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6-31G* basis set for atoms K through Zn

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Medium basis sets based upon contractions of Gaussian primitives are developed for the third-row elements K through Zn. The basis functions generalize the 6-31G and 6-31G* sets commonly used for atoms up to Ar. They use six primitive Gaussians for $1s$, $2s$, $2p$, $3s$, and $3p$ orbitals, and a split-valence pair of three and one primitives for valence orbitals, which are $4s$ and $5p$ for atoms K and Ca, and $4s$, $4p$, and $3d$ for atoms Sc through Zn. A 6-31G* set is formed by adding a single set of Gaussian polarization functions to the 6-31G set. They are Cartesian d-functions for atoms K and Ca, and Cartesian f-functions for atoms Sc through Zn. Comparison with experimental data shows relatively good agreement with bond lengths and angles for representative vapor-phase metal complexes. © *1998 American Institute of Physics.* [S0021-9606(98)30428-6]

I. INTRODUCTION

Virtually all *ab initio* calculations of properties for molecules containing more than two atoms require Gaussian basis sets. The optimal basis set should be flexible enough to allow realistic calculation of the desired properties, should equally well describe all parts of the molecule to keep the calculation balanced, and at the same time it should be as small as possible, because the computational costs rise sharply with basis set size.

The series of split-valence basis sets $I-JK$G developed in recent years[1] has been quite successful in a variety of molecular calculations. In this notation, the integer I represents the degree of contraction (number of primitive Gaussians) for single functions representing the innershell atomic orbitals. The valence atomic orbitals are covered by inner and outer parts, with contractions J and K, respectively. The most popular of this series are the small 3-21G and moderate 6-31G sets. Both were originally defined for atoms up to argon. In 1987, the 3-21G set was extended to first-row transition metals by Dobbs and Hehre,[2] who also reviewed other such basis sets developed prior to that time. 6-31G, however, is only available for atoms up to argon.

In many molecular environments, the split-valence bases must be augmented by diffuse and polarization functions. The notation used is $I-JK+$G**, where + indicates diffuse functions on atoms with $Z>2$, the first * denotes a single uncontracted set of polarization functions with angular quantum number one higher than that of the highest occupied atomic orbital (again for $Z>2$), and the second * is used for a similar set of polarization functions on hydrogen and helium. Each basis set should be associated with corresponding diffuse and polarization parameters.

Schäfer, Horn, and Ahlrichs[3] designed a variety of basis sets for the first through third row atoms with split valence

sets comparable to 6-31G. They chose a {63311/53/41} structure for the atoms Sc–Zn. This designates five contractions in the s-space, with 6, 3, 3, 1, and 1 Gaussian primitives in each, two contractions in the p-space with 5 and 3 primitives, and 2 d-contractions with 4 and 1 primitives. They also designed larger double zeta and triple zeta[4] sets.

An alternative way to develop the basis set is based on choosing the set of primitives optimized in the uncontracted atomic calculations, and choosing contractions afterwards in a way that ensures wave function flexibility in the valence region. The most popular basis sets of this type are based on Wachters[5] primitives, which come from full optimized uncontracted calculations. This design, although being computationally much less expensive, does not result in fully optimized sets. This method is useful for very accurate calculations on small systems. Examples of use of such basis sets can be found in work by Bauschlicher and co-workers.[6] An alternative method to generate uncontracted primitive exponents is the generator coordinate method used by Jorge and da Silva for heavier elements.[7] It has few adjustable parameters and consequently leads to a very large set of not fully optimized primitives. Such methods can be useful in atomic and very small molecular calculations.

The goal of the present work is the extension of the 6-31G basis to the third row atoms K through Zn. Combined with the large volume of earlier work on molecules with lighter atoms using the same basis, this should increase the range of inorganic and organometallic chemistry that can be handled efficiently by modern quantum-mechanical methods.

II. COMPUTATIONAL METHODS

Before describing the methods used to fix basis parameters, we need to discuss valence atomic orbitals in the third row of the periodic table. The inner shells are $(1s,2s,2p,3s,3p)$, each represented by single 6-Gaussian contractions. For potassium and calcium, only $4s$ is occupied in the atomic ground states. However, as already known for lithium, beryllium, sodium, and magnesium, the valence p-orbitals play a major role in their chemistry, so we choose

TABLE I. Dependence of the optimized d_{4p} coefficients in vanadium on the external field strength in the UHF calculation.

Field (a.u.)	$d_{4p,1}$	$d_{4p,2}$	$d_{4p,3}$	E
0.03	−0.2539	0.0910	0.9843	−942.834 8287 7
0.04	−0.1973	0.0807	0.9877	−942.869 6123 4
0.045	−0.1891	0.0801	0.9877	−942.889 6631 6
0.05	−0.1887	0.0820	0.9870	−942.911 2516 2
0.055	−0.1943	0.0865	0.9856	−942.934 2195 6

to classify $4p$ as valence and define inner and outer parts for the 3 1 split, accordingly. Thus for K and Ca, the basis has a total of 17 functions. For the transition metals scandium to zinc, on the other hand, $3d$ orbitals are occupied in atomic ground states and these clearly have to be treated as valence orbitals. They are incorporated in the basis and represented by 3 1 split Gaussians as elsewhere.

An important point concerns the nature of the d-functions used. Strictly, there are five $3d$ atomic orbitals which should be split into a total of ten functions. However, a case can be made for using a ''Cartesian'' set based on six primitives $\{xx,yy,zz,xy,yz,zx\}\exp(-\alpha r^2)$. Although this step increases the number of basis functions by two, it has the advantage of simplifying coding (some distributed programs cannot handle pure d-Gaussians). Further it is consistent with the 3-21G basis of Dobbs and Hehre, and with the polarization functions of 6-31G* basis for the first- and second-row elements. Thus for the range Sc to Zn, the 6-31G basis will contain a total of 29 functions.

We note at this point that Schäfer, Horn, and Ahlrichs do not include any $4p$ functions in their split-valence basis for K–Zn.[3] While some valency can no doubt be described using only $4s$ and $3d$ functions, it seems likely that $4p$ functions are also needed, particularly for high coordination numbers. We therefore retain $4p$ functions for all atoms in the range K–Zn.

Our procedure for obtaining 6-31G parameters is similar to that used for second-row elements,[8,9] with a few differences. We have minimized the total energy of selected states, using the ATOM-SCF program,[10] modified by us to allow variation of exponents and contraction coefficients at the same time, and to use the modified Powell method of conjugate gradients.[11,12] This program uses spin-restricted open shell Hartree–Fock theory (ROHF), whereas spin-unrestricted theory (UHF) was used for lighter elements. There is no evidence that this has a significant effect on the final values. Further, the ATOM-SCF program uses pure d-functions (based on spherical harmonics). Thus our param-

TABLE II. The UHF energies of atoms K through Zn with UHF wave functions.

Atom	6-31G	6-31G*
K(^2S)	−599.119 027	−599.119 261
Ca(^1S)	−676.707 923	−676.708 039
Sc(^2D)	−759.674 203	−759.677 039
Ti(^3F)	−848.327 855	−848.333 176
V(^4F)	−942.787 478	−942.792 465
Cr(^5D)	−1043.191 917	−1043.194 561
Mn(^6S)	−1149.722 055	−1149.722 555
Fe(^5D)	−1262.266 962	−1262.269 260
Co(^4F)	−1381.197 761	−1381.201 473
Ni(^3F)	−1506.609 605	−1506.612 758
Cu(^2D)	−1638.639 638	1638.641 169
Zn(^1S)	−1777.482 753	−1777.483 106

TABLE III. 6-31G basis set for potassium.

α	d_s	d_p
3.159 442(4)	1.828 010(−3)	
4.744 330(3)	1.399 403(−2)	
1.080 419(3)	6.887 129(−2)	
3.042 338(2)	2.369 760(−1)	
9.724 586(1)	4.829 040(−1)	
3.302 495(1)	3.404 795(−1)	
6.227 625(2)	−2.502 976(−3)	4.094 637(−3)
1.478 839(2)	−3.315 550(−2)	3.145 199(−2)
4.732 735(1)	−1.226 387(−1)	1.351 558(−1)
1.751 495(1)	5.353 643(−2)	3.390 500(−1)
6.922 722	6.193 860(−1)	4.629 455(−1)
2.768 277	4.345 878(−1)	2.242 638(−1)
1.184 802(1)	1.277 689(−2)	−1.221 377(−2)
4.079 211	2.098 767(−1)	−6.900 537(−3)
1.763 481	−3.095 274(−3)	2.007 466(−1)
7.889 270(−1)	−5.593 884(−1)	4.281 332(−1)
3.503 870(−1)	−5.134 760(−1)	3.970 156(−1)
1.463 440(−1)	−6.598 035(−2)	1.104 718(−1)
7.168 010(−1)	−5.237 772(−2)	3.164 300(−2)
2.337 410(−1)	−2.798 503(−1)	−4.046 160(−2)
3.867 500(−2)	1.141 547	1.012 029
1.652 100(−2)	1.000 000	1.000 000

TABLE IV. 6-31G basis set for calcium.

α	d_s	d_p
3.526 486(4)	1.813 501(−3)	
5.295 503(3)	1.388 493(−2)	
1.206 020(3)	6.836 162(−2)	
3.396 839(2)	2.356 188(−1)	
1.086 264(2)	4.820 639(−1)	
3.692 103(1)	3.429 819(−1)	
7.063 096(2)	2.448 225(−3)	4.020 371(−3)
1.678 187(2)	3.241 504(−2)	3.100 601(−2)
5.382 558(1)	1.226 219(−1)	1.337 279(−1)
2.001 638(1)	−4.316 965(−2)	3.367 983(−1)
7.970 279	−6.126 995(−1)	4.631 281(−1)
3.212 059	−4.487 540(−1)	2.257 532(−1)
1.419 518(1)	1.084 500(−2)	−1.289 621(−2)
4.880 828	2.088 333(−1)	−1.025 198(−2)
2.160 390	3.150 338(−2)	1.959 781(−1)
9.878 990(−1)	−5.526 518(−1)	4.357 933(−1)
4.495 170(−1)	−5.437 997(−1)	3.996 452(−1)
1.873 870(−1)	−6.669 342(−2)	9.713 636(−2)
1.032 271	−4.439 720(−2)	−4.298 621(−1)
3.811 710(−1)	−3.284 563(−1)	6.935 829(−3)
6.513 100(−2)	1.163 010	9.705 933(−1)
2.601 000(−2)	1.000 000	1.000 000

TABLE V. 6-31G basis set for scandium.

α	d_s	d_p
3.908 898(4)	1.803 263(−3)	
5.869 792(3)	1.380 769(−2)	
1.336 910(3)	6.800 396(−2)	
3.766 031(2)	2.347 099(−1)	
1.204 679(2)	4.815 690(−1)	
4.098 032(1)	3.445 652(−1)	
7.862 852(2)	2.451 863(−3)	4.039 530(−3)
1.868 870(2)	3.259 579(−2)	3.122 570(−2)
6.000 935(1)	1.238 242(−1)	1.349 833(−1)
2.225 883(1)	−4.359 890(−2)	3.424 793(−1)
8.885 149	−6.177 181(−1)	4.623 113(−1)
3.609 211	−4.432 823(−1)	2.177 524(−1)
2.984 355(1)	−2.586 302(−3)	−6.096 652(−3)
9.542 383	7.188 424(−2)	−2.628 884(−2)
4.056 790	2.503 260(−1)	5.091 001(−2)
1.704 703	−2.991 003(−1)	3.798 097(−1)
7.062 340(−1)	−7.446 818(−1)	5.170 883(−1)
2.795 360(−1)	−1.799 776(−1)	1.829 772(−1)
1.065 609	6.482 978(−2)	−2.938 440(−1)
4.259 330(−1)	3.253 756(−1)	9.235 323(−2)
7.632 000(−2)	−1.170 806	9.847 930(−1)
2.959 400(−2)	1.000 000	1.000 000
α_d	d_d	
1.114 701(1)	8.747 672(−2)	
2.821 043	3.795 635(−1)	
8.196 200(−1)	7.180 393(−1)	
2.214 680(−1)	1.000 000	

TABLE VII. 6-31G basis set for vanadium.

α	d_s	d_p
4.735 433(4)	1.784 513(−3)	
7.110 787(3)	1.366 754(−2)	
1.619 591(3)	6.736 122(−2)	
4.563 379(2)	2.330 552(−1)	
1.460 606(2)	4.806 316(−1)	
4.975 791(1)	3.474 802(−1)	
9.681 484(2)	2.410 599(−3)	3.995 005(−3)
2.302 821(2)	3.207 243(−2)	3.104 061(−2)
7.414 591(1)	1.245 942(−1)	1.347 747(−1)
2.764 107(1)	−3.482 177(−2)	3.437 279(−1)
1.111 475(1)	−6.167 374(−1)	4.628 759(−1)
4.543 113	−4.509 844(−1)	2.135 547(−1)
3.764 050(1)	−3.233 199(−3)	−6.494 056(−3)
1.228 238(1)	7.130 744(−2)	−2.753 453(−2)
5.233 366	2.543 820(−1)	5.516 284(−2)
2.208 950	-2.933 887(−1)	3.879 672(−1)
9.178 800(−1)	−7.415 695(−1)	5.090 258(−1)
3.634 120(−1)	−1.909 410(−1)	1.803 840(−1)
1.392 781	6.139 703(−2)	−1.891 265(−1)
5.439 130(−1)	3.061 130(−1)	8.005 453(−2)
9.147 600(−2)	−1.154 890	9.877 399(−1)
3.431 200(−2)	1.000 000	1.000 000
α_d	d_d	
1.605 025(1)	8.599 899(−2)	
4.160 063	3.802 996(−1)	
1.243 265	7.127 659(−1)	
3.442 770(−1)	1.000 000	

TABLE VI. 6-31G basis set for titanium.

α	d_s	d_p
4.315 295(4)	1.791 872(−3)	
6.479 571(3)	1.372 392(−2)	
1.475 675(3)	6.762 830(−2)	
4.156 991(2)	2.33 7642(−1)	
1.330 006(2)	4.810 696(−1)	
4.527 222(1)	3.462 280(−1)	
8.746 826(2)	2.431 008(−3)	4.017 679(−3)
2.079 785(2)	3.233 027(−2)	3.113 966(−2)
6.687 918(1)	1.242 520(−1)	1.349 077(−1)
2.487 347(1)	−3.903 905(−2)	3.431 672(−1)
9.968 441	−6.171 789(−1)	4.625 760(−1)
4.063 826	−4.473 097(−1)	2.154 603(−1)
3.364 363(1)	−2.940 358(−3)	−6.311 620(−3)
1.087 565(1)	7.163 103(−2)	−2.697 638(−2)
4.628 225	2.528 915(−1)	5.316 847(−2)
1.950 126	−2.966 401(−1)	3.845 549(−1)
8.094 520(−1)	−7.432 215(−1)	5.127 662(−1)
3.204 740(−1)	−1.853 520(−1)	1.811 135(−1)
1.224 148	6.351 465(−2)	−2.112 070(−1)
4.842 630(−1)	3.151 404(−1)	7.771 998(−2)
8.409 600(−2)	−1.162 595	9.898 214(−1)
3.203 600(−2)	1.000 000	1.000 000
α_d	d_d	
1.369 085(1)	8.589 418(−2)	
3.513 154	3.784 671(−1)	
1.040 434	7.161 239(−1)	
2.869 620(−1)	1.000 000	

TABLE VIII. 6-31G basis set for chromium.

α	d_s	d_p
5.178 981(4)	1.776 182(−3)	
7.776 849(3)	1.360 476(−2)	
1.771 385(3)	6.706 925(−2)	
4.991 588(2)	2.323 104(−1)	
1.597 982(2)	4.802 410(−1)	
5.447 021(1)	3.487 653(−1)	
1.064 328(3)	2.399 669(−3)	3.986 997(−3)
2.532 138(2)	3.194 886(−2)	3.104 662(−2)
8.160 924(1)	1.250 868(−1)	1.350 518(−1)
3.048 193(1)	−3.221 866(−2)	3.448 865(−1)
1.229 439(1)	−6.172 284(−1)	4.628 571(−1)
5.037 722	−4.525 936(−1)	2.110 426(−1)
4.156 291(1)	−3.454 216(−3)	−6.722 497(−3)
1.367 627(1)	7.218 428(−2)	−2.806 471(−2)
5.844 390	2.544 820(−1)	5.820 028(−2)
2.471 609	−2.934 534(−1)	3.916 988(−1)
1.028 308	−7.385 455(−1)	5.047 823(−1)
4.072 500(−1)	−1.947 157(−1)	1.790 290(−1)
1.571 464	5.892 219(−2)	−1.930 100(−1)
6.055 800(−1)	2.976 055(−1)	9.605 620(−2)
9.856 100(−2)	−1.147 506	9.817 609(−1)
3.645 900(−2)	1.000 000	1.000 000
α_d	d_d	
1.841 930(1)	8.650 816(−2)	
4.812 661	3.826 699(−1)	
1.446 447	7.093 772(−1)	
4.004 130(−1)	1.000 000	

TABLE IX. 6-31G basis set for manganese.

α	d_s	d_p
5.634 714(4)	1.771 580(−3)	
8.460 943(3)	1.357 081(−2)	
1.927 325(3)	6.690 605(−2)	
5.432 343(2)	2.318 541(−1)	
1.739 905(2)	4.799 046(−1)	
5.936 005(1)	3.495 737(−1)	
1.165 412(3)	2.388 751(−3)	3.977 318(−3)
2.773 276(2)	3.181 708(−2)	3.103 112(−2)
8.947 278(1)	1.254 670(−1)	1.351 894(−1)
3.348 256(1)	−2.955 431(−2)	3.457 387(−1)
1.354 037(1)	−6.175 160(−1)	4.629 205(−1)
5.557 972	−4.544 458(−1)	2.090 592(−1)
4.583 532(1)	−3.665 856(−3)	−6.887 578(−3)
1.518 777(1)	7.231 971(−2)	−2.846 816(−2)
6.500 710	2.544 486(−1)	6.031 832(−2)
2.751 583	−2.910 380(−1)	3.938 961(−1)
1.145 404	−7.359 860(−1)	5.013 769(−1)
4.536 870(−1)	−1.997 617(−1)	1.792 264(−1)
1.757 999	5.628 572(−2)	−5.035 024(−1)
6.670 220(−1)	2.897 491(−1)	2.345 011(−1)
1.051 290(−1)	−1.140 653	9.14157(−1)
3.841 800(−2)	1.000 000	1.000 000

α_d	d_d
2.094 355(1)	8.672 702(−2)
5.510 486	3.841 883(−1)
1.665 038	7.069 071(−1)
4.617 330(−1)	1.000 000

TABLE XI. 6-31G basis set for cobalt.

α	d_s	d_p
6.614 899(4)	1.759 787(−3)	
9.933 077(3)	1.348 162(−2)	
2.262 816(3)	6.649 342(−2)	
6.379 154(2)	2.307 939(−1)	
2.044 122(2)	4.792 919(−1)	
6.982 538(1)	3.514 097(−1)	
1.378 841(3)	2.376 276(−3)	3.971 488(−3)
3.282 694(2)	3.167 450(−2)	3.108 174(−2)
1.060 946(2)	1.262 888(−1)	1.357 439(−1)
3.983 275(1)	−2.584 552(−2)	3.476 827(−1)
1.618 622(1)	−6.183 491(−1)	4.626 340(−1)
6.667 788	−4.567 008(−1)	2.051 632(−1)
5.452 355(1)	−3.993 004(−3)	−7.290 772(−3)
1.829 783(1)	7.409 663(−2)	−2.926 027(−2)
7.867 348	2.542 000(−1)	6.564 150(−2)
3.340 534	−2.921 657(−1)	4.000 652(−1)
1.393 756	−7.318 703(−1)	4.950 236(−1)
5.513 260(−1)	−2.040 784(−1)	1.758 240(−1)
2.151 947	5.379 843(−2)	−2.165 496(−1)
8.110 630(−1)	2.759 971(−1)	1.240 488(−1)
1.210 170(−1)	−1.129 692	9.724 064(−1)
4.303 700(−2)	1.000 000	1.000 000

α_d	d_d
2.559 306(1)	9.004 748(−2)
6.800 990	3.931 703(−1)
2.051 647	6.976 844(−1)
5.556 710(−1)	1.000 000

TABLE X. 6-31G basis set for iron.

α	d_s	d_p
6.113 262(4)	1.766 111(−3)	
9.179 342(3)	1.353 038(−2)	
2.090 857(3)	6.673 128(−2)	
5.892 479(2)	2.314 823(−1)	
1.887 543(2)	4.797 058(−1)	
6.444 629(1)	3.501 976(−1)	
1.259 980(3)	2.438 014(−3)	4.028 019(−3)
2.998 761(2)	3.224 048(−2)	3.144 647(−2)
9.684 917(1)	1.265 724(−1)	1.368 317(−1)
3.631 020(1)	−3.139 902(−2)	3.487 236(−1)
1.472 996(1)	−6.207 593(−1)	4.617 931(−1)
6.066 075	−4.502 914(−1)	2.043 058(−1)
5.043 485(1)	−3.873 256(−3)	−7.017 128(−3)
1.683 929(1)	7.196 598(−2)	−2.877 660(−2)
7.192 086	2.556 591(−1)	6.181 383(−2)
3.053 420	−2.882 837(−1)	3.954 946(−1)
1.273 643	−7.342 822(−1)	4.989 059(−1)
5.040 910(−1)	−2.049 353(−1)	1.791 251(−1)
1.950 316	5.694 869(−2)	−4.593 796(−1)
7.367 210(−1)	2.882 915(−1)	2.852 139(−1)
1.141 770(−1)	−1.138 159	9.076 485(−1)
4.114 800(−2)	1.000 000	1.000 000

α_d	d_d
2.314 994(1)	8.876 935(−2)
6.122 368	3.896 319(−1)
1.846 601	7.014 816(−1)
5.043 610(−1)	1.000 000

TABLE XII. 6-31G basis set for nickel.

α	d_s	d_p
7.139 635(4)	1.753 003(−3)	
1.072 084(4)	1.343 122(−2)	
2.442 129(3)	6.627 041(−2)	
6.884 265(2)	2.302 508(−1)	
2.206 153(2)	4.790 186(−1)	
7.539 373(1)	3.523 444(−1)	
1.492 532(3)	2.370 714(−3)	3.967 554(−3)
3.554 013(2)	3.160 566(−2)	3.109 479(−2)
1.149 534(2)	1.266 335(−1)	1.359 517(−1)
4.322 043(1)	−2.417 037(−2)	3.485 136(−1)
1.759 710(1)	−6.187 775(−1)	4.625 498(−1)
7.257 765	−4.576 770(−1)	2.035 186(−1)
5.935 261(1)	−4.162 002(−3)	−7.421 452(−3)
2.002 181(1)	7.425 111(−2)	−2.953 410(−2)
8.614 561	2.541 360(−1)	6.731 852(−2)
3.660 531	−2.903 477(−1)	4.016 660(−1)
1.528 111	−7.302 121(−1)	4.926 623(−1)
6.040 570(−1)	−2.076 057(−1)	1.756 893(−1)
2.379 276	5.157 888(−2)	−1.887 663(−1)
8.858 390(−1)	2.707 611(−1)	1.015 199(−1)
1.285 290(−1)	−1.124 770	9.790 906(−1)
4.519 500(−2)	1.000 000	1.000 000

α_d	d_d
2.819 147(1)	9.098 881(−2)
7.523 584	3.958 208(−1)
2.271 228	6.947 154(−1)
6.116 030(−1)	1.000 000

TABLE XIII. 6-31G basis set for copper.

α	d_s	d_p
7.679 438(4)	1.748 161(−3)	
1.153 070(4)	1.339 602(−2)	
2.626 575(3)	6.610 885(−2)	
7.404 903(2)	2.298 265(−1)	
2.373 528(2)	4.787 675(−1)	
8.115 818(1)	3.530 739(−1)	
1.610 814(3)	2.364 055(−3)	3.963 307(−3)
3.836 367(2)	3.153 635(−2)	3.110 223(−2)
1.241 733(2)	1.269 452(−1)	1.361 350(−1)
4.674 678(1)	−2.262 840(−2)	3.492 914(−1)
1.906 569(1)	−6.192 080(−1)	4.624 780(−1)
7.871 567	−4.585 393(−1)	2.020 102(−1)
6.445 732(1)	−4.33 1075(−3)	−7.523 725(−3)
2.185 212(1)	7.412 307(−2)	−2.975 687(−2)
9.405 343	2.542 108(−1)	6.849 654(−2)
3.999 168	−2.874 843(−1)	4.027 141(−1)
1.670 297	−7.291 436(−1)	4.908 490(−1)
6.596 270(−1)	−2.113 951(−1)	1.759 268(−1)
2.600 088	5.027 577(−2)	−1.702 911(−1)
9.630 940(−1)	2.650 040(−1)	9.310 133(−2)
1.361 610(−1)	−1.120 155	9.814 336(−1)
4.733 200(−2)	1.000 000	1.000 000

α_d	d_d	
3.085 341(1)	9.199 905(−2)	
8.264 985	3.985 021(−1)	
2.495 332	6.917 897(−1)	
6.676 580(−1)	1.000 000	

TABLE XIV. 6-31G basis set for zinc.

α	d_s	d_p
8.240 094(4)	1.743 329(−3)	
1.237 255(4)	1.335 966(−2)	
2.818 351(3)	6.594 365(−2)	
7.945 717(2)	2.294 151(−1)	
2.547 232(2)	4.785 453(−1)	
8.713 880(1)	3.537 753(−1)	
1.732 569(3)	2.361 459(−3)	3.963 125(−3)
4.127 149(2)	3.150 177(−2)	3.113 411(−2)
1.336 780(2)	1.272 774(−1)	1.363 931(−1)
5.038 585(1)	−2.145 928(−2)	3.501 266(−1)
2.058 358(1)	−6.197 652(−1)	4.623 179(−1)
8.505 940	−4.590 180(−1)	2.004 995(−1)
6.936 492(1)	−4.440 098(−3)	−7.689 262(−3)
2.362 082(1)	7.505 253(−2)	−2.997 982(−2)
1.018 471(1)	2.533 111(−1)	7.082 411(−2)
4.334 082	−2.881 897(−1)	4.046 141(−1)
1.810 918	−7.267 052(−1)	4.882 325(−1)
7.148 410(−1)	−2.133 439(−1)	1.751 970(−1)
2.823 842	4.898 543(−2)	−1.586 763(−1)
1.039 543	2.592 793(−1)	8.379 327(−2)
1.432 640(−1)	−1.115 711	9.840 547(−1)
4.929 600(−2)	1.000 000	1.000 000

α_d	d_d	
3.370 764(1)	9.262 648(−2)	
9.061 106	4.002 980(−1)	
2.738 383	6.896 608(−1)	
7.302 940(−1)	1.000 000	

eters are optimized for pure functions, even though the final basis is specified with Cartesian functions.

The functional form of the 6-31G set orbitals is defined as

$$\phi_{kl}(\mathbf{r}) = \sum_{i=1}^{n_k} d_{kl,i} g_l(\alpha_{k,i}, \mathbf{r})$$

$$n_1 = n_2 = n_3 = 6; \quad n_4 = 3; \quad n_5 = 1, \tag{1}$$

where $l = s$ or p, the exponents of s and p primitives are constrained to be equal to each other in the same shell, k goes from 1 to 5, and $g(\alpha, \mathbf{r})$ are normalized Gaussian-type functions. The elements Sc–Zn also have d-type functions of the same form

$$\phi_{kd}(\mathbf{r}) = \sum_{i=1}^{n_k+1} d_{kd,i} g_l(\alpha_{kd,i}, \mathbf{r}).$$

Since all these elements have a vacant $4p$ molecular orbital in the Hartree–Fock function, all d_{4p} and d_{5p} coefficients are initially constrained to be zero. All remaining α and d coefficients are optimized to give the lowest ROHF energy for high spin, high orbital angular momentum states, namely $K(^2S)$, $Ca(^1S)$, $Sc(^2D)$, $Ti(^3F)$, $V(^4F)$, $Cr(^5D)$, $Mn(^6S)$, $Fe(^5D)$, $Co(^4F)$, $Ni(^3F)$, $Cu(^2D)$, and $Zn(^1S)$. With ex-

ception of $K(^2S)$, these states have a fully occupied $4s$ orbital. Optimization on such states may lead to the lack of diffuse d-type primitives which was shown by Hay to be important for the description of s^1d^{n-1} and s^0d^n states.[13] The use of $Cu(^2S)$ state for parameter optimization, however, had only a minor effect on the basis set. The largest difference was in the outermost d-type primitive, which has the value of 0.562 588 2 in the $Cu(^2S)$ optimized set, compared to 0.667 657 5 for $Cu(^2D)$ optimization. Nevertheless, for systems in which configurations with higher d-electron occupation play an important role, the use of 6-31+G type set, which is 6-31G augmented with the set of diffuse functions, may be desirable. These additional diffuse functions require further study.

The $3s$ inner orbital required a special consideration. The comparison of d_{3s} coefficients reveals different node structure for the different atoms. All transition metals have a (1,2,3) structure for the $3s$ orbital. This notation indicates that the orbital has the first d_{3s} coefficient of one sign, the next two have different sign, and the last three have their signs equal to the first. The $3s$ orbital of Ca has (3,3) node structure, and $3s$ orbital of K has (2,4) structure. Each node structure often supports a local minimum, since the transition from one structure to the other goes through the loss of one primitive at the transition point. We performed optimization at different node structures of $3s$ orbital for all atoms, choosing at the end the one corresponding to the global minimum.

The different node structures lead to differences in the ROHF energies of the order 1 μH.

The basis functions corresponding to the $4p$ atomic orbitals cannot be determined in this way, since these orbitals are unoccupied in all the atomic states considered. Exponents and s-coefficients have been found but the inner three d_{4p} coefficients are indeterminate. We made an attempt to optimize these by studying an excited state, as was done for lighter elements. Such a procedure encountered two major problems. First, the proximity of many excited states to each other made convergence in some cases very difficult to achieve. When the convergence was forced by a variety of techniques, the resulting $4p$ functions did not demonstrate a consistent trend across the row. Therefore, we decided to use the ground state UHF energy in the presence of the external electric field as an optimization criterion. The UHF energy was chosen over ROHF for purely technical reasons, and we used the GAUSSIAN-94 program for these calculations.[14] The uniform external field is the simplest form of the simulation of a bonding molecular environment. The field dependence of the optimized d_{4p} coefficients on vanadium revealed a parabolic dependence with zero derivative around 0.045 a.u. of field strength. The data is shown in Table I. A similar extremum in zinc was found for the field of about 0.055 a.u. We, therefore, chose the field of 0.045 for all atoms. The UHF energies obtained with 6-31G basis sets are shown in Table II, and the basis sets themselves are in Tables (III–XIV). They can be also downloaded through the Northwestern University Chemistry Department server.[15]

The 6-31G* polarization sets are obtained by adding a single polarization function to the split-valence 6-31G sets described above. Such functions add flexibility to the basis set in the region of chemical bonds. For K and Ca atoms we used a single set of six uncontracted Cartesian d-functions. The use of Cartesian d-functions is consistent with the 6-31G* set for second-row elements. For atoms Sc through Zn we chose a set of 10 Cartesian f-functions. The alternative would be a set of seven pure f-functions. The Cartesian representation adds three extra p-functions to the valence space, but it has the advantage of simpler coding. This brings the number of basis functions to a total of 23 for K and Ca, and to 39 for Sc through Zn.

The value of the polarization function exponent was optimized by minimizing the energy of fluorides, carbonyls, and carbonyl hydrides. We have also performed the f-function optimization on diatomic hydrides. Unfortunately, in many cases this resulted in either too diffuse f-functions, probably associated with the Rydberg states of the molecule, or too tight f-functions, when their main role was the improvement of the $3p$ orbital. This is because higher angular momentum functions do not significantly contribute to the bonding in diatomic hydrides. The fluoride compounds somewhat underestimated the optimal value of the polarization exponent by drawing it towards the fluorine core. The carbonyl compounds give the most realistic values of the polarization exponents. The optimized values of polarization exponents were averaged to a single value of 0.2 for the d-function exponent for K and Ca, and to 0.8 for the f-function exponent for atoms Sc through Zn. The values of

TABLE XV. Dependence of the optimized polarization exponent for various molecules. All geometries are optimized on the 6-31G level.

Molecule	Polarization exp.	Recommended exp.
K_2O	0.0808	
KOH	0.0598	
KF	0.0801	0.2
KCl	0.1933	
KH	0.2589	
$Ca(CH_3)_2$	0.4458	
$Ca(OH)_2$	0.0815	
CaF_2	0.1081	0.2
CaO	0.1641	
CaH	0.2404	
$CaCl_2$	0.1655	
ScF_3	0.4034	0.8
TiF_4	0.5150	0.8
VF_5	0.5503	
$V(CO)_6$	0.7311	0.8
VO	0.6628	
CrF_6	0.5895	0.8
$Cr(CO)_6$	0.8216	
$MnH(CO)_5$	1.0213	0.8
$Fe(CO)_5$	1.0795	0.8
CoF_3	0.8090	0.8
$CoH(CO)_4$	1.2060	
NiF_2	2.081	0.8
$Ni(CO)_2$	0.8900	
CuF	0.2235	0.8
CuF_2	0.8067	
ZnF_2	0.4965	0.8

optimal d- and f-functions for different compounds are given in Table XV, and the UHF energies obtained with 6-31G* basis sets are shown in Table II. They are lower than the 6-31G energies for two reasons. First, the Cartesian d- and f-type Gaussians contain functions of lower angular momentum. These functions improve the description of the occupied orbitals. Second, unlike ATOM-SCF, the GAUSSIAN 94 program does not impose the angular symmetry on atomic orbitals. This leads to the contamination of s orbitals with d-functions, and p orbitals with f functions, which further lowers the energy for atoms not in S state.

III. PERFORMANCE

We have performed a number of geometry optimization calculations with the 6-31G* basis set for the molecules for which there is experimental data on their geometric parameters in the gas phase. The results are summarized in Table XVI. The overall discrepancy between experimental values and those calculated with the 6-31G* set is rather significant. The bond lengths are strongly overestimated in K_2, CaO, and $Fe(CO)_5$ molecules. In order to analyze the discrepancy, we performed additional calculations in these cases.

TABLE XVI. Calculated and experimental equilibrium geometries. Bond lengths are given in angstroms, angles are in degrees.

Molecule	Point group	Parameter	6-31G	6-31G*	Expt.
K_2[a]		r(K K)	4.192	4.202	3.923
KOH[b]	$C_{\infty v}$	r(K O)	2.263	2.244	2.212
		r(O H)	0.951	0.944	0.91
KCl[a]		r(K Cl)	2.845	2.777	2.79
CaO[c]		r(Ca O)	2.226	2.038	1.822
TiCl$_4$[c]	T_d	r(Ti Cl)	2.202	2.202	2.170
VOCl$_3$[d]	C_{3v}	r(V O)	1.518	1.490	1.570
		r(V Cl)	2.162	2.138	2.142
		$\angle$ ClVCl	110.6	110.5	111.3
Cr(CO)$_6$[c]	O_h	r(Cr C)	1.968	1.987	1.92
		r(C O)	1.137	1.119	1.16
MnH[a]		r(Mn H)	1.789	1.789	1.731
Fe(CO)$_5$[e]	D_{3h}	r_{ax}(Fe C)	2.050	2.035	1.807
		r_{eq}(Fe C)	1.830	1.859	1.827
		r_{aver}(C O)	1.134	1.117	1.153
Ni(CO)$_4$[c]	T_d	r(Ni C)	1.850	1.866	1.838
		r(C O)	1.134	1.117	1.141
CuF[a]		r(Cu F)	1.754	1.729	1.743
ZnH[a]		r(Zn H)	1.630	1.615	1.595

[a]Experimental geometry from Ref. 22.
[b]Experimental geometry from Ref. 23.
[c]Experimental geometry from Ref. 24.
[d]Experimental geometry from Ref. 25.
[e]Experimental geometry from Ref. 26.

The Hartree–Fock method is known to overestimate significantly the iron-ligand bond lengths.[16] Our MP2 (second-order Moller–Plesset) geometry optimization for iron pentacarbonyl significantly reduced the Fe–C bond lengths, making them even shorter than the experimental ones. This result is consistent with the calculated iron-ligand distance for ferrocene[17] and FeCO$^+$,[18] where the Hartree–Fock model also significantly overestimates Fe–C bond length, while MP2 underestimates it. Good agreement with experimental Fe(CO)$_5$ geometry can be achieved through the complete active space second-order perturbation theory (CASPT2)[19] and coupled-cluster[20] methods.

The uncontraction of the valence basis function and addition of two extra polarization functions had only minor effect on the bond distance in K_2. The overestimation of the bond length in potassium dimer was also observed in the pseudopotential calculation and is attributed to the missing core-valence interaction terms.[21] In the case of all-electron calculations such overestimation can, therefore, be also attributed to the neglected correlation between core and valence electrons.

The overestimation of the bond length in CaO can be attributed to the basis set deficiency. Addition of a second polarization d function to calcium with the exponent of 2.0 leads to the optimized bond length of 1.8745 Å, which is an improvement of the agreement with experiment by 75%. A further study of the basis set requirements for the systems with multiple bonds might be necessary.

The performance of the 6-31G* basis set for the rest of the molecules gives an agreement with experiment similar to that for the molecules with second-row elements.[9]

IV. CONCLUSIONS

The 6-31G* polarization basis set has been extended to elements K through Zn. It can be used both in the Cartesian or spherical harmonic representation of the basis functions of higher angular momentum. The Hartree–Fock calculations on a sample set of molecules shows that for single bonded metal-ligand systems the agreement with experimental geometries is similar to that for the second-row atoms. The agreement is worse for multiple bonded systems, often due to the shortcomings of the Hartree–Fock model.

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