not provide a generally satisfactory description of equilibrium bond lengths or of electric dipole moments for many of the normal valent compounds considered. While its description of single-bond lengths in hypervalent compounds is reasonably good, the method fails entirely to reproduce the multiple bond distances found in these systems. Overall the performance of the 3-21G representations for third- and fourth-row, main-group elements closely follows that of the corresponding second-row basis sets.^{3b}

Addition of *d*-type functions to the 3-21G basis sets, leads to marked improvements in the majority of systems considered. In particular, equilibrium bond distances in both normal and hypervalent compounds are now generally in excellent agreement with experimental distances. Electric dipole moments are also greatly improved, indicating the role of *d* functions in the description of the bonding of heavy, main-group elements. Normal mode vibrational frequencies calculated at the 3-21G^(*) level overestimate experimental values (by 10%–12%), consistent with experience with first- and second-row elements. While hydrogenation energies for saturated compounds are reasonably well described, those for unsaturated systems and for hypervalent molecules are not. The 3-21G^(*) basis

set is proposed as the simplest method of choice for widespread application to the properties of molecules incorporating third- and fourth-row, main-group elements.

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