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# Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements

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The 6-31G* and 6-31G** basis sets previously introduced for first-row atoms have been extended through the second-row of the periodic table. Equilibrium geometries for one-heavy-atom hydrides calculated for the two-basis sets and using Hartree–Fock wave functions are in good agreement both with each other and with the experimental data. HF/6-31G* structures, obtained for two-heavy-atom hydrides and for a variety of hypervalent second-row molecules, are also in excellent accord with experimental equilibrium geometries. No large deviations between calculated and experimental single bond lengths have been noted, in contrast to previous work on analogous first-row compounds, where limiting Hartree–Fock distances were in error by up to a tenth of an angstrom. Equilibrium geometries calculated at the HF/6-31G level are consistently in better agreement with the experimental data than are those previously obtained using the simple split-valance 3-21G basis set for both normal- and hypervalent compounds. Normal-mode vibrational frequencies derived from 6-31G* level calculations are consistently larger than the corresponding experimental values, typically by 10%–15%; they are of much more uniform quality than those obtained from the 3-21G basis set. Hydrogenation energies calculated for normal- and hypervalent compounds are in moderate accord with experimental data, although in some instances large errors appear. Calculated energies relating to the stabilities of single and multiple bonds are in much better accord with the experimental energy differences.

## INTRODUCTION

There are currently several Gaussian-type basis sets available for use in practical *ab initio* molecular orbital calculations. These range from simple minimal basis sets in which there is only one basis function for each atomic orbital, to more flexible split-valence basis sets in which valence atomic orbitals are each represented by two basis functions, to polarization basis sets which, in addition, incorporate functions of higher angular quantum number than are occupied in the atomic ground state. While minimal basis sets, such as the extensively applied STO-3G representation,[1] do not give good descriptions of relative energies, force constants and electric dipole moments, they do fare reasonably well in the calculation of molecular equilibrium geometries. STO-3G representations have now been developed for the first 54 elements of the periodic table; as they may be applied to reasonably large molecules, the minimal basis set method is perhaps the most widely reaching of any nonempirical molecular orbital scheme developed to date.

A systematic series of small split-valence basis sets

has also been developed.[2] These are designated $K$-$LMG$, where $K$, $L$, and $M$ are integers denoting the number of Gaussians used to expand inner-shell atomic orbitals, and the inner- and outer-components of the valence-shell functions, respectively. At present, the most efficient of these is the 3-21G basis set ($K = 3$, $L = 2$, $M = 1$), which is now defined for first- and second-row elements.[3] In general, split-valence basis sets offer an improved description of molecular properties over the minimal representations, and at the same time are still small enough to be broadly applicable. Unfortunately, split-valence basis sets are still not completely successful in their description of relative molecular energies. Neither are they adequate for computations beyond the single-determinant framework[4]; here basis sets which incorporate functions of higher angular quantum number than are required for the ground state atom appear to be necessary. Split-valence representations are also not suitable for the description of the binding in hypervalent molecules, species for which the normal valence octet of an atom has been expanded to accommodate increased coordination. Such molecules are common among compounds of second-row elements, and become increasingly prevalent with increasing atomic number. Any complete account of main-group chemistry must eventually deal with them.

As commented above, further improvements in basis sets may be realized by supplementing the split-valence

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TABLE I. 6-31G valence-shell basis functions for sodium to argon.[a]

| Atom | $\alpha_3'$ | $d'_{3s}$ | $d'_{3p}$ | $\alpha_3''$ |
|------|-------------|-----------|-----------|--------------|
| Na | 4.979 66(−1) | −2.485 03(−1) | −2.302 25(−2) | 2.595 44(−2) |
|    | 8.435 29(−2) | −1.317 04(−1) | 9.503 59(−1) | |
|    | 6.663 50(−2) | 1.233 52 | 5.985 79(−2) | |
| Mg | 9.293 40(−1) | −2.122 90(−1) | −2.241 92(−2) | 4.210 61(−2) |
|    | 2.690 35(−1) | −1.079 85(−1) | 1.922 70(−1) | |
|    | 1.173 79(−1) | 1.175 84 | 8.461 81(−1) | |
| Al | 1.277 90 | −2.276 06(−1) | −1.751 26(−2) | 5.565 77(−2) |
|    | 3.975 90(−1) | 1.445 83(−3) | 2.445 33(−1) | |
|    | 1.600 95(−1) | 1.092 79 | 8.049 34(−1) | |
| Si | 1.727 38 | −2.446 30(−1) | −1.779 51(−2) | 7.783 69(−2) |
|    | 5.729 22(−1) | 4.315 72(−3) | 2.535 39(−1) | |
|    | 2.221 92(−1) | 1.098 18 | 8.006 69(−1) | |
| P | 2.156 23 | −2.529 23(−1) | −1.776 53(−2) | 9.983 17(−2) |
|   | 7.489 97(−1) | 3.285 17(−2) | 2.740 58(−1) | |
|   | 2.831 45(−1) | 1.081 25 | 7.854 21(−1) | |
| S | 2.615 84 | −2.503 74(−1) | −1.451 05(−2) | 1.171 67(−1) |
|   | 9.221 67(−1) | 6.695 70(−2) | 3.102 63(−1) | |
|   | 3.412 87(−1) | 1.054 51 | 7.544 83(−1) | |
| Cl | 3.186 49 | −2.518 30(−1) | −1.429 93(−2) | 1.426 57(−1) |
|    | 1.144 27 | 6.158 90(−2) | 3.235 72(−1) | |
|    | 4.203 77(−1) | 1.060 18 | 7.435 07(−1) | |
| Ar | 3.860 28 | −2.555 92(−1) | −1.591 97(−2) | 1.738 88(−1) |
|    | 1.413 73 | 3.780 66(−2) | 3.246 46(−1) | |
|    | 5.166 46(−1) | 1.080 56 | 7.439 90(−1) | |

[a]For tabulation of inner-shell functions see Ref. 2(b).

representations with functions of higher angular quantum number (i.e., polarization functions). These added functions allow for a displacement of the center of electron density away from the individual nuclei. While such a displacement can be accomplished using unsupplemented minimal or split-valence basis sets, simply by relaxing the constraint that all basis functions be nuclear centered,[5] in practice such a tactic is plagued with difficulties. In particular, for systems with little or no symmetry, the only well-defined way to locate the off-center basis functions is by minimization of the total energy. This is clearly a cumbersome computational approach.

The inclusion of polarization functions in the basis set descriptions of first-row elements generally leads to marked improvement in calculated molecular properties, and there is no reason to believe that similar improvements in properties over those obtained from split-valence basis sets would not be noted for compounds containing second- and higher-row elements. With this in mind we have extended the now widely applied 6-31G* and 6-31G** polarization basis sets for first-row atoms[7] to include the elements sodium to argon.

## COMPUTATIONAL METHODS

6-31G* basis sets for second-row elements have been obtained in a manner similar to that previously employed for the corresponding first-row atoms.[7] Initially the series of 6-31G split-valence basis sets is defined according to Eq. (1):

$$\phi_{1s}(\mathbf{r}) = \sum_{k=1}^{6} d_{1s,k} g_s(\alpha_{1k}, \mathbf{r}) ,$$

$$\phi_{2s}(\mathbf{r}) = \sum_{k=1}^{6} d_{2s,k} g_s(\alpha_{2k}, \mathbf{r}) ,$$

$$\phi_{2p}(\mathbf{r}) = \sum_{k=1}^{6} d_{2p,k} g_p(\alpha_{2k}, \mathbf{r}) ,$$

$$\phi_{3s}'(\mathbf{r}) = \sum_{k=1}^{3} d_{3s,k}' g_s(\alpha_{3k}', \mathbf{r}) , \qquad (1)$$

$$\phi_{3p}'(\mathbf{r}) = \sum_{k=1}^{3} d_{3p,k}' g_p(\alpha_{3k}', \mathbf{r}) ,$$

$$\phi_{3s}''(\mathbf{r}) = d_{3s,k}'' g_s(\alpha_3'', \mathbf{r}) ,$$

$$\phi_{3p}''(\mathbf{r}) = d_{3p,k}'' g_p(\alpha_3'', \mathbf{r}) ,$$

where each of the 13 atomic basis functions comprises either a single Gaussian or a sum of Gaussians. Here, the expansion coefficients $d$ and Gaussian exponents $\alpha$ for inner-shell functions ($\phi_{1s}$, $\phi_{2s}$, $\phi_{2p}$) are assumed to be identical to those used in the corresponding 6-21G basis sets.[2(b)] For all elements except sodium and magnesium, coefficients and exponents for the inner- and outer-components of the valence atomic orbitals ($\phi_{3s}'$, $\phi_{3p}'$, and $\phi_{3s}''$ and $\phi_{3p}''$, respectively) were obtained by minimizing the UHF energy of the atomic ground state subject to an overall normalization condition. For magnesium optimization was carried out on the $^3P$ excited state $[(1s)^2(2s)^2(2p)^6(3s)(3p)]$ in order to obtain a reasonable simultaneous description of both valence $s$- and $p$-type orbitals. For sodium, the valence $s$-type basis

functions were first determined using the $^2S$ ground state $[(1s)^2(2s)^2(2p)^6(3s)]$ with a basis set devoid of $3p$-type functions. Valence $3p$-type functions were subsequently added, and their contraction coefficients determined using the $^2P$ excited state $[(1s)^2(2s)^2(2p)^6(3p)]$ holding all other contraction coefficients as well as all Gaussian exponents fixed. Numerical procedures have been discussed elsewhere.[6] Final $d$ and $\alpha$ values are presented in Table I.

The 6-31G* polarization sets are then obtained from the above split-valence representations by the addition of functions of higher angular quantum number than are required for the atom in its ground state. Here, as for the first-row 6-31G* basis sets, a single set of six second-order Gaussians ($x^2$, $y^2$, $z^2$, $xy$, $xz$, $yz$) is employed. This set is equivalent to the more familiar array of five pure $d$-functions ($x^2-y^2$, $3z^2-r^2$, $xy$, $xz$, $yz$), plus a single function of $s$-type symmetry. One could further augment the underlying 6-31G basis set by the addition of third-order ($f$-type) functions; however, early studies on compounds containing first-row elements indicated that the majority of the effect of basis set polarization is achieved by addition of $d$-functions alone.[8] Other basis set improvements, in particular,

TABLE II. Optimum exponents for molecules.[a]

| Atom | Molecule | $\alpha_d$ |
|------|----------|------------|
| Na | NaOH | 0.05 |
| | NaF | 0.07 |
| | NaCl | 0.23 |
| | NaH | 0.40 |
| Mg | MgO | 0.09 |
| | $MgF_2$ | 0.11 |
| | $MgH_2$ | 0.24 |
| | $Mg(CH_3)_2$ | 0.25 |
| Al | $AlH_3$ | 0.31 |
| | $Al_2O$ | 0.31 |
| | $AlF_3$ | 0.33 |
| | $Al(CH_3)_3$ | 0.34 |
| Si | $SiH_4$ | 0.40 |
| | $SiF_2$ | 0.52 |
| | $SiF_4$ | 0.66 |
| P | $PH_3$ | 0.46 |
| | HPO | 0.52 |
| | HCP | 0.53 |
| | $PF_3$ | 0.62 |
| S | $H_2S$ | 0.53 |
| | $CH_3SH$ | 0.58 |
| | CS | 0.60 |
| | $SO_3$ | 0.65 |
| | $SF_2$ | 0.68 |
| | $SO_2$ | 0.70 |
| | $SF_4$ | 0.72 |
| Cl | HCl | 0.60 |
| | $CH_3Cl$ | 0.70 |
| | $ClF_3$ | 0.76 |
| | $FClO_2$ | 0.79 |
| | $FClO_3$ | 0.81 |

[a]Calculations employ optimum HF/3-21G level equilibrium geometries.

TABLE III. Average $d$ exponents for molecules.

| Atom | $\alpha_d$ | Atom | $\alpha_d$ |
|------|-----------|------|-----------|
| Na | 0.175 | P | 0.55 |
| Mg | 0.175 | S | 0.65 |
| Al | 0.325 | Cl | 0.75 |
| Si | 0.45 | Ar | 0.85[a] |

[a]Extrapolated from values on lighter elements.

further partitioning of the valence-shell orbitals into more than two components, have been shown to be of considerable importance,[9] and it is likely that such developments should be pursued prior to the inclusion of $f$-type or higher-order functions.

The radial exponent $\alpha$ associated with the added $d$ functions is determined for each element as an average of exponents appropriate for typical molecules incorporating that element, the selection including both normal- and hypervalent compounds. Optimized $d$ exponents for the compounds considered appear in Table II. For most elements the $\alpha_d$ differ little from one another, and selection of an "average value" is straightforward. The major exceptions are sodium and magnesium where the $\alpha_d$ span a much wider range. Here, anomalously small exponents are noted for some of the more highly polar compounds (e.g., NaOH and MgO). This is consistent with previous work involving supplemented minimal basis sets[10] and suggests the relative unimportance of $d$-type functions in the bonding in these compounds. The selected average $\alpha$-values for second-row atoms are given in Table III. These are employed in all studies which follow.

6-31G* basis sets for second-row atoms are to be used in conjunction with the corresponding 6-31G* representations for the first-row.[7] Hydrogen atoms are not equipped with polarization ($p$-type) functions, but represented only by a pair of $s$-type basis functions. It has been found, however, that the properties of some molecules alter considerably upon the addition of hydrogen polarization functions to the basis set. This is particularly true for compounds in which hydrogen is bridging (e.g., the nonclassical ethyl cation). For these situations use of another basis set, termed 6-31G**, may be advantageous. It differs from 6-31G* only in that $p$-type polarization functions are also added to hydrogen atoms as well as to first- and second-row elements. Details of the added $p$-type functions are to be found in the original literature.[7]

It should be noted that a 6-31G* basis set for silicon has previously been published.[11] This is based on a 6-31G type basis set obtained by minimization of the energy of silicon atom in its $^3P$ ground state with respect to all Gaussian exponents and contraction coefficients. An exponent of 0.395 for the set of six second-order Gaussian functions was then selected on the basis of energy optimization for silane. Properties deriving from this basis set are not expected to differ greatly from those obtained from the present 6-31G* representation.

TABLE IV. Calculated and experimental equilibrium geometries for one heavy-atom hydrides (bond lengths in angstroms, angles in degrees).

| Molecule | Point group | Geometrical parameter | 3-21G | 6-31G* | 6-31G** | Exptl. |
|---|---|---|---|---|---|---|
| NaH$_3$[a] | $C_{\infty v}$ | $r$(NaH) | 1.926 | 1.914 | 1.912 | 1.887 |
| MgH$_2$ | $D_{\infty h}$ | $r$(MgH) | 1.726 | 1.718 | 1.714 | ... |
| AlH$_3$ | $D_{3h}$ | $r$(AlH) | 1.599 | 1.588 | 1.583 | ... |
| SiH$_4$[b] | $T_d$ | $r$(SiH) | 1.487 | 1.475 | 1.476 | 1.481 |
| PH$_3$[b] | $C_{3v}$ | $r$(PH) | 1.423 | 1.403 | 1.405 | 1.420 |
|  |  | <(HPH) | 96.1 | 95.4 | 95.6 | 93.3 |
| H$_2$S[b] | $C_{2v}$ | $r$(SH) | 1.350 | 1.326 | 1.327 | 1.336 |
|  |  | <(HSH) | 95.8 | 94.4 | 94.4 | 92.1 |
| HCl[a] | $C_{\infty v}$ | $r$(ClH) | 1.293 | 1.266 | 1.266 | 1.275 |

[a]Experimental data from: D. R. Stull and J. Prophet, *JANAF Thermochemical Tables*, 2nd ed., NSRDS-NBS (National Bureau of Standards, Washington, D.C., 1971), Vol. 37.
[b]Experimental data from: J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote, *Structure Data on Free Polyatomic Molecules*, Landolt–Börnstein, New Series, Group II, edited by K. H. Hellwege and A. M. Hellwege (Springer, Berlin, 1976), Vol. 7.

Development of basis sets for second-row atoms prior to 1977 has been detailed in a review by Dunning and Hay.[12] Subsequently, a contracted Gaussian basis has been published for second-row atoms and their anions.[13] However, neither this representation, nor any of its predecessors, included polarization functions. Recently both a minimal and a split-valence basis set, to which are added polarization functions, have been constructed,[14] MINI-$i$* and MIDI-$i$*. Use of the latter representation in the calculation of molecular properties leads to a significantly improved description relative to the unpolarized parent basis, MIDI-$i$*.

The MIDI-$i$* basis is prepared in a manner which differs slightly from that used in the present work. Three MIDI-$i$* representations were constructed, $i$ = 1, 3, and 4; the largest of which, MIDI-4*, is still much smaller than the 6-31G* basis. The constraint imposed on fabrication of the 6-31G* basis in which the same exponent is used for $s$- and $p$-functions of the same principal quantum number is released for MIDI-$i$* leading to an increase in the amount of work necessary in the integral evaluations. The 6-31G* representation differs also in composition from MIDI-$i$* which does not include polarization functions of $d$-symmetry on either Na or Mg, relying instead on the $p$-function to provide sufficient polarization. The radial exponents for MIDI-$i$ $p$ and $d$ polarization functions are optimized on the atom for maximum overlap between the polarization function and the molecular orbital, in contrast to those for 6-31G* which were obtained in molecular environments, and are in all cases smaller than the corresponding 6-31G* functions.

## PERFORMANCE OF THE BASIS SET

All calculations have been carried out using either the Gaussian-77[5] or Gaussian-80[6] computer programs.

## EQUILIBRIUM GEOMETRIES

Using the newly constructed basis sets, equilibrium geometries were calculated for one- and two-heavy-

atom hydrides including second-row elements, as well as for a number of simple molecules containing second-row atoms with expanded valence shells. In Table IV 6-31G* and 6-31G** equilibrium structures for the one-heavy-atom hydrides are compared with structures obtained both from experiment and from the 3-21G split-valence basis set.[2(b)] 6-31G* AH bond lengths are uniformly shorter than the corresponding 3-21G values, generally by one or more hundreths of an angstrom. Except for NaH they are also shorter than the experimental lengths. The 6-31G** bond lengths are not markedly different from those obtained using 6-31G*, the largest change being 0.005 Å for AlH$_3$. These values are also consistently shorter than calculated 3-21G level bond lengths[2(b)] and, with the exception of sodium hydride, than experimental distances. Despite the fact that both 6-31G* and 6-31G** bond lengths are consistently short, the calculated equilibrium structures at either of these levels represent improvements over 3-21G geometries.[2(b)] Overall, the mean absolute differences between calculated and measured bond distances are 0.014 and 0.016 Å for the 6-31G* and 6-31G** models, respectively. For comparison, the corresponding mean error is 0.016 Å at the 3-21G level.

It should be noted that previous experience with first-row elements has shown that bond lengths generally elongate when electron correlation effects are taken into account.[4] The reason for this may simply be thought of as the participation of excited state configurations which are often significantly antibonding. It is to be expected, therefore, that limiting Hartree–Fock level bond lengths will be shorter than measured values, and that extensions beyond the single-determinant level will bring these results into closer accord with experiment. Work in this direction is in progress.

6-31G* geometries for the larger set of two-heavy-atom, normal-valent molecules for which experimental data are available for comparison are given in Table V. As for the one heavy-atom hydrides, the structures are

TABLE V. Calculated and experimental equilibrium geometries for two heavy-atom hydrides (bond lengths in angstroms, angles in degrees).

| Molecule | Point group | Geometrical parameter | 3-21G | 6-31G* | Expt. |
|---|---|---|---|---|---|
| LiCl[a] | $C_{\infty v}$ | $r$(LiCl) | 2.112 | 2.072 | 2.021 |
| CH$_3$SiH$_3$ [b] | $C_{3v}$ | $r$(CSi) | 1.917 | 1.888 | 1.867 |
| | | $r$(CH) | 1.085 | 1.086 | 1.093 |
| | | $r$(SiH) | 1.490 | 1.478 | 1.485 |
| | | <(HCH) | 108.3 | 108.3 | 107.7 |
| | | <(HSiH) | 108.3 | 107.8 | 108.3 |
| HCP[b] | $C_{\infty v}$ | $r$(CP) | 1.548 | 1.515 | 1.540 |
| | | $r$(CH) | 1.057 | 1.063 | 1.069 |
| H$_2$CPH[c] | $C_s$ | $r$(CP) | 1.683 | 1.652 | 1.67 |
| | | $r$(CH$_{anti}$) | 1.073 | 1.076 | $\cdots$ |
| | | $r$(CH$_{syn}$) | 1.073 | 1.075 | $\cdots$ |
| | | $r$(PH) | 1.433 | 1.409 | $\cdots$ |
| | | <(PCH$_{anti}$) | 119.5 | 119.6 | $\cdots$ |
| | | <(PCH$_{syn}$) | 124.7 | 125.0 | $\cdots$ |
| | | <(HPC) | 98.8 | 98.9 | $\cdots$ |
| CH$_3$PH$_2$ [b,d] | $C_s$ | $r$(CP) | 1.908 | 1.861 | 1.862 |
| | | $r$(CH$_{tr}$) | 1.081 | 1.082 | 1.094 |
| | | $r$(CH$_g$) | 1.082 | 1.084 | 1.094 |
| | | $r$(PH) | 1.425 | 1.404 | 1.432 |
| | | <(PCH$_{tr}$) | 112.1 | 113.2 | 109.2 |
| | | <(PCH$_g$H$_g'$) | 123.5 | 123.9 | $\cdots$ |
| | | <(HgCH$_g'$) | 108.9 | 107.6 | $\cdots$ |
| | | <(CPHH') | 101.8 | 102.8 | $\cdots$ |
| | | <(HPH) | 95.6 | 95.1 | $\cdots$ |
| CS[a] | $C_{\infty v}$ | $r$(CS) | 1.562 | 1.520 | 1.535 |
| H$_2$CS[b] | $C_{2v}$ | $r$(CS) | 1.638 | 1.597 | 1.611 |
| | | $r$(CH) | 1.073 | 1.078 | 1.093 |
| | | <(HCH) | 116.5 | 115.5 | 116.9 |
| CH$_3$SH[b,e] | $C_s$ | $r$(CS) | 1.895 | 1.817 | 1.819 |
| | | $r$(CH$_{tr}$) | 1.078 | 1.082 | 1.091 |
| | | $r$(CH$_g$) | 1.077 | 1.081 | 1.091 |
| | | $r$(SH) | 1.352 | 1.327 | 1.336 |
| | | <(SCH$_{tr}$) | 105.6 | 106.7 | $\cdots$ |
| | | <(SCH$_g$H$_g'$) | 126.6 | 129.3 | $\cdots$ |
| | | <(H$_g$CH$_g'$) | 111.4 | 110.0 | 109.8 |
| | | <(CSH) | 97.9 | 97.9 | 96.5 |
| CH$_3$Cl[b] | $C_{3v}$ | $r$(CCl) | 1.892 | 1.785 | 1.781 |
| | | $r$(CH) | 1.073 | 1.078 | 1.096 |
| | | <(HCH) | 112.6 | 110.5 | 110.0 |
| PN[a] | $C_{\infty v}$ | $r$(PN) | 1.510 | 1.455 | 1.491 |
| NaOH[a] | $C_{\infty v}$ | $r$(NaO) | 1.870 | 1.922 | 1.95 |
| | | $r$(OH) | 0.962 | 0.941 | 0.96 |
| MgO[a] | $C_{\infty v}$ | $r$(MgO) | 1.776 | 1.738 | 1.749 |
| SiO[a] | $C_{\infty v}$ | $r$(SiO) | 1.536 | 1.487 | 1.509 |
| HPO[b,g] | $C_s$ | $r$(PO) | 1.544 | 1.460 | 1.512 |
| | | $r$(PH) | 1.447 | 1.431 | 1.433 |
| | | <(HPO) | 103.5 | 105.4 | 104.7 |
| HOCl[b] | $C_s$ | $r$(ClO) | 1.767 | 1.670 | 1.690 |
| | | $r$(OH) | 0.975 | 0.951 | 0.975 |
| | | <(HOCl) | 104.2 | 105.1 | 102.5 |
| NaF[a] | $C_{\infty v}$ | $r$(NaF) | 1.863 | 1.885 | 1.926 |
| SiH$_3$F [b] | $C_{3v}$ | $r$(SiF) | 1.635 | 1.594 | 1.596 |
| | | $r$(SiH) | 1.478 | 1.470 | 1.480 |
| | | <(HSiH) | 109.8 | 110.2 | 110.6 |
| ClF[a] | $C_{\infty v}$ | $r$(ClF) | 1.689 | 1.613 | 1.628 |
| Na$_2$ [a] | $D_{\infty h}$ | $r$(NaNa) | 3.228 | 3.130 | 3.078 |

TABLE V  (*Continued*)

| Molecule | Point group | Geometrical parameter | 3-21G | 6-31G* | Exptl. |
|---|---|---|---|---|---|
| NaCl[a] | $C_{\infty v}$ | $r$(NaCl) | 2.421 | 2.397 | 2.361 |
| Si$_2$H$_6$ [b] | $D_{3d}$ | $r$(SiSi) | 2.382 | 2.353 | 2.327 |
|  |  | $r$(SiH) | 1.488 | 1.478 | 1.486 |
|  |  | < (HSiH) | 108.8 | 108.5 | 107.8 |
| SiH$_3$Cl[b] | $C_{3v}$ | $r$(SiCl) | 2.191 | 2.067 | 2.048 |
|  |  | $r$(SiH) | 1.475 | 1.468 | 1.481 |
|  |  | < (HSiH) | 111.8 | 108.31 | 108.0 |
| P$_2$[a] | $D_{\infty h}$ | $r$(PP) | 1.930 | 1.859 | 1.894 |
| P$_2$H$_4$ [b,f] | $C_2$ | $r$(PP) | 2.356 | 2.214 | 2.219 |
|  |  | $r$(PH$_{int}$) | 1.421 | 1.401 | 1.417 |
|  |  | $r$(PH$_{ext}$) | 1.419 | 1.402 | 1.414 |
|  |  | < (PPH$_{int}$) | 99.1 | 101.2 | 99.1 |
|  |  | < (PPH$_{ext}$) | 95.5 | 96.8 | 94.3 |
|  |  | < (H$_{int}$ PH$_{ext}$) | 95.8 | 95.6 | 92.0 |
|  |  | $\omega$(H$_{int}$ PPH$_{ext}$) | 79.1 | 77.3 | 74.0 |
| H$_2$S$_2$ [b] | $C_2$ | $r$(SS) | 2.264 | 2.064 | 2.058 |
|  |  | $r$(SH) | 1.352 | 1.327 | 1.345 |
|  |  | < (SSH) | 96.7 | 99.2 | 98.1 |
|  |  | $\omega$(HSSH) | 93.7 | 89.9 | 90.8 |
| Cl$_2$[a] | $D_{\infty h}$ | $r$(ClCl) | 2.193 | 1.990 | 1.988 |

[a]See footnote a of Table IV for reference to experimental data.
[b]See footnote b of Table IV for reference to experimental data.
[c]C=P bond length estimated from investigations on $CH_2PCl$, $CF_2$=PH and $CH_2$= PH. M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. E. Simmons, J. C. S. Chem. Comm. 513 (1976).
[d]Subscripts tr, g, and *g'* refer to relative orientations of the CH bonds to the phosphorous lone pair of 180° and ±60°, respectively, PCH$_g$H$_g'$ refers to the angle between the PC bond and the line bisecting the H$_g$CH$_g'$ plane. CPHH' refers to the angle between the CP bond and the line bisecting the HPH plane.
[e]Subscripts tr, g, and *g'* refer to relative orientations of the SH and CH bonds of 180° and ±60°, respectively. SCH$_g$H$_g'$ refers to the angle between the SC bond and the line bisecting the H$_g$CH$_g'$ plane.
[f]Subscripts int and ext refer to the projection below:
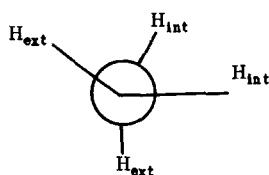


[g]H−P bond length assumed to be the same as in PH, M. Lam Thanh and M. Peyron, J. Chim. Phys. 61, 1531 (1964).

generally quite close to the experimental geometries. In most cases, the 6-31G* structures are improved relative to the 3-21G geometries. The mean absolute deviation from experiment for 6-31G* bond lengths between heavy atoms is 0.022 Å, compared to 0.067 Å for 3-21G distances. While the worst cases for 3-21G (e.g., the SS bond length in H$_2$S$_2$ and the CS distance in methane thiol) are well described at the 6-31G* level, deviations in multiple bond lengths are still significant. Thus, the P=O bond length in HPO is underestimated by 0.052 Å at the 6-31G* level, while that in PN is 0.036 Å shorter than the experimental value. Again, the application of correlated methods to the 6-31G* basis is expected to result in longer calculated bond lengths, and hence improved agreement with experiment.

Bond angles calculated using the 6-31G* basis set are marginally better than those obtained from 3-21G calculations; the mean absolute deviation from experiment for the former is 1.3° while for the latter it is 1.6°. Torsional angles are also slightly improved. For example, the HPPH angle in P$_2$H$_4$ is overestimated by 3.3° at 6-31G*, while the 3-21G value is 5.1° too large. In most cases, the bond angles are still somewhat at variance with those found experimentally. Prior work with first-row compounds,[3(a)] has shown that while bond angles calculated using multideterminant methods are not very different from those obtained from single-determinant calculations, in general they are in better accord with experiment. Thus, correlated treatments for second-row molecules will also probably result in

TABLE VI. Calculated and experimental equilibrium geometries for hypervalent molecules (bond lengths in angstroms, angles in degrees).

| Molecule | Point group | Geometrical parameter | 6-31G* | Exptl. |
|---|---|---|---|---|
| PF$_5$[a] | $D_{3h}$ | $r(PE_{eq})$ | 1.535 | 1.534 |
| | | $r(PF_{ax})$ | 1.568 | 1.577 |
| F$_3$PO[b] | $C_{3v}$ | $r(PO)$ | 1.425 | 1.436 |
| | | $r(PF)$ | 1.526 | 1.524 |
| | | $<(FPF)$ | 100.7 | 101.3 |
| F$_3$PS[b] | $C_{3v}$ | $r(PS)$ | 1.874 | 1.866 |
| | | $r(PF)$ | 1.535 | 1.538 |
| | | $<(FPF)$ | 99.6 | 99.6 |
| SO$_2$[b] | $C_{2v}$ | $r(SO)$ | 1.414 | 1.431 |
| | | $<(OSO)$ | 118.8 | 119.3 |
| SF$_4$[b] | $C_{2v}$ | $r(SF_{eq})$ | 1.544 | 1.545 |
| | | $r(SF_{ax})$ | 1.632 | 1.646 |
| | | $<(F_{eq}SF_{eq})$ | 102.7 | 101.6 |
| | | $>(F_{ax}SF_{ax})$ | 169.9 | 173.1 |
| F$_2$SO[b] | $C_s$ | $s(SO)$ | 1.409 | 1.413 |
| | | $r(SF)$ | 1.571 | 1.585 |
| | | $<(FSO)$ | 106.9 | 106.8 |
| | | $<(FSF)$ | 92.4 | 92.2 |
| NSF[b] | $C_s$ | $r(SN)$ | 1.431 | 1.448 |
| | | $r(SF)$ | 1.615 | 1.643 |
| | | $<(NSF)$ | 114.1 | 116.9 |
| SO$_3$[b] | $D_{3h}$ | $r(SO)$ | 1.405 | 1.420 |
| F$_4$SO[b] | $C_{2v}$ | $r(SO)$ | 1.404 | 1.403 |
| | | $r(SF_{eq})$ | 1.537 | 1.552 |
| | | $r(SF_{ax})$ | 1.582 | 1.575 |
| | | $<(F_{eq}SF_{eq})$ | 112.5 | 110.2 |
| | | $<(F_{ax}SF_{ax})$ | 164.5 | 178.6 |
| ClF$_3$[b] | $C_{2v}$ | $r(ClF_{ax})$ | 1.672 | 1.698 |
| | | $r(ClF_{eq})$ | 1.579 | 1.598 |
| | | $<(F_{ax}ClF_{ax})$ | 172.6 | 175.0 |
| ClF$_5$[a] | $C_{4v}$ | $r(ClF_{ax})$ | 1.590 | 1.65 |
| | | $r(ClF_{eq})$ | 1.630 | |
| | | $<(F_{ax}ClF_{eq})$ | 84.9 | 86.5 |
| FCLO$_2$[b] | $C_s$ | $r(ClO)$ | 1.419 | 1.418 |
| | | $r(ClF)$ | 1.617 | 1.697 |
| | | $<(OClO)$ | 114.3 | 115.2 |
| | | $<(OClF)$ | 102.3 | 101.7 |
| FClO$_3$[b] | $C_{3v}$ | $r(ClO)$ | 1.402 | 1.404 |
| | | $r(ClF)$ | 1.579 | 1.619 |
| | | $<(OClO)$ | 115.3 | 116.6 |

[a]See footnote a of Table IV for reference to experimental data.
[b]See footnote b of Table IV for reference to experimental data.

improved descriptions of equilibrium bond angles for normal-valent compounds.

As mentioned before, polarization basis sets such as 6-31G* should be much more successful than either minimal or split-valence representations in the calculation of properties of molecules which have expanded valence manifolds. Table VI compares the 6-31G* calculated and experimental equilibrium structures for a number of hypervalent molecules. The 6-31G* basis set performs admirably at this task; the mean absolute deviation from experiment for bond lengths is only 0.016

Å, and for bond angles is 1.3°. The largest difference in bond lengths is seen in ClF$_5$, where the calculated axial ClF distance is 0.06 Å shorter than the experimental value. However, the experimental length was obtained assuming equivalent axial and equatorial bonds. The angle between the axial fluorines in thionyltetrafluoride also appears to be seriously in error, deviating more than 14° from the experiment. Again the experimental value is suspect. While the bond lengths for F$_4$SO seem to be reasonably well established, reported values for the axial angle range from 138° to 186°. It is probable that the structures of hypervalent compounds can be further refined using post-Hartree—Fock methods, but the results of such studies have not yet been documented.

## NORMAL-MODE VIBRATION FREQUENCIES

Vibration frequencies obtained from the 6-31G* basis set are compared to experimental values in Table VII; 3-21G level frequencies have also been included for comparison. Computational methods have been discussed elsewhere.[17] Both directly measured frequencies and harmonic values (i.e., those corrected for anharmonic effects) are tabulated. The latter are more appropriate for comparison with the theoretical results which themselves are based on quadratic force fields.

With but a single exception (the $a_1$ symmetry mode in silane) frequencies calculated at the 6-31G* level are larger than experimental harmonic values, typically by 10–15%. In the mean they deviate by 12%. Although the mean absolute error in frequencies obtained using the smaller 3-21G basis set is actually smaller (9%), the theoretical results at this level are not as uniform as those derived from 6-31G*. This is indicated in a calculated standard deviation for 3-21G frequencies of 11% which is nearly twice the value of 6% noted for the 6-31G* calculations. The greatest differences in the two theoretical models occur for hypervalent compounds. Here 3-21G level frequencies are often 20–30% too low (indicating the inability of the model to properly account for the tight binding in these compounds). On the other hand, the 6-31G* results here are no worse than they are for the normal-valent systems considered. It is apparent that the 3-21G basis set is not suitable for the calculation of vibrational frequencies for the entire spectrum of molecules incorporating second-row elements, in contrast to its favorable performance for first-row systems.[2(a),18] The 6-31G* representation fares much better, and does appear to yield results of sufficient consistency to be of eventual use to the assignment of experimental frequencies.

## RELATIVE ENERGIES

Table VIII contains 6-31G* total energies for second-row atoms and for both the normal- and hypervalent compounds discussed previously. The total energies are significantly lower than energies derived from either the 3-21G basis set or from the parent 6-31G split-valence representation. The total energies themselves are not of particular interest; in general, energy differences are more pertinent to chemical problems.

TABLE VII. Calculated and experimental normal mode vibration frequencies (cm$^{-1}$).

| Molecule | Symmetry of mode | Description of mode | 3–21G | 6–31G* | Exptl.[a] Measured | Harmonic |
|---|---|---|---|---|---|---|
| SiH$_4$[c] | $a_1$ | sym. stretch | 2311 | 2233 | 2187 | 2377 |
| | $e$ | deg. deform. | 1046 | 1052 | 975 | 975 |
| | $t_2$ | deg. stretch | 2285 | 2385 | 2191 | 2319 |
| | | deg. deform. | 974 | 1017 | 914 | 945 |
| PH$_3$[d] | $a_1$ | sym. stretch | 2404 | 2666 | 2323 | 2452 |
| | | sym. deform. | 1093 | 1143 | 992 | 1041 |
| | $e$ | deg. stretch | 2398 | 2602 | 2328 | 2457 |
| | | deg. deform. | 1271 | 1278 | 1118 | 1154 |
| H$_2$S[e] | $a_1$ | sym. stretch | 2642 | 2918 | 2615 | 2722 |
| | | bend | 1323 | 1368 | 1183 | 1215 |
| | $b_1$ | asym. stretch | 2656 | 2930 | 2626 | 2733 |
| HCl[f] | $\sigma$ | | 2847 | 3188 | 2990 | 3042 |
| CS[f] | $\sigma$ | | 1284 | 1471 | 1285 | 1291 |
| CH$_3$Cl[g] | $a_1$ | sym. CH stretch | 3268 | 3252 | 2937 | 3062 |
| | | sym. deform | 1502 | 1536 | 1355 | 1393 |
| | | CCl stretch | 663 | 781 | 732 | 732 |
| | $e$ | deg. stretch | 3397 | 3368 | 3039 | 3209 |
| | | deg. deform | 1647 | 1640 | 1452 | 1520 |
| | | rock | 1097 | 1136 | 1017 | 1049 |
| SO$_2$[h] | $a_1$ | sym. stretch | 1114 | 1357 | 1151 | 1167 |
| | | bend | 497 | 592 | 518 | 526 |
| | $b_1$ | asym. stretch | 1297 | 1568 | 1362 | 1381 |
| SO$_3$[b,i] | $a_1'$ | sym. stretch | 926 | 1227 | 1065 | 1048 |
| | $a_2''$ | sym. deform. | 356 | 561 | 498 | 504 |
| | $e$ | deg. stretch | 1152 | 1555 | 1391 | 1409 |
| | $e''$ | deg. deform. | 440 | 584 | 530 | 539 |

[a]Measured experimental vibrational frequencies from: T. Shimanouchi, *Tables of Molecular Vibrational Frequencies*, Consolidated Vol. I., NSRDS–NBS 39 (National Bureau of Standards, Washington, D.C., 1972), unless otherwise noted.

[b]Measured experimental vibrational frequencies from: T. Shimanouchi, J. Phys. Chem. Ref. Data **6**, 993 (1977).

[c]Harmonic frequencies from I. W. Levin and W. T. King, J. Chem. Phys. **37**, 1375 (1962).

[d]Harmonic frequencies from J. L. Duncan and I. M. Mills, Spectrosc. Acta **20**, 523 (1964).

[e]Harmonic frequencies from H. C. Allen, Jr. and E. K. Plyler, J. Chem. Phys. **25**, 1132 (1956).

[f]See footnote a Table IV for reference to harmonic frequencies.

[g]Harmonic frequencies from W. T. King, I. M. Mills, and B. Crawford, Jr., J. Chem. Phys. **27**, 455 (1964).

[h]Harmonic frequencies from R. D. Shelton, A. H. Nielsen, and W. H. Fletcher, J. Chem. Phys. **21**, 2178 (1953).

[i]Harmonic frequencies from A. J. Dorney, A. R. Hoy, and I. M. Mills, J. Mol. Spectrosc. **45**, 253 (1973).

The energy lowerings (per heavy-atom) resulting from addition of polarization functions to the 6–31G basis set are given in Table IX. The lowerings reflect the usage of polarization functions by the molecules in their bonding. Molecules such as NaH and MgH$_2$, in which the bonding is primarily due to overlap of $s$-functions, appear to make little use of $d$-functions. Here, a polarization description has already been obtained in the parent 6–31G representation by the incorporation of unused $p$-functions. The addition of the set of six polarization functions does improve the energy of these molecules slightly, but the energy lowerings are probably due, in part, to the $s$-function which is included along with the $d$-functions. For molecules incorporating the remaining second-row elements (i.e., those which involve $p$-functions in bonding) $d$ functions are necessary in order to account for the polarization of the electron

distribution. Thus, one would expect significant energy lowerings. This is indeed the case as the data in Table IX indicate.

The observed energy lowerings for molecules incorporating second-row elements follow the same general pattern as those noted in the first-row,[7] although they are nearly twice as large. These differences in magnitude are probably due in large part to the fact that $d$-symmetry orbitals for second-row elements are energetically more accessible than those for the corresponding first-row atoms. Hence, the $d$-orbitals are themselves more able to make significant contributions to molecular bonding even for compounds which would be described as normal-valent. This line of reasoning is consistent with the observation that calculated equilibrium structures for compounds containing second-row

TABLE VIII. Calculated total energies for atoms and molecules (hartrees).

| Atom or molecule | $E$(6–31G*//6–31G*) | Atom or molecule | $E$(6–31G*//6–31G*) |
|---|---|---|---|
| Na | −160.373 28 | SiO | −363.778 84 |
| Mg | −199.595 61 | NaF | −261.301 70 |
| Al | −241.856 98 | $SiH_3F$ | −390.148 40 |
| Si | −288.831 79 | ClF | −558.819 52 |
| P | −340.690 20 | $Na_2$ | −323.681 18 |
| S | −397.475 96 | NaCl | −621.399 62 |
| Cl | −459.447 96 | $Si_2H_6$ | −581.305 10 |
| Ar | −526.773 74 | $SiH_3Cl$ | −790.183 41 |
|  |  | $P_2$ | −681.424 53 |
| NaH | −162.372 45 | $P_2H_4$ | −683.751 08 |
| $MgH_2$ | −200.715 57 | $H_2S_2$ | −796.174 40 |
| $AlH_3$ | −243.350 50 | $Cl_2$ | −918.912 82 |
| $SiH_4$ | −291.225 13 |  |  |
| $PH_3$ | −342.447 96 | $PF_5$ | −838.050 72 |
| $H_2S$ | −398.667 32 | $F_3PO$ | −714.028 42 |
| HCl | −460.059 98 | $F_3PS$ | −1036.659 17 |
|  |  | $SO_2$ | −547.169 01 |
| LiCl | −467.009 19 | $SF_4$ | −795.143 38 |
| $CH_3SiH_3$ | −330.272 41 | $F_2SO$ | −671.183 51 |
| HCP | −379.105 30 | NSF | −551.300 64 |
| $H_2CPH$ | −380.287 05 | $SO_3$ | −621.981 57 |
| $CH_3PH_2$ | −381.486 26 | $F_4SO$ | −869.966 97 |
| CS | −435.304 31 | $ClF_3$ | −757.484 44 |
| $H_2CS$ | −436.506 46 | $ClF_5$ | −956.139 24 |
| $CH_3SH$ | −437.700 32 | $FClO_2$ | −708.291 74 |
| $CH_3Cl$ | −499.093 15 | $FClO_3$ | −783.045 12 |
| PN | −395.125 75 |  |  |
| HPO | −416.124 70 |  |  |
| HOCl | −534.841 97 |  |  |
| NaOH | −237.272 47 |  |  |
| MgO | −274.323 83 |  |  |

elements depend far more on added $d$-functions than those for the analogous first-row systems. For example, the carbon–chlorine bond length in methyl chloride decreases by almost 0.1 Å in going from the 3-21G to the 6-31G* basis set; for comparison, the CF linkage in methyl fluoride decreases by only 0.04 Å. Another possible reason for the increase in energy lowering is the

TABLE IX. Energy lowerings per heavy-atom due to addition of second-order polarization functions (kcal mol$^{-1}$).

| Atom | Molecule | Energy lowering[a] |
|---|---|---|
| Na– | NaH | 0.9 |
| –Mg– | $MgH_2$ | 4.1 |
| Al (tetrahedral) | $AlH_3$ | 20.0 |
| Si (tetrahedral) | $SiH_4$ | 32.4 |
|  | $Si_2H_6$ | 28.4 |
| P (pyramidal) | $PH_3$ | 32.6 |
|  | $P_2H_4$ | 30.8 |
| P≡ | $P_2$ | 23.0 |
| S (bent) | $H_2S$ | 25.5 |
|  | $H_2S_2$ | 27.1 |
| Cl– | $Cl_2$ | 25.8 |
|  | HCl | 14.6 |

[a]$E$(6–31G*//6–31G*)–$E$(6–31G //6–31G).

fact that the valence $3s$, $3p$ functions on second-row elements are more diffuse and hence more polarizable than those $(2s, 2p)$ functions on first-row elements.

Total energies calculated using the 6-31G** basis, in which $p$-type functions have been added to the 6-31G* representation of hydrogen, are lower than their corresponding 6-31G* energies by anywhere from 0.1 to 4 kcal mol$^{-1}$ per hydrogen atom. The lowerings for the one-heavy-atom hydrides are summarized in Table X. The changes in energy are most significant for molecules such as HCl and $PH_3$ in which the $\pi_p$ character of the bonding interactions between the central atom and hydrogen may be enhanced. The energies of molecules with highly polar bonds are also significantly affected by the

TABLE X. Energy lowerings per hydrogen atom due to addition of $p$-functions (kcal mol$^{-1}$).

| Bond | Molecule | Energy lowering |
|---|---|---|
| Na–H | NaH | 0.1 |
| Mg–H | $MgH_2$ | 0.4 |
| Al–H | $AlH_3$ | 0.9 |
| Si–H | $SiH_4$ | 1.3 |
| P–H | $PH_3$ | 1.3 |
| S–H | $H_2S$ | 2.4 |
| Cl–H | HCl | 3.9 |

TABLE XI. Hydrogenation energies for two heavy-atom hydrides (kcal mol$^{-1}$).

| | 3-21G // 3-21G | 6-31G* //6-31G* | 6-31G** // 6-31G* | Exptl.[a] |
|---|---|---|---|---|
| LiCl + H$_2$ → LiH + HCl | 72 | 60 | 58 | 60 ± 3 |
| CH$_3$SiH$_3$[d,e] + H$_2$ → CH$_4$ + SiH$_4$ | −11 | −13 | −12 | −8 |
| HCP + 3H$_2$ → CH$_4$ + PH$_3$ | −89 | −99 | −97 | −68 ± 15 |
| H$_2$CPH + 2H$_2$ → CH$_4$ + PH$_3$ | −59 | −64 | −63 | ··· |
| CH$_3$PH$_2$ + H$_2$ → CH$_4$ + PH$_3$ | −16 | −19 | −19 | ··· |
| CS + 3H$_2$ → CH$_4$ + H$_2$S | −119 | −111 | −112 | −100 |
| H$_2$CS[c,e] + 2H$_2$ → CH$_4$ + H$_2$S | −62 | −64 | −65 | −54 |
| CH$_3$SH[d,e] + H$_2$ → CH$_4$ + H$_2$S | −20 | −22 | −23 | −16 |
| CH$_3$Cl + H$_2$ → CH$_4$ + HCl | −21 | −22 | −24 | −21 |
| PN + 3H$_2$ → PH$_3$ + NH$_3$ | −78 | −79 | −82 | −45 |
| HPO + 2H$_2$ → PH$_3$ + H$_2$O | −58 | −50 | −55 | ··· |
| HOCl + H$_2$ → H$_2$O + HCl | −54 | −64 | −69 | −61 ± 3 |
| NaOH + H$_2$ → NaH + H$_2$O | 16 | 10 | 9 | 21 ± 7 |
| MgO + 2H$_2$ → MgH$_2$ + H$_2$O | ··· | −93 | −96 | ··· |
| SiO + 3H$_2$ → SiH$_4$ + H$_2$O | −37 | −48 | −51 | −34 ± 3 |
| NaF + H$_2$ → NaH + HF | 30 | 33 | 31 | 34 ± 5 |
| SiH$_3$F + H$_2$ → SiH$_4$ + HF | 31 | 30 | 26 | 46 ± 15 |
| ClF + H$_2$ → HCl + HF | −63 | −73 | −80 | −78 |
| Na$_2$ + H$_2$ → NaH + NaH | 44 | 40 | 42 | 30 ± 10 |
| NaCl + H$_2$ → NaH + HCl | 73 | 60 | 58 | 52 ± 5 |
| Si$_2$H$_6$[b,e] + H$_2$ → SiH$_4$ + SiH$_4$ | −8 | −12 | −11 | −3 |
| SiH$_3$Cl + H$_2$ → SiH$_4$ + HCl | 15 | 16 | 13 | 33 ± 15 |
| P$_2$ + 3H$_2$ → PH$_3$ + PH$_3$ | −40 | −57 | −56 | −46 |
| P$_2$H$_4$[d,e] + H$_2$ → PH$_3$ + PH$_3$ | −8 | −11 | −10 | −5 |
| H$_2$S$_2$[d,e] + H$_2$ → H$_2$S + H$_2$S | −19 | −21 | −23 | −14 |
| Cl$_2$ + H$_2$ → HCl + HCl | −45 | −50 | −55 | −45 |

[a]All experimental thermochemical data and vibrational frequencies from reference given in Table IV footnote a unless otherwise noted.
[b]Experimental vibrational frequencies from: L. M. Sverdlov, M. A. Kovner, and E. P. Krainov, Vibrational Spectra of Polyatomic Molecules (Wiley, New York, 1974).
[c]Frequencies calculated using ab initio methods at the 3-21G level (Ref. 19).
[d]See footnote b Table VII for reference to experimental vibrational frequencies.
[e]Experimental thermochemical data from S. W. Benson, Thermochemical Kinetics (Wiley, New York, 1976).

addition of $p$ functions to hydrogen. Compared to the lowerings noted for the corresponding first-row hydrides[7] (e.g., 1.0 kcal mol$^{-1}$ for a CH bond in methane, 5.3 kcal mol$^{-1}$ for the linkage in hydrogen fluoride), the values here are small, and do not extend over as wide a range. These differences may be due to decreased polarity of the bonds between hydrogen and second-row elements relative to those for the analogous first-row compounds.

For each of the two-heavy atom hydrides in Table V, a simple hydrogenation reaction may be written. This set of reactions is shown in Table XI along with heats of reaction obtained from experimental data, where available, and from calculations using the 3-21G, 6-31G*, and 6-31G** basis sets. The experimental data have

been corrected to 0 °K and for zero-point vibrational energy.[19] Experimental uncertainties are ±1 kcal mol$^{-1}$ unless otherwise noted.

It is known that Hartree–Fock theory generally gives a poor description of the energies of reactions which result in bond cleavage. Here, electron correlation effects play a significant role. Hydrogenation reactions in which bonds between heavy atoms are severed, and new linkages to hydrogen are formed would, therefore, not be expected to be uniformly well described by a single-determinant model. The tabulated data concur. While calculated hydrogenation energies for singly bonded systems are reasonably close to experimental enthalpies (differing at most by 20 kcal mol$^{-1}$ and often within the experimental error limits), those for mole-

TABLE XII. Hydrogenation energies of hypervalent molecules (kcal mol$^{-1}$).

| | 3-21G // 3-21G | 6-31G* // 6-31G* | 6-31G** // 6-31G* | Exptl.[a] |
|---|---|---|---|---|
| $PF_5 + 4H_2 \rightarrow PH_3 + 5HF$ | 47 | 60 | 40 | 45 |
| $F_3PO + 4H_2 \rightarrow PH_3 + H_2O + 3HF$ | 5 | 43 | 26 | $34 \pm 2$ |
| $F_3PS + 4H_2 \rightarrow PH_3 + H_2S + 3HF$ | 2 | 10 | 14 | $32 \pm 15$ |
| $SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$ | −149 | −87 | −100 | −60 |
| $SF_4 + 3H_2 \rightarrow H_2S + 4HF$ | −126 | −97 | −116 | $−89 \pm 5$ |
| $F_2SO + 3H_2 \rightarrow H_2S + H_2O + 2HF$ | −120 | −75 | −91 | $−71 \pm 5$ |
| $NSF + 3H_2 \rightarrow NH_3 + H_2S + HF$ | −136 | −109 | −118 | $\cdots$ |
| $SO_3 + 4H_2 \rightarrow H_2S + 3H_2O$ | −233 | −132 | −150 | −97 |
| $F_4SO + 4H_2 \rightarrow H_2S + H_2O + 4HF$ | −210 | −135 | −159 | $\cdots$ |
| $ClF_3 + 2H_2 \rightarrow HCl + 3HF$ | −288 | −207 | −222 | −184 |
| $ClF_5 + 3H_2 \rightarrow HCl + 5HF$ | −405 | −348 | −371 | $−298 \pm 15$ |
| $FClO_2 + 3H_2 \rightarrow HCl + HF + 2H_2O$ | −304 | −259 | −276 | $\cdots$ |
| $FClO_3 + 4H_2 \rightarrow HCl + HF + 3H_2O$ | −426 | −340 | −363 | −269 |

[a]See footnote a Table IV for reference to experimental thermochemical data and vibrational frequencies.

cules incorporating multiple bonds are quite poor, in error by as much as 60 kcal mol$^{-1}$.

Energies of complete hydrogenation of hypervalent compounds are given in Table XII. Here values calculated using the 6-31G* and 6-31G** basis sets are considerably closer to experimental values than those obtained at the 3-21G level. This observation differs from that made for the normal-valent two-heavy-atom hydrides (where the overall performance of the three basis sets was similar) and is consistent with the notion that $d$-type functions are required for the proper description of the bonding in such compounds. Even at the 6-31G* and 6-31G** levels calculated hydrogenation energies are in error by as much as 60 kcal mol$^{-1}$. Here too, theoretical models which account in part for electron correlation effects should fare considerably better.

It is apparent from the previous discussion that hydrogenation energies calculated within the framework of single-determinant Hartree–Fock theory are subject to considerable error. While the total number of electron pairs is conserved in the hydrogenation process, drastic changes occur in the makeup of those bonding pairs. For example, in the reaction of carbonyl sulfide with three hydrogen molecules to produce a molecule of methane and one of hydrogen sulfide, four CH and two SH linkages have been formed at the expense of the $\sigma$ and $\pi$ bonds previously connecting carbon and sulfur and

the three HH bonds. If the changes in bonding were less dramatic (i.e., the total number of bonds involving a given pair of elements maintained and only bond types interconverted) correlation effects might be less significant and reaction energies might be uniformly well described by simple Hartree–Fock models. The data in Table XIII suggest that formal reactions in which a molecule incorporating an unsaturated linkage is converted to the appropriate number of molecules each incorporating a single bond between the same pair of elements, do appear to be relatively well treated by single-determinant models. Even basis sets as simple as 3-21G describe to reasonable accuracy the energies of these processes which relate the stabilities of multiple and single bonds. The 6-31G* and 6-31G** representations fare even better, the largest deviation from experiment being only 8 kcal mol$^{-1}$, in both cases. Unfortunately, comparisons are limited due to a lack of experimental thermochemical data on unsaturated molecules with second-row elements. The level of success does, however, suggest the utility of the theory in providing accurate estimates of the thermochemistry of such compounds given only the corresponding data on saturated systems.

## CONCLUSION

The 6-31G* polarization basis set for first-row elements has been extended to the second-row. The inclu-

TABLE XIII. Calculated and experimental energies of reactions relating multiple and single bonds (kcal mol$^{-1}$).

| Reaction | 3-21G // 3-21G | 6-31G* // 6-31G* | 6-31G** // 6-31G* | Exptl. |
|---|---|---|---|---|
| $HC \equiv P + 2CH_4 + 2PH_3 \rightarrow 3CH_3PH_2$ | −42 | −42 | −41 | $\cdots$ |
| $C \equiv S + 2CH_4 + 2H_2S \rightarrow 3CH_3SH$ | −58 | −45 | −43 | −51 |
| $H_2C = S + CH_4 + H_2S \rightarrow 2CH_3SH$ | −22 | −20 | −20 | −21 |
| $P \equiv P + 4PH_3 \rightarrow 3PH_2PH_2$ | −22 | −25 | −25 | −33 |

sion of supplementary functions of $d$-symmetry allows for the proper description of bonding in molecules containing atoms with expanded valence manifolds. The work presented in this paper leads to the following conclusions.

(1) Equilibrium structures for both normal- and hypervalent molecules are in close acoord with available experimental values. The 6-31G* structures are considerably improved over the corresponding 3-21G structures, especially for hypervalent molecules.

(2) Normal-mode vibrational frequencies obtained using the 6-31G* representation, while larger by 10–15% than the corresponding experimental values, are much more consistent than those from 3-21G calculations. Errors in calculated frequencies for hypervalent molecules are comparable to those for normal-valent compounds.

(3) Hydrogenation energies at the 6-31G* level are in most cases closer to the experimental values than the corresponding 3-21G energies. Deviations are somewhat larger for hypervalent molecules than for normal-valent compounds.

While the 6-31G* basis set is relatively costly to apply, the resulting properties are of high quality. Prior experience with first-row compounds has shown that this basis set is among the smallest to which correlated methods may be applied. Hence, the extension of the 6-31G* and 6-31G** representations to the elements sodium through argon will provide a sound basis for correlated studies on compounds containing second-row elements.

[1](a) First-row: W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. 51, 2657 (1969); (b) Second-row: W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, ibid. 52, 2769 (1970); (c) Third-row, main group: W. J. Pietro, B. A. Levi, W. J. Hehre, and R. F. Stewart, Inorg. Chem. 19, 2225 (1980); (d) Fourth-row main group: W. J. Pietro, R. F. Hout, Jr., E. S. Blurock, W. J. Hehre, D. J. DeFrees, and R. F. Stewart, ibid. 20, 3650 (1981); (e) First- and second-row transition metals: W. J. Pietro and W. J. Hehre, Organometallics (submitted).

[2](a) First-row: J. S. Binkley, J. A. Pople, and W. J. Hehre, J. Am. Chem. Soc. 102, 939 (1980); (b) Second-row: M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, ibid. (to be published).

[3]For other contracted basis sets for second-row elements see: (a) A. D. McLean and G. S. Chandler, J. Chem. Phys. 72, 5639 (1980); (b) T. H. Dunning, Jr. and P. J. Hay, in Methods of Electronic Structure Theory, edited by H. F. Schaefer, III (Plenum, New York, 1977).

[4]See, for example: (a) D. J. DeFrees, B. A. Levi, S. K. Pollack, W. J. Hehre, J. S. Binkley, and J. A. Pople, J. Am. Chem. Soc. 101, 4085 (1979); (b) C. E. Dykstra and H. F. Schaefer, in The Chemistry of Ketenes and Allenes, edited by S. Patai (Wiley, New York).

[5]Such an approach has been utilized by Carlsen who obtained equilibrium geometries for a number of polyatomic molecules in excellent agreement with those derived from near-limiting Hartree–Fock procedures simply by using the 4-31G split-valence basis set (Ref. 5) supplemented by a single set of Gaussian $s$- and $p$-type functions placed along chemical bonds. N. R. Carlsen, Chem. Phys. Lett. 51, 192 (1977).

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[12]T. H. Dunning, Jr. and P. J. Hay in Methods of Electronic Structure Theory, edited by H. F. Schaefer III (Plenum, New York, 1977), Vol. 4, p. 1.

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[17]R. F. Hout, Jr., B. A. Levi, and W. J. Hehre, J. Am. Chem. Soc. (to be published).

[18]J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. DeFrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout, Jr. and W. J. Hehre, Int. J. Quant. Chem. (in press).

[19]Heats of formation were corrected to 0 K using $\Delta H(0)$ = $\Delta H(298) - (H_{298} - H_0)_{\text{compound}} + \sum (H_{298} - H_0)_{\text{elements}}$, where the corrections $H_{298} - H_0$ can be calculated from statistical mechanics. In practice, when correcting heats of reaction, it is not necessary to calculate the corrections for the elements which are involved as the contributions from each side of the reaction will cancel. Assuming a rigid-rotor/harmonic oscillator model, at temperatures high enough that the rotation may be treated classically, $H_{298} - H_0$ is given as

$$H(T) - H_0^0 = \tfrac{3}{2}RT + \tfrac{3}{2}RT + \left\{ \sum_{j=1}^{3N-6} \theta_{\nu j} R / [\exp(\theta_{\nu j}/T) - 1] \right\} + RT \; ,$$

for a nonlinear molecule, and as

$$H(T) - H_0^0 = RT + \tfrac{3}{2}RT + \left\{ \sum_{j=1}^{3N-5} \theta_{\nu j} R / [\exp(\theta_{\nu j}/T) - 1] \right\} + RT$$

for a linear molecule. These equations are valid for nearly all cases. The major exception is $H_2$, for which a nonclassical treatment of the rotation is required even at fairly high temperatures; the resulting value of the correction $H_{298} - H_0$, is 2.024 kcal mol$^{-1}$. Where available, experimental frequencies were used; in cases where they were not, frequencies were obtained theoretically from 3-21G level calculations. On the average such frequencies are larger than their corresponding experimental values by 11%. Therefore all calculated frequencies were scaled by 0.89 before use.

The heats of formation were also corrected for the zero point energy of vibration $E_{\text{zero point}} = \tfrac{1}{2} \sum_{j=1}^{N} \theta_{\nu j} R$, where $N$ is the number of normal modes, $3N-6$ for nonlinear molecules, $3N-5$ for linear molecules. Normal modes which correspond to torsions or inversions and with frequencies less than 500 cm$^{-1}$ were treated as rotations. For each such mode the vibrational component of the enthalpy correction is replaced by a rotational term $\tfrac{1}{2}RT$.