

# A systematic study of basis set effects in *ab initio* SCF calculations: Well-tempered GTF basis set calculations on transition metal halides

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Geometric structure and one-electron properties were calculated from the SCF wave functions of  $\text{ScF}_3$ ,  $\text{YF}_3$ ,  $\text{CuF}$ ,  $\text{AgF}$ ,  $\text{CuCl}$ , and  $\text{AgCl}$ . The large well-tempered Gaussian basis sets were used in the SCF calculations. The results thought to be approaching the near-Hartree-Fock quality were compared with results of previous calculations in which smaller basis sets were used. The comparison indicates that most of the information on these transition metal compounds, obtainable from near-Hartree-Fock calculations, may be reliably predicted using the smaller basis sets.

## I. INTRODUCTION

The truly unambiguous prescription for performing molecular calculations free of basis set truncation errors is using large basis sets.<sup>1</sup> With this idea in mind, a new family of high quality well-tempered Gaussian-type function (WT-GTF) basis sets, capable of producing near-Hartree-Fock atomic and molecular wave functions, was prepared for atoms Li through Hg.<sup>2,3</sup> The basis functions have well-spaced exponent values common for *s*, *p*, *d*, and *f* radial functions which were optimized in calculations on the atomic ground states.

The WT-GTF basis sets were used in SCF studies of a set of excited electronic configurations of transition metal atoms<sup>4</sup> and on the ground states of  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{Na}_2$ , and  $\text{P}_2$ ,<sup>2</sup> followed by MC-SCF studies on  $\text{N}_2$  and  $\text{P}_2$ .<sup>5</sup> In these test calculations the quality of the SCF results was approaching near-Hartree-Fock accuracy.

In the present study, the SCF calculations were performed on the ground states of halides containing first and second row transition metal atoms ( $\text{ScF}_3$ ,  $\text{YF}_3$ ,  $\text{CuF}$ ,  $\text{AgF}$ ,  $\text{CuCl}$ , and  $\text{AgCl}$ ), using the WT-GTF basis sets. Presented are computed data on the equilibrium geometries, dissociation energies, and some one-electron properties. Since the basis set truncation errors in these calculations are expected to be very small, we use them as a high quality reference to which we compare the results of previous calculations<sup>6</sup> performed using smaller Gaussian basis sets. As a result, we draw very encouraging conclusions on the quality of the

smaller bases. (The molecular SCF calculations were performed with the SPDFG program package.<sup>7</sup> The six components of the Cartesian *d*-type functions were used in all calculations. The one-electron properties were calculated using the POLYATOM code.<sup>8</sup>)

## II. CONTRACTION SCHEME FOR MOLECULAR CALCULATIONS

In order to reduce the computer time required for molecular calculations and to obtain a contraction scheme which leads to molecular results that are stable with respect to the basis set, we studied the performance of different contraction patterns derived from Raffennetti's general contraction scheme.<sup>9</sup> These pilot SCF calculations were performed for the ground state of  $\text{CuF}$  molecule at  $r(\text{Cu-F}) = 3.5$  a.u.

The different contraction patterns designed (*P* to *W*) are displayed in Fig. 1. A solid vertical line connects all basis functions that form one contracted function. The symbol \* represents an uncontracted function from the original WT set. The symbol + represents a function (whose exponent is taken from the exponent pool) which is added to the block. Let us take as an example the contraction pattern *P*. The WT atomic basis sets are  $\text{Cu}-(20/12/9)^3$  and  $\text{F}-(14/9)^2$ . From Fig. 1, the resulting basis set *P* for molecular calculations may be written as

$$\text{Cu}[(1-16)_{1s}(1-16)_{2s}(1-16)_{3s}(1-16)_{4s}(17)(18)(19)(20)/(5-15)_{2p}(5-15)_{3p}(16)/(9-15)_{3d}(16)(17)], \\ \text{F}[(1-10)_{1s}(1-10)_{2s}(11)(12)(13)(14)/(6-10)_{2p}(11)(12)(13)(14)/(11)(12)(13)],$$

or  $\text{Cu}-[8/3/3]$ ,  $\text{F}-[6/5/3*]$ . (When going from the left to the right of Fig. 1, namely from *P* to *W*, the contraction scheme is specified only if some change is introduced. Thus, the bases *S* to *V* have the same contraction in the *s* block as the basis *R*.)

The contraction pattern *P* is equivalent to the Raffennetti's general scheme<sup>9</sup> although the uncontracted functions (\*) are not duplicated in the contracted expansions.

The molecular basis set *Q* is obtained from *P* by deleting the innermost primitive functions in the expansions of the contracted *s* functions. A single contracted function made from the deleted functions is added instead. This results in virtually no loss in the quality of the total energy and other

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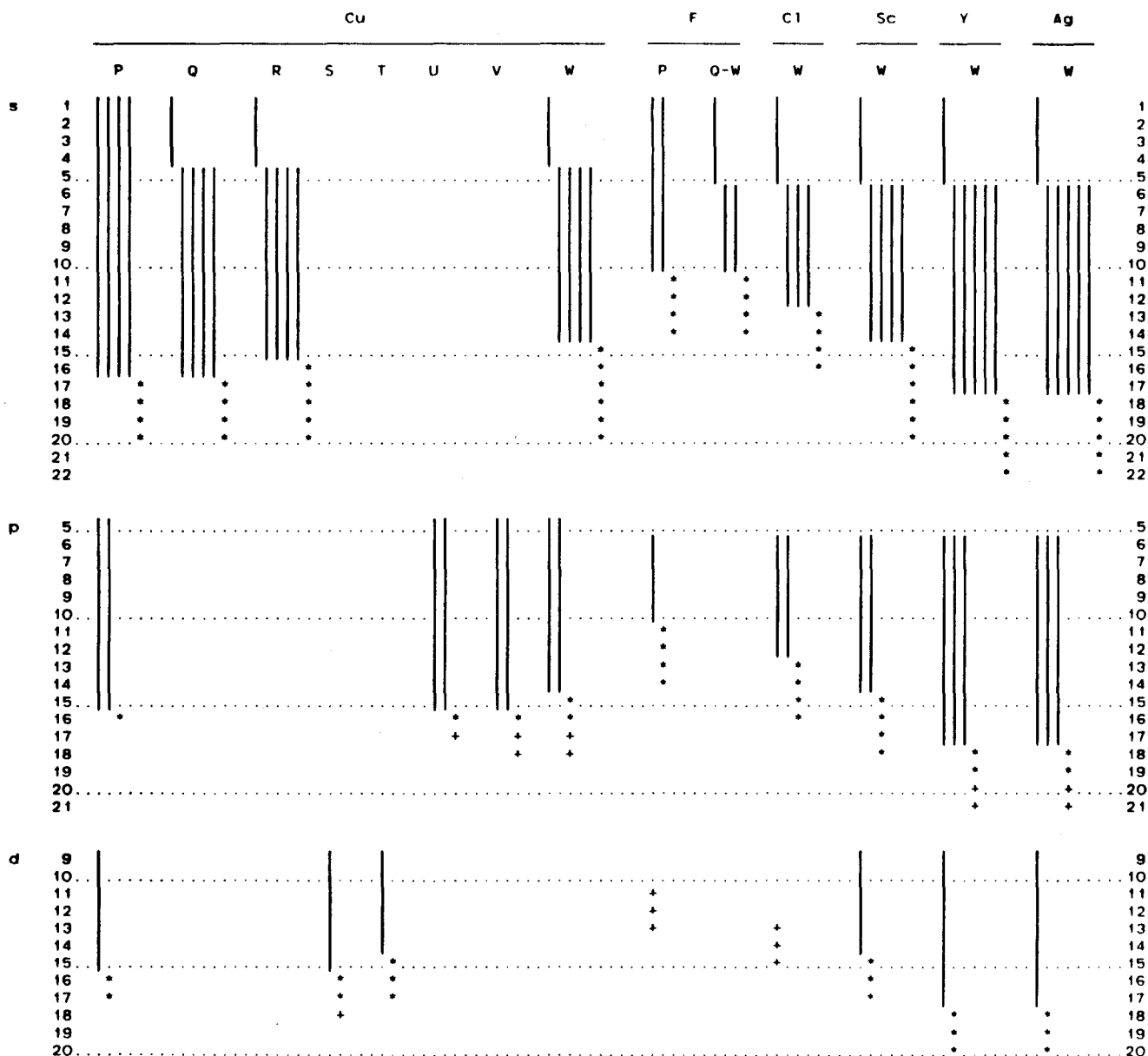


FIG. 1. Well-tempered basis sets for molecular calculations. A solid line connects all GTF that form one contracted function. The symbol \* represents a function in the original WT set that is released. The symbol + represents a function (whose exponent is taken from the exponent pool) that is added to the block.

properties listed in Table I, and shortens the time for computing the integrals over the contracted basis. Because of this, we take the *Q* rather than the *P* basis set as a starting point for further modifications.

The changes introduced in bases *R* to *W* affect only the basis set on the metal atom. Releasing the outermost (16th) GTF in the *s* contracted functions leads to basis set *R*. The small effects of this change in the results (Table I) show that saturation of the block has been accomplished. (Again, shorter expansions lead to savings in the integral evaluation.)

We have also studied the effects of improvements of the *d* block by adding one more function (*R* → *S*) or by releasing the outermost component (*R* → *T*). Both steps slightly improve the results. It is satisfactory to see that releasing the outermost function is more efficient (in terms of the total

energy and the computer time) than adding a more diffuse one to the original set.

The extension of the *p* block has a greater impact on the results (Table I). The addition of the first *p* function (*T* → *U*) results in a lowering of 0.001 82 hartree in the total energy. The second additional *p* function (*U* → *V*) brings about a further stabilization of 0.000 22 hartree which indicates that the *p* block is now almost saturated. The participation of the additional *p* functions in the valence SCF molecular orbitals also indicates the need for these polarization functions.

Finally, basis set *W* brings about further flexibility of the valence space. At this stage all properties have reached stable values. Therefore, we decided to use the *W*-like molecular basis sets in all the calculations. These basis sets are also depicted in Fig. 1.

TABLE I. CuF: energy and one-electron properties. Different contraction schemes for well-tempered basis sets.<sup>a</sup>

| Basis sets               |            |            |            |            |            |            |            |            |            |  |
|--------------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|--|
|                          | Expt       | P          | Q          | R          | S          | T          | U          | V          | W          |  |
| Total energy + 1738      |            | -0.457 590 | -0.457 589 | -0.457 613 | -0.457 636 | -0.457 667 | -0.459 489 | -0.459 710 | -0.459 799 |  |
| CPU time/s               |            | 3 300      | 1 940      | 1 647      | 1 874      | 1 672      | 1 790      | 1 898      | 1 734      |  |
| integrals                |            | 21.7       | 23.1       | 24.6       | 32.6       | 32.1       | 36.7       | 41.4       | 47.0       |  |
| iteration                |            | 3 590      | 2 650      | 2 420      | 2 900      | 2 610      | 2 870      | 3 110      | 3 120      |  |
| Dipole moment            | -5.77(0.2) | -7.098 9   | -7.098 6   | -7.097 5   | -7.092 2   | -7.095 5   | -6.904 6   | -6.884 3   | -6.884 3   |  |
| Second moment            |            | -15.495 9  | -15.489 9  | -15.490 4  | -15.495 3  | -15.491 5  | -15.516 4  | -15.554 7  | -15.553 7  |  |
| zz                       |            | -21.139 4  | -21.153 4  | -21.149 3  | -21.155 3  | -21.145 6  | -20.992 1  | -20.964 2  | -20.970 5  |  |
| Quadrupole moment        |            | -5.643 5   | -5.663 6   | -5.658 9   | -5.659 9   | -5.654 1   | -5.475 6   | -5.409 5   | -5.416 8   |  |
| Third moment             |            | -4.982 0   | -4.986 3   | -4.985 4   | -4.977 4   | -4.983 8   | -4.807 2   | -4.800 9   | -4.799 9   |  |
| zzx                      |            | -24.449 2  | -24.445 8  | -24.435 0  | -24.404 7  | -24.434 5  | -23.744 0  | -23.618 5  | -23.643 2  |  |
| zzz                      |            | -9.503 1   | -9.487 0   | -9.478 7   | -9.472 5   | -9.483 0   | -9.322 3   | -9.215 7   | -9.243 6   |  |
| Octupole moment          |            | 135.444 4  | 135.444 6  | 135.443 9  | 135.443 6  | 135.443 9  | 135.443 9  | 135.443 4  | 135.442 4  |  |
| Potential at Cu          |            | 26.769 97  | 26.770 1   | 26.770 07  | 26.769 98  | 26.769 99  | 26.765 55  | 26.764 37  | 26.764 3   |  |
| F                        |            | 0.102 18   | 0.102 28   | 0.102 17   | 0.102 10   | 0.092 69   | 0.093 60   | 0.093 49   | 0.092 63   |  |
| Electric field Cu        |            | 0.005 55   | 0.005 59   | 0.005 59   | 0.005 60   | 0.005 62   | 0.005 83   | 0.005 83   | 0.005 80   |  |
| F                        |            | 0.970 40   | 0.974 64   | 0.970 94   | 0.962 75   | 0.946 49   | 0.909 40   | 0.919 18   | 0.978 07   |  |
| Elec. field Grad. Cu     |            | -0.888 64  | -0.884 07  | -0.884 45  | -0.885 44  | -0.886 71  | -0.827 38  | -0.812 69  | -0.812 06  |  |
| F                        |            | 36.48      | 36.64      | 36.50      | 36.19      | 35.58      | 34.19      | 34.56      | 36.77      |  |
| NQCC <sup>c</sup> Cu-63  | 21.95(0.1) | 31.92      | 32.06      | 31.94      | 31.67      | 31.14      | 29.92      | 30.24      | 32.17      |  |
| Cu-65                    | 20.32(0.1) | 122.920    | 122.922    | 122.920    | 122.931    | 122.918    | 122.841    | 122.878    | 122.881    |  |
| $\langle r^2 \rangle$    |            | 16 462.1   | 16 462.3   | 16 462.1   | 16 462.1   | 16 462.0   | 16 462.0   | 16 462.0   | 16 462.0   |  |
| Charge density Cu        |            | 442.179    | 442.206    | 442.206    | 442.206    | 442.206    | 442.217    | 442.221    | 442.222    |  |
| F                        |            | 0.911      | 0.911      | 0.911      | 0.910      | 0.912      | 0.859      | 0.850      | 0.853      |  |
| Mulliken gross charge Cu |            | -0.068     | -0.070     | -0.071     | -0.069     | -0.072     | 0.021      | 0.031      | 0.029      |  |
| Overlap population       |            |            |            |            |            |            |            |            |            |  |

<sup>a</sup>All calculations correspond to  $r(\text{Cu-F}) = 3.5$  a.u. Total energies in hartree units, dipole moment in Debye, second and quadrupole moments in Buckingham, third and octupole moments in units of  $10^{-34}$  esu cm, all other properties in atomic units. Experimental values from Refs. 10 and 11.

<sup>b</sup> $\Theta(\text{zz}) = -2\Theta(\text{xx}) = -2\Theta(\text{yy})$ .

<sup>c</sup> $\Omega(\text{zz}) = -2\Omega(\text{xx}) = -2\Omega(\text{yy})$ .

<sup>d</sup> $q(\text{zz}) = -2q(\text{xx}) = -2q(\text{yy})$ .

<sup>e</sup>Nuclear quadrupole coupling constant,  $eqQ/h$  (MHz). The nuclear quadrupole moments were taken from Ref. 11.

TABLE II.  $R_e$ ,  $\bar{\nu}_e$ , and  $D_e$  for  $\text{ScF}_3$ ,  $\text{CuF}$ ,  $\text{CuCl}$ ,  $\text{YF}_3$ ,  $\text{AgF}$ , and  $\text{AgCl}$ . Well-tempered basis set  $W$ .

| Molecule       | $R_e$ (Å) |       | $\bar{\nu}_e$ ( $\text{cm}^{-1}$ ) |      | $D_e$ (eV) <sup>a</sup> |      |
|----------------|-----------|-------|------------------------------------|------|-------------------------|------|
|                | $W$       | Expt  | $W$                                | Expt | $W$                     | Expt |
| $\text{ScF}_3$ | 1.857     | 1.91  | 634                                | ...  | 14.73                   | ...  |
| $\text{CuF}$   | 1.827     | 1.745 | 561                                | 623  | 2.43                    | 4.42 |
| $\text{CuCl}$  | 2.182     | 2.051 | 353                                | 417  | 2.77                    | 3.93 |
| $\text{YF}_3$  | 2.017     | ...   | 579                                | ...  | 15.58                   | ...  |
| $\text{AgF}$   | 2.078     | 1.983 | 467                                | 513  | 2.06                    | 3.64 |
| $\text{AgCl}$  | 2.444     | 2.281 | 292                                | 343  | 2.52                    | 3.22 |

<sup>a</sup>The values for  $\text{ScF}_3$  and  $\text{YF}_3$  are not corrected for the zero-point energy. Experimental values from Refs. 12–14.

### III. RESULTS OF MOLECULAR CALCULATIONS

We have performed SCF calculations on the ground states of  $\text{ScF}_3$  ( $D_{3h}$ ),  $\text{YF}_3$  ( $D_{3h}$ ),  $\text{CuF}$ ,  $\text{AgF}$ ,  $\text{CuCl}$ , and  $\text{AgCl}$  using the well-tempered basis sets  $W$ . The results of these calculations are collected in Tables II to V and Figs. 2 to 8.

The values of the equilibrium metal–ligand distance obtained are in reasonable agreement with the experimental ones (see Table II, Fig. 2), with differences ranging between 3%–7% (0.05–0.16 Å), with the calculated values being larger than the experimental ones. This behavior coincides with that observed in calculations with extended basis sets.<sup>16</sup> An exception to this rule is found in  $\text{ScF}_3$ ; however, in this case the experimental measurement was not accurate.<sup>12</sup> The largest deviations from the experiment are found among the chlorine and silver compounds. These values would decrease if corrections beyond the HF level are considered. (The non-relativistic calculations on  $\text{AgH}$  and  $\text{Ag}_2$  by McLean<sup>17</sup> show a shortening of the Ag–H and Ag–Ag equilibrium distances of 0.07 Å as a consequence of the correlation corrections. A shortening of 4% in the Ag–H distance was found due to relativistic effects by Lee and McLean.<sup>18</sup>)

The totally symmetric vibrational frequencies are shown in Table II and Fig. 2. They compare satisfactorily with the experimental values, which are uniformly larger than the calculated ones.

The calculated values of the dissociation energy are 1–2 eV (20%–50%) smaller than the experimental data. It can be seen that our SCF results lead to an incorrect sequence of the dissociation energy in compounds sharing the same metal. Thus, the experimental sequence is  $\text{AgCl} < \text{AgF}$ ;  $\text{CuCl} < \text{CuF}$  and our calculations show the opposite trend:  $\text{AgCl} > \text{AgF}$ ;  $\text{CuCl} > \text{CuF}$ . Presumably the correct sequence could be attained beyond the Hartree–Fock level.

Finally, in Tables III to V and Figs. 4 to 8 we present the variation of some one-electron properties with the metal–ligand distance.

It seems that the use of the large and ( $s,p,d$ )-saturated WT-GTF basis sets<sup>2,3</sup> in combination with the contraction

pattern  $W$ , which ensures a wide flexibility of the molecular basis sets, guarantees that the molecular results presented here are approaching the near-Hartree–Fock accuracy. As commented below, we expect the effect of the  $f$ -type polarization functions to be small for these properties.

### IV. COMPARISON OF MOLECULAR RESULTS OBTAINED WITH THE WT AND SMALLER BASIS SETS

Recently a large family of Gaussian basis sets (GB) for molecular calculations was compiled.<sup>19</sup> Only the minimal basis sets were presented; however, more flexible basis sets may be obtained through splitting of the valence part, addition of suitable polarization functions, etc.

A systematic study of the use of the various minimal basis sets,<sup>6,20</sup> their split-valence versions, and extended sets with additional  $p$ -,  $d$ -, or  $f$ -type polarization functions<sup>6</sup> was conducted for the ground state of molecules containing transition metal atoms:  $\text{ScF}_3$ ,  $\text{TiCl}_4$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{Ni}(\text{CO})_4$ ,  $\text{CuF}$ ,  $\text{CuCl}$ ,  $\text{Zn}(\text{CH}_3)_2$ ,  $\text{ZrCl}_4$ , and  $\text{Cd}(\text{CH}_3)_2$ . These studies<sup>6,20</sup> aimed at establishing what level of refinement of the molecular basis set is necessary in order to produce reliable molecular results for the compounds and properties investigated.

Since the basis set truncation errors of the WT molecular results presented here are expected to be very small, we are now in a position to analyze the quality of the previous GB molecular calculations<sup>6</sup> by comparing them directly with the near-Hartree–Fock WT calculations.

The molecular results that we compare here are geometries, vibrational frequencies, dissociation energies, multipole moments, electric field gradients at the nuclei, and charge densities at the nuclei (Figs. 2 to 8). The molecules are  $\text{ScF}_3$ ,  $\text{CuF}$ ,  $\text{CuCl}$ , (Ref. 6) and  $\text{YF}_3$ ,  $\text{AgF}$ ,  $\text{AgCl}$  (this work). (For lucidity and compactness of the presentation we display the results in graphical form. The underlying numerical data are available from us upon request.)

The GB results used in the comparison are those corresponding to basis sets VII, IX, and X in Ref. 6. Though we use here the same nomenclature as in Ref. 6, it is convenient to recall the meaning of VII–X briefly:

| Name | F             | Cl              | Sc,Cu                   | Y,Ag                       |
|------|---------------|-----------------|-------------------------|----------------------------|
| VII  | (521/41)      | (5321/521)      | (53321/5211*1*/41)      | (433321/43211*1*/421)      |
| IX   | (521/41/1*1*) | (5321/521/1*1*) | (53321/5211*1*/41)      | (433321/43211*1*/421)      |
| X    | (521/41/1*1*) | (5321/521/1*1*) | (53321/5211*1*/41/1*1*) | (433321/43211*1*/421/1*1*) |

TABLE III. ScF<sub>3</sub>, YF<sub>3</sub>: energy and one-electron properties vs  $r(\text{Sc-F})$  or  $r(\text{Y-F})$ . Well-tempered basis set  $W^a$ .

|                                       | $r(\text{Sc-F})$ |            |            |            |            | $r(\text{Y-F})$ |            |            |  |  |
|---------------------------------------|------------------|------------|------------|------------|------------|-----------------|------------|------------|--|--|
|                                       | 3.3              | 3.4        | 3.5        | 3.6        | 3.7        | 3.8             | 3.9        | 4.0        |  |  |
| Total energy ( $A = 1058, B = 3630$ ) | -4.480 227       | -4.497 181 | -4.502 849 | -4.499 650 | -4.475 853 | -4.480 272      | -4.477 454 | -4.468 905 |  |  |
| Second moment $xx = yy$               | -38.612 5        | -39.661 1  | -40.743 9  | -41.860 9  | -48.926 4  | -50.177 6       | -51.465 2  | -52.788 9  |  |  |
| $zz$                                  | -24.367 5        | -24.500 6  | -24.625 8  | -24.743 6  | -29.646 5  | -29.743 1       | -29.835 5  | -29.923 5  |  |  |
| Quadrupole moment $zz^b$              | 14.245 0         | 15.160 4   | 16.118 1   | 17.117 3   | 19.279 9   | 20.434 5        | 21.629 7   | 22.865 4   |  |  |
| Third moment $xxx = -xyy$             | -10.306 7        | -11.303 5  | -12.387 1  | -13.560 8  | -16.232 0  | -17.679 6       | -19.232 7  | -20.894 5  |  |  |
| Octupole moment $xxx = -xyy$          | -25.766 8        | -28.258 7  | -30.967 7  | -33.902 0  | -40.580 1  | -44.199 0       | -48.081 9  | -52.236 2  |  |  |
| Potential at Sc/Y                     | 85.680 46        | 85.644 31  | 85.610 62  | 85.579 21  | 203.628 4  | 203.601 7       | 203.576 4  | 203.552 5  |  |  |
| F                                     | 26.640 31        | 26.639 65  | 26.639 65  | 26.640 22  | 26.662 33  | 26.662 93       | 26.663 99  | 26.665 43  |  |  |
| Electric field F x                    | 0.019 08         | 0.013 77   | 0.009 52   | 0.006 11   | 0.010 21   | 0.006 85        | 0.004 17   | 0.002 04   |  |  |
| Elec. field grad. Sc/Y $zz^c$         | -2.156 88        | -1.970 03  | -1.799 05  | -1.644 70  | -3.306 68  | -3.063 56       | -2.837 15  | -2.628 53  |  |  |
| F $xx^a$                              | 0.184 00         | 0.062 65   | -0.061 48  | -0.186 80  | 0.109 59   | 0.010 66        | -0.089 39  | -0.189 02  |  |  |
| $zz$                                  | -0.260 04        | -0.180 63  | -0.103 06  | -0.027 35  | -0.199 10  | -0.132 90       | -0.068 95  | -0.007 47  |  |  |
| $\langle r^2 \rangle$                 | 369.568          | 389.316    | 409.650    | 430.568    | 464.431    | 486.613         | 509.386    | 532.750    |  |  |
| Charge density Sc/Y                   | 6127.30          | 6127.24    | 6127.19    | 6127.14    | 40 916.0   | 40 915.9        | 40 915.9   | 40 915.8   |  |  |
| F                                     | 442.267          | 442.261    | 442.262    | 442.269    | 442.258    | 442.257         | 442.260    | 442.266    |  |  |
| Mulliken gross charge Sc/Y            | 2.408            | 2.412      | 2.414      | 2.415      | 2.520      | 2.514           | 2.509      | 2.505      |  |  |
| F                                     | -0.803           | -0.804     | -0.805     | -0.805     | -0.840     | -0.838          | -0.836     | -0.835     |  |  |
| Sc/Y-F bond overlap population        | -0.289           | -0.174     | -0.083     | -0.013     | -0.365     | -0.240          | -0.144     | -0.069     |  |  |

<sup>a</sup> Same units as in Table I.  $x, y$ , and  $z$  are the molecular axes: the molecule has  $D_{3h}$  symmetry, the  $C_3$  axis being  $z$ ; one F atom is on the  $x$  axis.<sup>b</sup>  $\Theta(zz) = -2\Theta(xx) = -2\Theta(yy)$ .<sup>c</sup>  $q(zz) = -2q(xx) = -2q(yy)$ .<sup>d</sup>  $q(zz) = -2[q(xx) + q(yy)]$ .

TABLE IV. CuF, AgF: energy and one-electron properties vs  $r(\text{Cu-F})$  or  $r(\text{Ag-F})$ . Well-tempered basis set  $W^a$ .

|                                       | Expt            | $r(\text{Cu-F})$ |            |            |            |            | $r(\text{Ag-F})$ |            |            |  |  |
|---------------------------------------|-----------------|------------------|------------|------------|------------|------------|------------------|------------|------------|--|--|
|                                       |                 | 3.3              | 3.4        | 3.5        | 3.6        | 3.8        | 3.9              | 4.0        | 4.1        |  |  |
| Total energy ( $A = 1738, B = 5297$ ) |                 | -4.457 637       | -4.459 719 | -4.459 799 | -4.458 362 | -B.176 760 | -B.177 904       | -B.177 622 | -B.176 250 |  |  |
| Dipole moment                         |                 |                  |            |            |            |            |                  |            |            |  |  |
|                                       | CuF: -5.77(0.2) | -6.369 9         | -6.625 5   | -6.884 3   | -7.146 7   | -7.523 9   | -7.811 1         | -8.099 4   | -8.388 0   |  |  |
|                                       | AgF: -6.22      |                  |            |            |            |            |                  |            |            |  |  |
| Second moment $xx = yy$               |                 | -15.644 3        | -15.592 9  | -15.553 7  | -15.524 0  | -22.743 8  | -22.708 9        | -22.678 9  | -22.652 2  |  |  |
| $zz$                                  |                 | -20.094 2        | -20.528 7  | -20.970 5  | -21.421 5  | -32.483 1  | -33.134 3        | -33.807 2  | -34.503 1  |  |  |
| Quad. moment $zz^b$                   |                 | -4.449 9         | -4.935 8   | -5.416 8   | -5.897 5   | -9.739 3   | -10.425 4        | -11.128 4  | -11.850 9  |  |  |
| Third moment $zxx = zyy$              |                 | -4.359 5         | -4.581 9   | -4.799 9   | -5.014 6   | -5.654 9   | -5.889 2         | -6.121 6   | -6.352 3   |  |  |
| $zzz$                                 |                 | -20.912 4        | -22.240 4  | -23.643 2  | -25.126 1  | -33.849 7  | -36.023 0        | -38.308 8  | -40.707 0  |  |  |
| Octupole moment $zzz^c$               |                 | -7.833 9         | -8.494 7   | -9.243 6   | -10.082 2  | -16.885 0  | -18.355 6        | -19.943 8  | -21.650 0  |  |  |
| Potential at Cu/Ag                    |                 | 135.450 4        | 135.446 7  | 135.442 4  | 135.437 8  | 263.480 3  | 263.475 4        | 263.470 5  | 263.465 7  |  |  |
| F                                     |                 | 26.754 31        | 26.759 37  | 26.764 3   | 26.769 13  | 26.785 97  | 26.790 31        | 26.794 65  | 26.798 99  |  |  |
| Electric field Cu/Ag $zz^d$           |                 | 0.097 33         | 0.095 14   | 0.092 63   | 0.089 90   | 0.096 96   | 0.093 70         | 0.090 49   | 0.087 35   |  |  |
| $F_z$                                 |                 | 0.011 66         | 0.008 37   | 0.005 80   | 0.003 79   | 0.007 23   | 0.005 01         | 0.003 29   | 0.001 96   |  |  |
| Elec. field grad. Cu/Ag $zz^d$        |                 | 1.104 91         | 1.043 69   | 0.978 07   | 0.911 73   | 2.008 02   | 1.842 38         | 1.691 59   | 1.554 54   |  |  |
| $F_{zz}$                              |                 | -0.737 07        | -0.775 87  | -0.812 06  | -0.843 46  | -0.667 76  | -0.689 69        | -0.707 57  | -0.722 92  |  |  |
| NQCC <sup>e</sup> Cu-63               | 21.95(0.1)      | 41.54            | 39.24      | 36.77      | 34.28      |            |                  |            |            |  |  |
| Cu-65                                 | 20.32(0.1)      | 36.35            | 34.33      | 32.17      | 29.99      |            |                  |            |            |  |  |
| $\langle r^2 \rangle$                 |                 | 113.020          | 117.870    | 122.881    | 128.050    | 167.145    | 173.399          | 179.827    | 186.429    |  |  |
| Charge density Cu/Ag                  |                 | 16 462.5         | 16 462.2   | 16 462.0   | 16 461.8   | 72 323.5   | 72 323.3         | 72 323.0   | 72 322.9   |  |  |
| F                                     |                 | 442.185          | 442.204    | 442.222    | 442.239    | 442.215    | 442.228          | 442.240    | 442.251    |  |  |
| Mulliken gross charge Cu/Ag           |                 | 0.868            | 0.860      | 0.853      | 0.848      | 0.880      | 0.875            | 0.871      | 0.869      |  |  |
| Overlap population                    |                 | -0.037           | -0.002     | 0.029      | 0.055      | -0.164     | -0.111           | -0.068     | -0.032     |  |  |

<sup>a</sup> Same units as in Table I. Experimental values from Refs. 10 and 14. Experimental values from Refs. 10 and 11.<sup>b</sup>  $\Theta(zz) = -2\Theta(xx) = -2\Theta(yy)$ .<sup>c</sup>  $\Omega(zzz) = -2\Omega(zxx) = -2\Omega(zyy)$ .<sup>d</sup>  $q(zz) = -2q(xx) = -2q(yy)$ .<sup>e</sup> Nuclear quadrupole coupling constant,  $Q/h$  (MHz). The nuclear quadrupole moments were taken from Ref. 11.

TABLE V. CuCl, AgCl: energy and one-electron properties vs  $r(\text{Cu-Cl})$  or  $r(\text{Ag-Cl})$ . Well-tempered basis set  $W^a$ .

|                                       | Expt                                     | $r(\text{Cu-Cl})$ |            |            |            |            | $r(\text{Ag-Cl})$ |            |            |  |  |
|---------------------------------------|--|-------------------|------------|------------|------------|------------|-------------------|------------|------------|--|--|
|                                       |  | 4.0               | 4.1        | 4.2        | 4.3        | 4.5        | 4.6               | 4.7        | 4.8        |  |  |
| Total energy ( $A = 2098, B = 5657$ ) |  | -4.542 723        | -4.543 580 | -4.543 308 | -4.542 138 | -B.265 599 | -B.266 245        | -B.266 005 | -B.265 053 |  |  |
| Dipole moment                         | AgCl: -5.70                              | -6.714 0          | -6.942 4   | -7.177 0   | -7.417 4   | -8.055 1   | -8.310 8          | -8.571 4   | -8.836 4   |  |  |
| Second moment $xx = yy$               |  | -24.834 4         | -24.827 6  | -24.823 9  | -24.822 8  | -32.158 3  | -32.144 2         | -32.133 1  | -32.124 8  |  |  |
| $zz$                                  |  | -24.648 0         | -24.860 0  | -25.085 8  | -25.324 8  | -37.945 0  | -38.436 0         | -38.948 2  | -39.480 9  |  |  |
| Quadrupole moment $zz^b$              |  | 0.186 4           | -0.032 4   | -0.261 9   | -0.502 0   | -5.786 7   | -6.291 9          | -6.815 1   | -7.356 1   |  |  |
| Third moment $zxx = zyy$              |  | -12.796 5         | -13.229 0  | -13.663 5  | -14.099 6  | -17.357 9  | -17.859 8         | -18.362 6  | -18.865 8  |  |  |
| $zzz$                                 |  | -42.793 4         | -44.489 5  | -46.258 1  | -48.101 2  | -63.062 7  | -65.654 7         | -68.359 5  | -71.178 1  |  |  |
| Octupole moment $zzz^c$               |  | -4.403 9          | -4.802 5   | -5.267 6   | -5.802 2   | -10.988 9  | -12.075 3         | -13.271 8  | -14.580 8  |  |  |
| Potential at Cu/Ag                    |  | 135.428 5         | 135.426 2  | 135.423 5  | 135.420    | 263.459 6  | 263.456 5         | 263.453 2  | 263.449 9  |  |  |
| Cl                                    |  | 64.504 19         | 64.506 49  | 64.508 84  | 64.511 24  | 64.523 21  | 64.525 61         | 64.528 04  | 64.530 50  |  |  |
| Electric field Cu/Ag $z$              |  | 0.072 64          | 0.072 48   | 0.071 91   | 0.071 03   | 0.077 93   | 0.076 38          | 0.074 70   | 0.072 92   |  |  |
| Cl $z$                                |  | 0.006 97          | 0.006 32   | 0.005 81   | 0.005 40   | 0.006 58   | 0.005 97          | 0.005 48   | 0.005 09   |  |  |
| Electric field grad. Cu/Ag $zz^d$     |  | 0.696 26          | 0.673 11   | 0.647 77   | 0.620 92   | 1.422 76   | 1.337 02          | 1.254 77   | 1.176 91   |  |  |
| Cl $zz$                               |  | -1.091 18         | -1.155 09  | -1.212 07  | -1.261 26  | -1.068 82  | -1.101 33         | -1.129 69  | -1.154 22  |  |  |
| NQCC <sup>e</sup> Cu-63               | 16.12(0.2)                               | 26.18             | 25.31      | 24.35      | 23.34      | -21.35     | -22.00            | -22.56     | -23.05     |  |  |
| Cl-35                                 | CuCl: -32.28(0.15)<br>AgCl: -36.50(0.10) | -21.79            | -23.07     | -24.21     | -25.19     |            |                   |            |            |  |  |
| $\langle r^2 \rangle$                 |  | 226.832           | 235.405    | 244.728    | 254.019    | 329.276    | 341.000           | 352.995    | 365.259    |  |  |
| Charge density Cu/Ag                  |  | 16 462.6          | 16 462.4   | 16 462.2   | 16 462.1   | 72 324.0   | 72 323.8          | 72 323.5   | 72 323.4   |  |  |
| Cl                                    |  | 3 189.57          | 3 189.58   | 3 189.60   | 3 189.62   | 3 189.6    | 3 189.60          | 3 189.61   | 3 189.62   |  |  |
| Mulliken gross charge Cu/Ag           |  | 0.673             | 0.671      | 0.670      | 0.671      | 0.731      | 0.730             | 0.730      | 0.731      |  |  |
| Overlap population                    |  | 0.350             | 0.355      | 0.358      | 0.360      | 0.210      | 0.226             | 0.238      | 0.248      |  |  |

<sup>a</sup> All units as in Table I. Experimental values from Refs. 10, 13, and 14.<sup>b</sup>  $\Theta(zz) = -2\Theta(xx) = -2\Theta(yy)$ .<sup>c</sup>  $\Omega(zzz) = -2\Omega(zxx) = -2\Omega(zyy)$ .<sup>d</sup>  $q(zz) = -2q(xx) = -2q(yy)$ .<sup>e</sup> Nuclear quadrupole coupling constant,  $Q/h$  (MHz). The nuclear quadrupole moments were taken from Ref. 11.

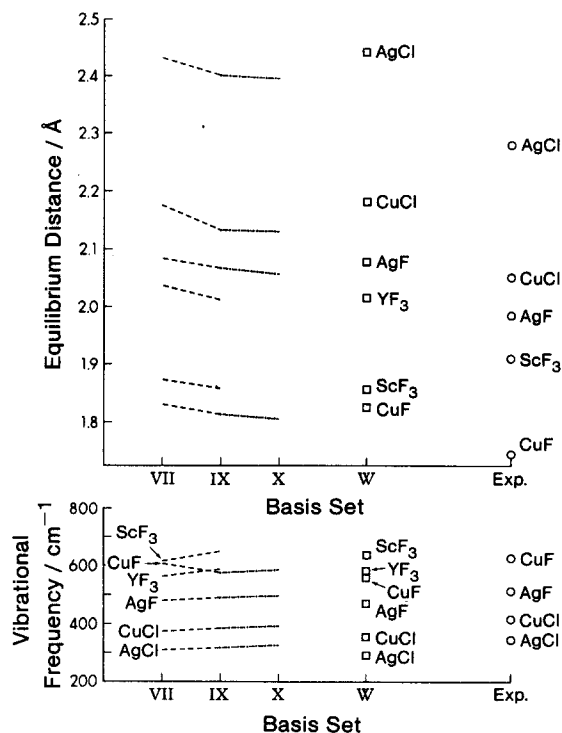


FIG. 2. Equilibrium distances (in angstroms) and totally symmetric vibrational frequencies (in  $\text{cm}^{-1}$ ).

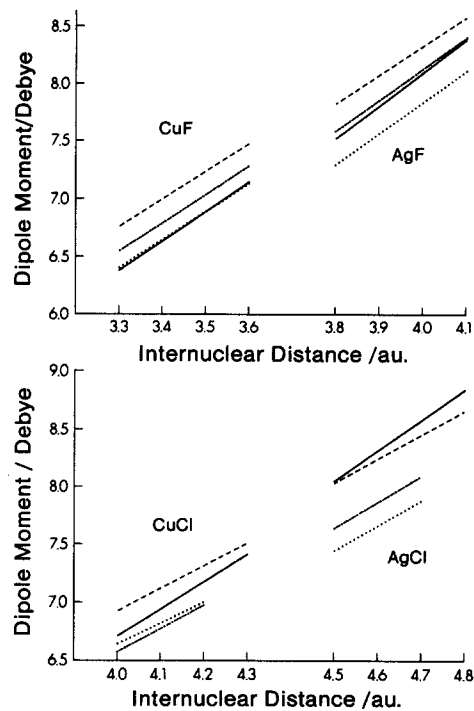


FIG. 4. Molecular dipole moments (in Debye). (---VII, ----IX, ...X, —W.)

Basis set IX is obtained from VII by addition of two  $d$ -type polarization functions on F and Cl. Addition of two  $f$ -type polarization functions to the transition metal atoms on set IX leads to set X.

It should be noticed that set IX is the only one among the GB sets which is equivalent to  $W$ , in the sense that both have the similar set of polarization functions.

#### A. Geometries, vibrational frequencies, and dissociation energies

The GB, WT, and experimental values of these proper-

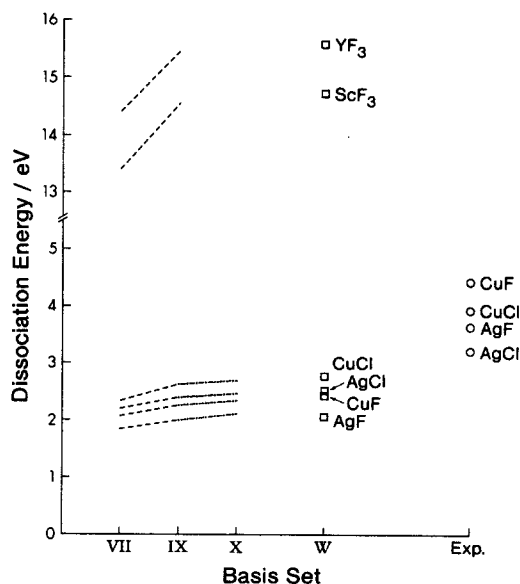


FIG. 3. Dissociation energies (in eV).

ties are plotted in Figs. 2 and 3.

The values of the equilibrium metal-ligand distances calculated with bases VII and IX differ from the  $W$  values by 0.00 to 0.05 Å. The values of the vibrational frequencies cal-

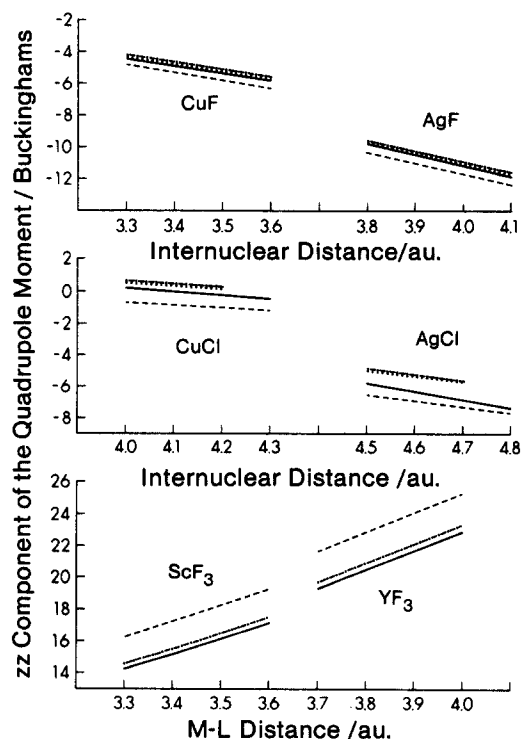


FIG. 5. Molecular quadrupole moments (in Buckingham) referred to the center of mass. The component along the principal symmetry axis is shown. (---VII, ----IX, ...X, —W.)



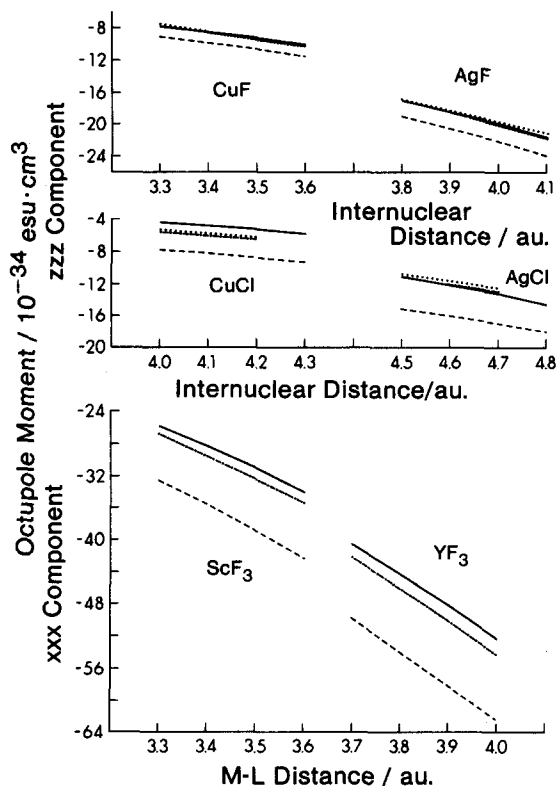


FIG. 6. Molecular octupole moments (in units of  $10^{-34}$  esu  $\text{cm}^3$ ) referred to the center of mass. The component along the metal-ligand axis is shown. (---VII, .....IX, ---X, —W.)

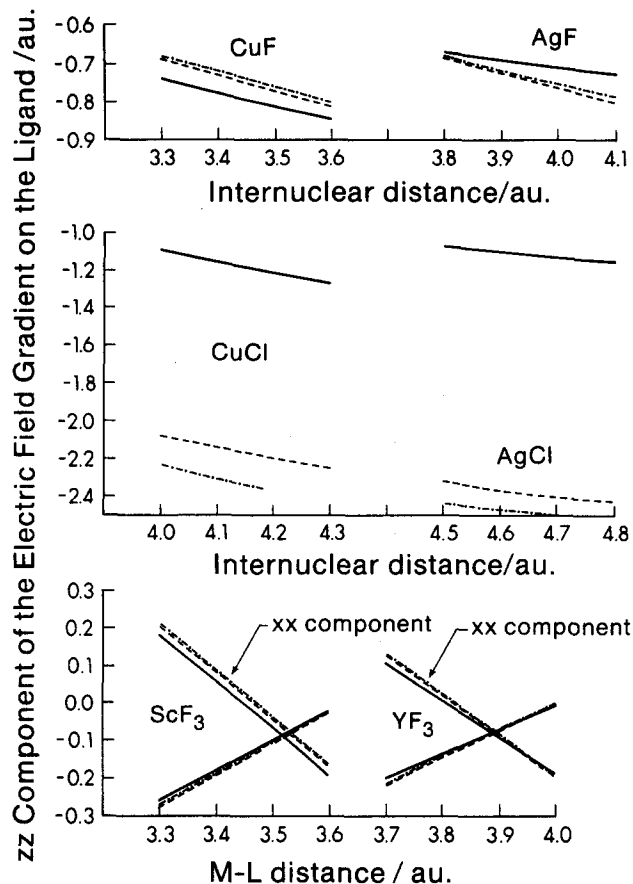


FIG. 8. Electric field gradient on the ligand (in a.u.). The component along the principal symmetry axis and along the Sc/Y-F axis are shown. (---VII, .....IX, —W.)

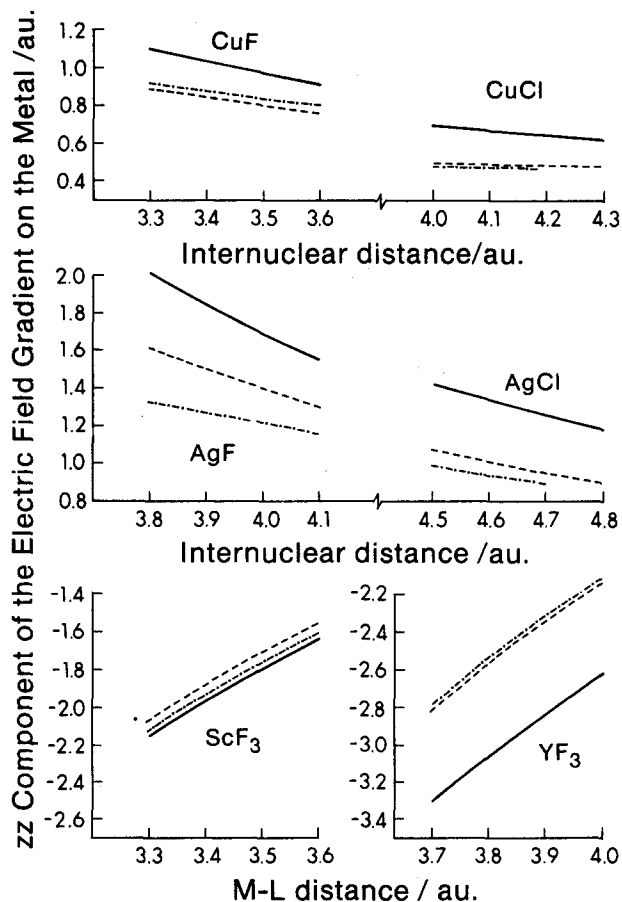


FIG. 7. Electric field gradient on the metal (in a.u.). The component along the principal symmetry axis is shown. (---VII, .....IX, —W.)

culated with bases VII and IX are also very close to the *W* ones. In CuF the inclusion of *d*-type polarization functions on the F basis set (basis IX) seems to be necessary in order to reproduce the sequence obtained at the *W* level. The values of the dissociation energies  $D_e$  improve steadily when going from basis VII through IX to *W*; for  $\text{ScF}_3$  and  $\text{YF}_3$ , the *d* polarization functions increase the value of  $D_e$  by more than 1 eV.

At this point, the high quality of the GB sets IX in predicting these properties becomes apparent; the effect of the *d* polarization functions on the ligand is, in general, small.

## B. One-electron properties

In Figs. 4 to 8 we show the GB and *W* results at different values of the metal-ligand distance.

### 1. Multipole moments

The results of the dipole moment in CuF, AgF, CuCl, and AgCl (Fig. 4) show that the GB results converge to the *W* limit only in the two fluorides. Nevertheless, the largest discrepancy, which occurs in AgCl, is of about 0.4 D ( $\approx 5\%$ ).

The quadrupole and octupole moments (Fig. 5 and 6) show a very good agreement (and convergence) between the

best GB result, IX, and the well tempered in the four diatomics and in  $\text{ScF}_3$  and  $\text{YF}_3$  as well. Again, the  $d$  polarization functions on the ligand are more important for  $\text{ScF}_3$  and  $\text{YF}_3$  than for the other molecules.

## 2. Electric field gradient at the nuclei

The values of the electric field gradient at the metallic site  $q(M)$  (Fig. 7) show that the GB results for the Cu and Sc compounds tend to and are very close to the  $W$  ones. However, the GB results on the Ag and Y compounds do not converge to the  $W$  ones and, furthermore, differ from the  $W$  values by 15%–35%.

The values of the electric field gradient at the fluorine atom (Fig. 8) are similar in IX and  $W$  basis sets. However, the values at the chlorine site are quite poor. Again, the GB results do not converge to the  $W$  ones and differ from the  $W$  values by 100%–120%. The discrepancies for the GB values of  $q(\text{Ag})$ ,  $q(\text{Y})$ , and  $q(\text{Cl})$  are analyzed below.

## 3. Charge density at the nuclei

The results of the best GB  $spd$  basis set IX, are still lower than the  $W$  ones. The discrepancies are always below 14%.

Finally, it can be seen that for all the molecules, the variation of the properties mentioned above with the metal–ligand distance is quite independent of the basis set and in many cases, the discrepancies GB– $W$  are smaller than the variation of the particular property with the internuclear distance.

## 4. Analysis of individual orbital contributions to the properties

In an attempt to ascertain the origin of the discrepancies mentioned above, we analyzed the individual molecular orbital contributions to the properties. We can group the properties as follows:

| Group | Properties                   | Main contribution                        |
|-------|------------------------------|--|
| 1     | charge density at the nuclei | 1s orbitals                              |
|       | $q(\text{metal})$            | inner core orbitals with $l$ nonzero     |
|       | $q(\text{ligand})$           | <i>idem</i> , plus valence contributions |
| 3     | multipole moments            | all                                      |

### Contribution

|        |  |
|--------|--|
| 2p     | $q(\text{Ag,IX-P}) - q(\text{Ag,IX})$    |
| 3p     | $q(\text{Ag,IX-PP}) - q(\text{Ag,IX-P})$ |
| 3d     | $q(\text{Ag,IX-PD}) - q(\text{Ag,IX-P})$ |
| total  |  |
| 2p3p3d | $q(\text{Ag,IX-PPD}) - q(\text{Ag,IX})$  |

(Note that the main contribution refers to MOs though it is expressed in terms of the prevailing atomic functions in the particular MO.)

A series of calculations were done in which some atomic contracted functions of basis set IX were improved by substituting them with the corresponding well-tempered atomic orbitals. These basis sets are shown in Table VI. The dots indicate that the corresponding function of basis IX is still used. The letters  $W$  indicate which contracted function of IX is replaced by the corresponding WT atomic orbital (or at least a large contracted function made up from the WT atomic orbital). As an example, basis set IX-S of AgCl means

$\text{Ag}[(1-18)_{\text{WT}} 33321/43211*1*/421],$

$\text{Cl}[(1-12)_{\text{WT}} 321/521/1*1*].$

The results obtained with the bases IX-S to IX-PPD inform about the effect of better representations of the inner-core atomic functions as shown in Table VI for AgCl at  $r(\text{Ag-Cl}) = 4.5$  a.u.

## 5. Calculation IX-S

The improvement of the 1s contracted functions reduces the discrepancies between the IX and  $W$  values of the charge densities at the nuclei from 14% to 0.6% for Ag and from 9% to 0.4% for Cl. Besides, the difference between the total energies is reduced by 70% (from 4.111 to 1.244 hartree). All other properties listed in Table VI remain virtually unchanged.

## 6. Calculations IX-P → IX-PPD

The results of these calculations corroborate the conclusions of the analysis in terms of individual orbital contributions commented above. It is shown that the electric field gradient on Ag,  $q(\text{Ag})$ , is very sensitive to improvements of the representation of the inner-core functions 2p, 3p, and 3d. It can be seen (Table VI) that the relative importance of the individual components is  $2p > 3d \approx 3p$ , and that their contributions are additive:

### Value (a.u.)

|       |
|-------|
| 0.202 |
| 0.082 |
| 0.108 |
| 0.391 |
| 0.392 |

Thus, upon the improvement of the basis set from IX to IX-PPD the discrepancy with the results of  $W$  basis set was reduced from 32% to 5%.

In analogous calculations, the improvement of the values of  $q(\text{Ag})$  for AgF and  $q(\text{Y})$  for  $\text{YF}_3$  (Table VII) shows that in order to calculate this property with high accuracy a

TABLE VI. AgCl: substitution of WT atomic functions in the basis set IX. Effects on the total energy and one-electron properties.  $r(\text{Ag-Cl}) = 4.5 \text{ a.u.}^a$ 

| Basis set                      | Ag |     |     |     | Cl  |    |     |     | Expt         | IX         | IX-S       | IX-P       | IX-PP      | IX-PD      | IX-PPD     | W          |
|--------------------------------|----|-----|-----|-----|-----|----|-----|-----|--------------|------------|------------|------------|------------|------------|------------|------------|
| IX                             | (4 | 3   | 3   | 2   | 1   | (5 | 3   | 2   |              |            |            |            |            |            |            |            |
| IX-S                           | (W | ... | ... | ... | ... | (W | ... | ... |              | (W         | ...        | ...        | ...        | ...        | ...        |            |
| IX-P                           | (. | ... | ... | ... | ... | (. | ... | ... |              | (.         | ...        | ...        | ...        | ...        | ...        |            |
| IX-PP                          | (. | ... | ... | ... | ... | (. | ... | ... |              | (.         | ...        | ...        | ...        | ...        | ...        |            |
| IX-PD                          | (. | ... | ... | ... | ... | (. | ... | ... |              | (.         | ...        | ...        | ...        | ...        | ...        |            |
| IX-PPD                         | (. | ... | ... | ... | ... | (. | ... | ... |              | (.         | ...        | ...        | ...        | ...        | ...        |            |
| Total energy + 5653            |    |     |     |     |     |    |     |     |              | -0.156 533 | -3.021 884 | -0.814 962 | -0.872 414 | -1.111 160 | -1.167 708 | -4.265 599 |
| Dipole moment                  |    |     |     |     |     |    |     |     | -5.70        | -7.640 5   | -7.637 0   | -7.661 3   | -7.658 5   | -7.669 0   | -7.666 1   | -8.055 1   |
| Quadrupole moment $zz^b$       |    |     |     |     |     |    |     |     |              | -4.825 5   | -4.820 3   | -4.864 8   | -4.862 1   | -4.875 3   | -4.872 6   | -5.786 7   |
| Octupole moment $zzz^c$        |    |     |     |     |     |    |     |     |              | -10.992 3  | -10.977 5  | -10.994 6  | -10.988 2  | -11.019 8  | -11.013 4  | -10.988 9  |
| Electric field grad. Ag $zz^d$ |    |     |     |     |     |    |     |     |              | 0.975 15   | 0.967 98   | 1.177 08   | 1.258 94   | 1.284 76   | 1.367 49   | 1.422 76   |
| Cl $zz$                        |    |     |     |     |     |    |     |     |              | -2.437 51  | -2.444 56  | -2.096 57  | -2.097 17  | -2.093 26  | -2.093 88  | -1.068 82  |
| NQCC <sup>e</sup> Cl-35        |    |     |     |     |     |    |     |     | -36.50(0.10) | -48.68     | -48.82     | -41.87     | -41.89     | -41.81     | -41.82     | -21.35     |
| Charge density Ag              |    |     |     |     |     |    |     |     |              | 62 086.1   | 72 745.7   | 62 085.4   | 62 083.8   | 62 017.2   | 62 015.4   | 72 324.0   |
| Cl                             |    |     |     |     |     |    |     |     |              | 2 912.90   | 3 202.78   | 2 912.94   | 2 912.94   | 2 912.94   | 2 912.94   | 3 189.60   |

<sup>a</sup> Same units as in Table I. Experimental values from Refs. 14 and 15.<sup>b</sup>  $\Theta(zz) = -2\Theta(xx) = -2\Theta(yy)$ .<sup>c</sup>  $\Omega(zzz) = -2\Omega(zzx) = -2\Omega(zyy)$ .<sup>d</sup>  $q(zz) = -2q(xx) = -2q(yy)$ .<sup>e</sup> Nuclear quadrupole coupling constant,  $Q/h$  (MHz). The nuclear quadrupole moments were taken from Ref. 11.

TABLE VII. Electric field gradient at the nuclei (a.u.).

| $r(M-L)/(a.u.)$ |     |                | IX         | IX-core WT <sup>a</sup> | $W$        | XI <sup>b</sup> |
|-----------------|-----|----------------|------------|-------------------------|------------|-----------------|
| CuCl            | 4.0 | Cu             | 0.476 25   | 0.495 75                | 0.696 26   |                 |
|                 |     | Cl             | - 2.238 34 | - 1.880 71              | - 1.091 18 |                 |
| AgF             | 3.8 | Ag             | 1.322 16   | 1.985 42                | 2.008 02   |                 |
|                 |     | F              | - 0.678 10 | - 0.675 36              | - 0.667 76 |                 |
| AgCl            | 4.5 | Ag             | 0.975 15   | 1.367 49                | 1.422 76   | 0.904 28        |
|                 |     | Cl             | - 2.437 51 | - 2.093 88              | - 1.068 82 | - 1.043 92      |
| YF <sub>3</sub> | 3.7 | Y( <i>zz</i> ) | - 2.831 88 | - 3.040 64              | - 3.306 68 |                 |
|                 |     | F( <i>xx</i> ) | 0.131 69   | 0.132 85                | 0.109 59   |                 |
|                 |     | ( <i>zz</i> )  | - 0.209 14 | - 0.209 94              | - 0.199 10 |                 |

<sup>a</sup> Basis sets: CuCl IX-*P*, AgF IX-*PPD*, AgCl IX-*PPD*, YF<sub>3</sub> IX-*PPD*.

<sup>b</sup> Basis XI differs from basis IX in the chlorine basis set, which was obtained from the (432/42) in Ref. 19: (4311/411/1\*1\*). The tabulated data on the diatomics correspond to the component along the bond axis.

good representation of the inner-core functions in the basis sets of the *4d* elements is required. It is also seen in Table VII that improvement of the *2p* function on Cu is not even necessary.

It should be noticed that all properties other than the electric field gradients at the nuclei remain virtually unchanged.

The electric field gradient on the Cl,  $q(\text{Cl})$ , in AgCl calculated using the IX-*P* basis shows (Table VI) that the initial discrepancy between results IX and  $W$  can be reduced by 25% if the contracted function representing the *2p* orbital of Cl is improved. (The same result is observed in the IX-*P* calculation on CuCl shown in Table VII.) The calculations IX-*PP*, IX-*PD*, and IX-*PPD* show that the value of  $q(\text{Cl})$  is independent of the changes of the inner-core functions of Ag.

The remaining discrepancy [which is greater than that observed for  $q(M)$  values] suggests that the GB valence basis functions used for Ag and Cl (see Sec. IV) may be slightly unbalanced. It is suspected that the quality of the Cl valence basis set is significantly superior to the quality of the Ag valence basis set. An additional calculation on AgCl at  $r(\text{Ag-Cl}) = 4.5$  a.u. was designed to elucidate the problem. Basis set IX was used for Ag and the poorer basis set (432/42),<sup>19</sup> split and augmented with two *d* polarization functions as in the original basis IX, (4311/411/1\*1\*), was used for chlorine. (The new basis set is called XI in Table VII.) This combination of atomic bases was chosen according to the criterion that both give similar errors of the energy of the valence atomic orbitals relative to the HF solutions.<sup>19</sup> The results of the calculation show virtually no change of the values of all the properties, except the value of the electric field gradient on the chlorine which is now  $-1.0439$  a.u. (Table VII), very different from the  $q(\text{Cl}, \text{IX}) = -2.4375$  a.u., but very close to the  $q(\text{Cl}, W) = -1.0688$  a.u. (The total energy in this calculation is  $-5652.781\ 82$  hartree.)

### C. Effects of *f*-type polarization functions

The similarity of the SCF wave functions obtained with GB basis set IX and the basis set  $W$  allows us to expect that

the effects of *f*-type polarization functions added to both bases would lead to similar changes, too. We have extended basis set IX to X by addition of two *f*-type polarization functions whose exponents have been taken from the WT pool; these two functions give the maximum overlap with the *d* valence atomic orbitals. The results obtained for the diatomics show a very small effect in most properties, as can be seen from Figs. 2 to 8. The effects of the *f*-type functions shown here are very similar to those found by McLean<sup>17</sup> for AgH at the SCF level. He found that the equilibrium Ag-H distance did not change (we find a change of 0.010 Å for AgF and 0.006 Å for AgCl), the dissociation energy increased by 0.115 eV (this work: 0.11 eV for AgF, 0.07 eV for AgCl), and the dipole moment calculated at the equilibrium distance changed by 0.29 D (this work: 0.29 D for AgF, 0.20 D for AgCl). Therefore, we can expect very small changes in the SCF results obtained with the  $W$  basis set upon addition of *f*-type functions. However, McLean<sup>17</sup> showed that a serious superposition error could appear in molecular CI calculations if the *f*-type functions were not included in the basis set of the metal, due to the important  $d \rightarrow f$  atomic excitations.

## V. CONCLUSIONS

The availability of the large well-tempered basis sets makes it possible to calculate very accurate molecular SCF wave functions which may be used in the analysis of smaller basis sets as tools for reliable prediction of molecular characteristics.

The results for the transition metal molecules studied here show that the GB basis sets, which are much smaller than the WT ones, can be used in the SCF calculation of geometries, vibrational frequencies, dissociation energies, and most of the one-electron properties, since reasonable deviations from extended basis sets calculations occur. However, if one is interested in the electric field gradient at the nuclei, the inner *p*-, and *d*-type contracted functions should be improved, and any imbalance, albeit small, should be avoided.

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