Fully optimized contracted Gaussian basis sets for atoms Li to Kr

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Various contracted Gaussian basis sets for atoms up to Kr are presented which have been determined by optimizing atomic self-consistent field ground state energies with respect to all basis set parameters, i.e., orbital exponents and contraction coefficients.

INTRODUCTION

Chemical bonding usually does not affect inner shells of atoms. Atomic contributions from the valence shell, however, may contract or expand and be polarized depending on the actual bonding situation. The smallest (atom centered) basis set which can be expected to reliably account for these effects, e.g., in self-consistent field (SCF) treatments, is of SVP (split valence polarization) type, which means that inner shell atomic orbitals (AOs) are described by a single basis function, two basis functions are provided for each valence shell AO, augmented by a set of polarization functions.

CGTO (contracted Gaussian-type orbital) basis sets can, of course, be obtained by segmented or generalized contraction of atom optimized GTO basis sets. Since we will not deal with this popular and successful procedure, we refer the reader to recent reviews.1-5 It should be noted, however, that the basis sets obtained by segmented contraction are clearly not fully optimized, i.e., the basis set parameters do not minimize an appropriate measure for accuracy such as the atomic ground state energy. Atom optimized basis sets in a generalized contraction are clearly fully optimized.6 Since we consider it advantageous to use fully optimized segmented CGTO sets, we will present various basis sets of this kind, especially SV basis sets.

The most widely and successfully used atom optimized basis sets of SV type have been determined by Pople et al., the 4-31 G (Ref. 7) and 6-31 G (Ref. 8) basis sets. The main and probably only drawback of 4-31 G bases, to give an example, concerns the relatively poor energy especially for second row elements: the 4-31 G atomic energies for Al to Cl are even higher than those of Huzinaga’s (9~5~) basis.9 The SV type 4-31 G basis does not appear to be an efficient contraction of a (12s8p) primitive basis.2

SV contractions can be conveniently obtained from atom optimized SZ (single zeta) basis sets by decontracting valence AOs. SZ basis sets are available for various numbers of GTOs per AO for atoms up to Rn from the work of Huzinaga and co-workers.10 These SZ sets have proved invaluable to us since their study provided important hints for the design of fully atom optimized CGTO sets presented in this article.

METHOD OF COMPUTATION, ACCURACY, AND NOMENCLATURE

The methodology of GTO basis set optimization has been developed and described in detail by Faegri and Alm-
\[ L = k + l + m + 1. \]  

It is convenient for the present purpose not to require normal-
ization of CGTOs since the SCF energy does not de-
pend on the normalization of AOs. Differentiation of the
CGTO \( \sigma_{i,j,k} \) with respect to one of its exponents \( \eta_i \) or con-
traction coefficients \( d_j \) yields

\[
\frac{\partial \sigma_{i,j,k}}{\partial \eta_i} = d_j \frac{\partial g_{i,k}}{\partial \eta_i} - \frac{1}{2} \left( L + \frac{1}{2} \right) \eta_i g_{i,k} - d_j (r - r_A)^2 g_{i,k}. 
\]

\[
\frac{\partial \sigma_{i,j,k}}{\partial d_j} = g_{i,k}. 
\]

The Eqs. (1)–(11) fully specify the gradient of \( E_{SCF} \)
with respect to the individual \( \eta_i \) and \( d_j \) in CGTOs in terms of
matrix elements of one- and two-electron operators (which are clearly independent of \( \eta_i \) and \( d_j \)).

The analytic gradients computed in this way were then
used to home in onto a local minimum of the energy by means of a relaxation procedure also used for geometry
optimizations. We did not compute second derivatives.

Since the relaxation procedure is designed to home in on
minima we are confident that (at least) a local minimum of
the corresponding atomic energy has been found in all
cases. The relaxation procedure is not very satisfactory.
There is clearly strong coupling of parameters to be opti-
mized and the convergence occasionally requires assis-
tance, e.g., first freezing some parameters or resetting the
approximate hessian to a diagonal matrix. After some ex-
erience with a reasonable choice of starting parameters
(scaling of CGTOs from a neighbor atom, using the ap-
proximate hessian from a previous optimization at a neigh-
bor atom), the procedure converged automatically al-
though up to 150 iterations were necessary to converge the
energy to \( 10^{-11} \) a.u. (in some cases only to \( 10^{-10} \) a.u.), the
density to \( 10^{-9} \), and all parameters to 7 decimal figures.
The optimization was terminated when gradients were
within numerical noise. The virial coefficient was always
\( \pm 10^{-8} \), although this was not enforced by global scaling.

The following nomenclature will be used to character-
bize basis sets: \((k,l,m)\) denotes a GTO basis with \( k \) GTOs of \( s \) type, \( l \) GTOs of \( p \) type and \( m \) GTOs of \( d \) type; \( [s_1,...,l_1;...,m_1] \) denotes the contraction pattern (e.g.,
\( s_1 \) GTOs of \( s \) type in the first CGTO).

**FULLY ATOM-OPTIMIZED CGTO BASIS SETS UP TO Kr**

**SV basis sets**

The smallest (in the valence shell) SV basis just con-
tains two uncontracted GTOs in the valence shell. Pursu-
ing Huzinaga's SZ sets it occurred to us that such a "min-
imal choice" might be useful provided there is a core AO of
the same \( l \) quantum number. The \( 432/42 \) basis of Huzi-

\[ \text{Huzinaga et al.}^{10} \] for \( P(4S) \), to give an example, is only 16 mH
higher in energy than the \( 433/43 \) basis. It was hoped
that this loss in energy might be further reduced by fully
optimizing a SV basis from the very start.

Having decided to use a 2 GTO valence shell representation,
it remained to determine the SZ description of inner
shells. We have been led here by considerations which will
be sketched now for a typical example. Consider the 2p
and 3p shells of second row atoms. The number \( p_1 \) of \( p \) type
GTOs to describe the 2p AO was obtained from calcu-
lations employing \( p_1 = 4, 5, 6 \). It turned out that for \( p_1 < 5 \)
the valence (3p) \( p \) GTOs tended to improve the 2p AOs,
whereas for \( p_1 = 5 \) or \( p_1 = 6 \) this was not the case: the 2
GTO representation of the 3p shell remained stable for
\( p_1 > 5 \).

Considerations basically identical to the one just de-
scribed led to the following choice; SV basis sets: (a) 1st
row elements—Li, Be: \([51] \), i.e., \((7)/[3]\) or \([511] \), i.e.,
\((7,4)/[3,2] \) (Be \( 3P \)), B–Ne: \([511,31] \), i.e., \((7,4)/[3,2] \); (b) 2nd
row elements—Na, Mg: \([5311,5] \), i.e., \((10,5)/[4] \) or
\([5311,511] \), i.e., \((10,7)/[4,3] \) (Mg \( 3P \)), Al–Ar: \([5311,511] \),
\((10,7)/[4,3] \); (c) 3rd row elements—K, Ca: \([6331,5311] \), i.e., \((14,8)/[5,2] \) or \([6331,5311] \), i.e.,
\((14,10)/[5,4] \) (Ca \( 3P \)), Sc–Zn: \([6331,5314] \), i.e.,
\((14,8,5)/[5,2,2] \) or \([6331,5314] \), i.e., \((14,8,6)/[5,2,2] \),
Ga–Kr: \([6331,5314] \), i.e., \((14,10,5)/[5,4,2] \).

The above reasoning does not help to fix the chosen
\((31) \) representation for the 2p shell of first row atoms.
Since most integral programs "like" higher contractions
we have decided for a larger basis in cases of doubt.
Although a \((21) \) representation for 2p could have also been
considered for B to F, this appeared to be unbalanced com-
pared to the \((5) \) representation for 1s, especially for ele-
ments at the right end of the period. Our choice has been
vindicated by test calculations to be discussed below.

Some comments are to be made on alkali metals. When
optimizing basis sets of the size of the present SV basis,
only one of the two uncontracted \( s \) functions stays in the
valence region, i.e., the total minimum is not of SV type.
We therefore first optimized the corresponding SZ basis
sets and then split the valence \( s \) exponent and optimized
the splitting factor. It turned out that for Li and K this led
to a good starting point for a full optimization, which then
homed in on a local minimum of the energy with two
functions in the valence region.\(^{16} \) For Na we could not
locate such a minimum, although there might be a very
shallow one.

**Larger basis sets**

For comparison we have also optimized CGTO basis
sets of DZ (double zeta) type; DZ basis sets: (a) 1st
row elements—Li, Be: \([511] \), i.e., \((8)/[4] \), B–Ne: \([511,31] \),
i.e., \((8,4)/[4,2] \); (b) 2nd row elements—Na, Mg: \([521111,41] \), i.e.,
\((11,5)/[6,2] \), Al–Ar: \([521111,4111] \), i.e., \((11,7)/
[6,4] \); (c) 3rd row elements—K, Ca: \([621111,331111] \), i.e.,
\((14,9,5)/[8,5,3] \), Sc–Zn: \([621111,331111,311] \), i.e.,
\((14,11,5)/[8,6,2] \), as well as the corresponding uncon-
tracted basis sets. To our surprise it turned out that Huzi-

\[ \text{Huzinaga's atom optimized GTO basis sets}^{9} \] are in part far
from being optimized. Although we achieve relatively mi-

or lowerings of atomic ground state energies \( [e.g., by 3 \]
\( mH \) for the \((11,7) \) basis for the \( 4S \) state of P], the orbital
TABLE I. RHF-SCF energies in hartrees for present basis sets for atoms Li to Ar. SV, DZ, TZ as described in the text.

<table>
<thead>
<tr>
<th>Atom</th>
<th>State</th>
<th>SV</th>
<th>DZ</th>
<th>TZ</th>
<th>HF limit (Ref. 24)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>۰S</td>
<td>-7.425 064</td>
<td>-7.430 999</td>
<td>-7.432 617</td>
<td>-7.432 727</td>
</tr>
<tr>
<td>Be</td>
<td>۱۱۱P</td>
<td>-14.553 727</td>
<td>-14.570 335</td>
<td>-14.572 335</td>
<td>-14.573 023</td>
</tr>
<tr>
<td>C</td>
<td>۲۴۱P</td>
<td>-37.641 143</td>
<td>-37.676 346</td>
<td>-37.687 291</td>
<td>-37.688 619</td>
</tr>
<tr>
<td>N</td>
<td>۴۴۴S</td>
<td>-54.332 925</td>
<td>-54.379 482</td>
<td>-54.398 890</td>
<td>-54.400 934</td>
</tr>
<tr>
<td>O</td>
<td>۳۳۴P</td>
<td>-74.713 746</td>
<td>-74.773 732</td>
<td>-74.806 289</td>
<td>-74.809 398</td>
</tr>
<tr>
<td>Ne</td>
<td>۴۴۴S</td>
<td>-128.376 407</td>
<td>-128.461 528</td>
<td>-128.540 811</td>
<td>-128.547 10</td>
</tr>
<tr>
<td>Na</td>
<td>۲۲۴S</td>
<td>-161.791 703</td>
<td>-161.838 183</td>
<td>-161.851 998</td>
<td>-161.858 91</td>
</tr>
<tr>
<td>Mg</td>
<td>۴۴۴S</td>
<td>-199.533 593</td>
<td>-199.591 591</td>
<td>-199.607 443</td>
<td>-199.614 63</td>
</tr>
<tr>
<td>Al</td>
<td>۲۲۳P</td>
<td>-241.878 870</td>
<td>-241.883 166</td>
<td>-241.877 999</td>
<td>-241.876 71</td>
</tr>
<tr>
<td>S</td>
<td>۳۳۳P</td>
<td>-397.361 194</td>
<td>-397.433 828</td>
<td>-397.473 030</td>
<td>-397.482 07</td>
</tr>
<tr>
<td>Cl</td>
<td>۲۲۳P</td>
<td>-526.623 385</td>
<td>-526.758 128</td>
<td>-526.802 631</td>
<td>-526.817 51</td>
</tr>
<tr>
<td>Ar</td>
<td>۱۱۱S</td>
<td>-526.623 385</td>
<td>-526.758 128</td>
<td>-526.802 631</td>
<td>-526.817 51</td>
</tr>
</tbody>
</table>

The terms so obtained in Oₖ have no component of other atomic terms of the same spin, e.g., ³A₂ₕ has no ³Pₗ component. For the d⁴ and d⁶ configurations one has to use a full contraction of the d GTOs to maintain L symmetry (same radial function for eₗ and t₂ₕ), i.e., one has to optimize the energy with respect to orbital exponents and contraction coefficients by means of gradient techniques as described above, even if a (partially) uncontracted d basis is desired.

**Comparison of atomic SCF ground state energies**

In Tables I and II we have listed atomic ground state restricted Hartree–Fock self-consistent field (RHF-SCF) energies obtained with present fully optimized basis sets. We consider N(⁴S), P(⁴S), and Mn(⁶S) in some detail to give the reader an idea of accuracies of various basis sets (Tables III–V).

The present SV basis of type (7,4)/[3,2] for N(⁴S) is 8 mH lower in energy than the 4-31 G basis, although 4-31 G is based on an (8,4) (GTO) set. The 68 mH deviation of the SV energy from the HF limit results mainly from deficiencies in the 1s part. Extension from (5 1 l/3 1) to 161 l/31 recovers already 12 mH without leading to any noticeable improvement in the valence region. The DZ basis loses only 5.5 mH through contraction (with optimization of all parameters), roughly 25% of the distance to the HF limit. The present (9,5) basis is 0.4 mH lower in energy than the corresponding Huzinaga basis. Our (10,6) basis is also 0.2 mH lower than the corresponding Huzinaga basis and 1.8 mH higher than the HF limit. Contraction of this basis—and optimization of all parameters—implies a loss of only 0.2 mH.

Considering the basis sets of SV type for P(⁴S)—present, 4-31 G, and 6-31 G—the present SV basis is much

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TABLE II. RHF-SCF energies in hartrees for present basis sets for atoms K to Kr. SV, DZ, TZ as described in the text. Energies marked with an asterisk refer to optimized basis sets with six d GTOs. Occupancy of transition metals is 3d^54s^1, except for Ni(3D):3d^84s^1, Ni(5S):3d^10, Cu(3S):3d^94s^1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Basis</th>
<th>5s</th>
<th>5p</th>
<th>3d</th>
<th>HF limit (Ref. 24)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>3s</td>
<td>-599.076 962</td>
<td>-599.148 385</td>
<td>-599.164 79</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>1s</td>
<td>-676.660 070</td>
<td>-676.740 256</td>
<td>-676.758 18</td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>3p</td>
<td>-676.622 455</td>
<td>-676.701 640</td>
<td>&lt;...&gt;</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>3f</td>
<td>-759.625 235</td>
<td>-759.713 573</td>
<td>-759.735 72</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>4f</td>
<td>-848.282 096</td>
<td>-848.379 067</td>
<td>-848.406 00</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>5s</td>
<td>-942.745 719</td>
<td>-942.851 763</td>
<td>-942.884 33</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>6s</td>
<td>-1043.196 070</td>
<td>-1043.309 807 &lt;...&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>7s</td>
<td>-1043.155 118</td>
<td>-1043.270 664</td>
<td>-1043.309 8</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>8s</td>
<td>-1149.694 241</td>
<td>-1149.819 721</td>
<td>-1149.866 2</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>9s</td>
<td>-1262.25 1794</td>
<td>-1262.387 575</td>
<td>-1262.443 7</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>10s</td>
<td>-1381.201 346</td>
<td>-1381.347 858</td>
<td>-1381.414 6</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>11s</td>
<td>-1506.574 107</td>
<td>-1506.729 374</td>
<td>-1506.870 9</td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>12s</td>
<td>-1506.625 423*</td>
<td>-1506.792 258</td>
<td>-1506.870 9</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>13s</td>
<td>-1506.574 107</td>
<td>-1506.729 374</td>
<td>-1506.870 9</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>14s</td>
<td>-1506.397 399</td>
<td>-1506.550 369</td>
<td>-1506.615 804*</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>15s</td>
<td>-1506.454 934*</td>
<td>-1506.615 804*</td>
<td>-1506.615 804*</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>16s</td>
<td>-1638.688 105</td>
<td>-1638.853 786</td>
<td>-1638.904 562*</td>
<td></td>
</tr>
<tr>
<td>Kr</td>
<td>17s</td>
<td>-1777.560 282</td>
<td>-1777.741 472</td>
<td>-1777.848 1</td>
<td></td>
</tr>
</tbody>
</table>

closer to 6-31 G [derived from a (16,10) primitive basis] than to 4-31 G [derived from (12,8)], although it is obtained from a (10,7) GTO basis. As further evidence for the quality of the present SV basis we have plotted in Fig. 1 the radial density distribution of the 3p SCF AO. Although we “offer” only two GTOs for the valence shell, we

have the same quality for the 3p AO for 0<r<2 a₀ (roughly the maximum of the radial density distribution) as the 4-31 G basis, whereas the latter leads to markedly larger deviations (more than a factor of two) from the near HF limit [e.g., a (17,12) GTO basis set] result at r>2 a₀. For the 3s AO the relative accuracy of the SV basis is even better.

The energy error of the present SV basis (5311/511) with respect to the HF solution of 12 mH is mainly due to deficiencies in the description of the 1s AO. An extension from (5311/511) to (6311/511) recovers already 48% of the distance to the HF limit. Again we have not found any effect of this improved 1s AO representation on the valence shell.

The present DZ contraction of an (11,7) GTO basis implies a loss of only 4.8 mH in energy as compared to a deviation of 31 mH to the HF limit. Our test calculations, in part discussed below, do not point to a sufficient advantage of this DZ basis over the present SV basis. For more accurate calculations we therefore recommend to go directly to the TZ (12,9)/[7,5] basis with contraction pattern [51211/5111]. The corresponding energy is only 6.9 mH above the HF limit and the contraction of the (12,9) basis (with optimization) incurs a loss of only 1 mH.

A series of tests was performed for the [Ar](4s^23d^5) 6S state of Mn to assess accuracies and potential shortcomings

TABLE III. RHF-SCF energies for various basis sets for N(4S) ground state, ordered according to the energy.

<table>
<thead>
<tr>
<th>Basis</th>
<th>E_{SCF}/a.u. +54</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-31 G (Ref. 7)</td>
<td>-0.325 299*</td>
</tr>
<tr>
<td>SV (511/31)</td>
<td>-0.332 925</td>
</tr>
<tr>
<td>(611/31)</td>
<td>-0.344 963</td>
</tr>
<tr>
<td>DZ (5111/31)</td>
<td>-0.379 482</td>
</tr>
<tr>
<td>6-31 G (Ref. 8)</td>
<td>-0.302 275*</td>
</tr>
<tr>
<td>(8,4)</td>
<td>-0.385 045</td>
</tr>
<tr>
<td>(9,5) Huzinaga (Ref. 9)</td>
<td>-0.395 473</td>
</tr>
<tr>
<td>[51111/311]</td>
<td>-0.395 684</td>
</tr>
<tr>
<td>(9,5)</td>
<td>-0.395 885</td>
</tr>
<tr>
<td>TZ (51111/411)</td>
<td>-0.398 880</td>
</tr>
<tr>
<td>(10,6) Huzinaga (Ref. 9)</td>
<td>-0.398 925</td>
</tr>
<tr>
<td>(10,6)</td>
<td>-0.399 097</td>
</tr>
<tr>
<td>HF limit (Ref. 24)</td>
<td>-0.400 934</td>
</tr>
</tbody>
</table>

*RHF-SCF energies calculated with TURBOMOLE. Pople et al. give the following UHF energies: -340.320 188 a.u. for 4-31 G, -340.690 20 a.u. for 6-31 G.

TABLE IV. RHF-SCF energies for various basis sets for P(4S) ground state, ordered according to the energy.

<table>
<thead>
<tr>
<th>Basis</th>
<th>E_{SCF}/a.u. +1149</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-31 G (Ref. 7)</td>
<td>-0.320 156*</td>
</tr>
<tr>
<td>SV (5311/511)</td>
<td>-0.597 366</td>
</tr>
<tr>
<td>(6311/511)</td>
<td>-0.656 000</td>
</tr>
<tr>
<td>DZ (521111/4111)</td>
<td>-0.688 104</td>
</tr>
<tr>
<td>(11,7) Huzinaga (Ref. 9)</td>
<td>-0.689 484</td>
</tr>
<tr>
<td>(11,7)</td>
<td>-0.692 914</td>
</tr>
<tr>
<td>TZ (5121111/5111)</td>
<td>-0.711 921</td>
</tr>
<tr>
<td>(12,9)</td>
<td>-0.712 856</td>
</tr>
<tr>
<td>HF limit (Ref. 24)</td>
<td>-0.718 78</td>
</tr>
</tbody>
</table>

TABLE V. RHF-SCF energies for various basis sets for Mn (5S) ground state, ordered according to the energy.

<table>
<thead>
<tr>
<th>Basis</th>
<th>E_{SCF}/a.u. +1149</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huzinaga (Ref. 10)</td>
<td>-0.787 333/53/5</td>
</tr>
<tr>
<td>Present</td>
<td>-0.536 53311/53/41</td>
</tr>
<tr>
<td>Wachters (Ref. 17)</td>
<td>-0.694 651111/5311/311</td>
</tr>
<tr>
<td>Present</td>
<td>-0.787 63311/73/5</td>
</tr>
<tr>
<td>DZ</td>
<td>-0.820 6121111/5311/311</td>
</tr>
<tr>
<td>Wachters (Ref. 17)</td>
<td>-0.832 (14,5,5)</td>
</tr>
<tr>
<td>Present</td>
<td>-0.835 (14,5,5)</td>
</tr>
<tr>
<td>Clementi (Ref. 25)</td>
<td>-0.866 STO*</td>
</tr>
<tr>
<td>HF limit (Ref. 24)</td>
<td>-0.866</td>
</tr>
</tbody>
</table>

S*Slater-type orbitals (STO).
of various basis sets. Table V contains the SCF energies we have obtained, ordered according to the energy, where “present” always implies full optimization of all parameters. On the basis of these results we selected \{63311/53/41\} as optimal basis of SV type. The SCF energy differs by 172 mH from the HF limit, of which 100 mH (58\%) can be recovered by just extending to \{83311/73/41\}, i.e., by a better description of the 1s and 2p AOs. This extension has no visible effect on the outer shell description. The remaining discrepancy, i.e., \{83311/73/41\} vs the HF limit (of 72 mH) reflects errors in the approximation of outer shells, mainly the 2s AO. If a better description than the present SV basis is desired, we recommend the present fully optimized Wachters type contraction \{62111111/331111\} which is only 46 mH higher in energy than the HF limit and only 12 mH higher than the uncontracted Wachters basis.\(^{17}\) We finally note that careful optimization lowers the energy of the Wachters basis by 3.7 mH (11\% of the distance to the HF limit) and that the present \{53311/53/41\} energy is even lower than the best SZ \{5333/53/53\}\(^{10}\) result.

As an additional indication of the appropriateness of the present SV basis we compare the present orbital exponents with those obtained by Wachters for the most diffuse functions: 0.703 (present)/0.652 (Wachters), 0.106/0.084, 0.040/0.031 for the three outermost s functions; 3.337/3.477, 1.379/1.341, 0.539/0.505 for the three outermost p functions; 1.212/1.103, 0.388/0.337 for the two most diffuse d functions. The relatively minor deviations strongly indicate similar quality in the description of 3s, 3p, 3d, and 4s, at least if the most diffuse GTO of 3s and 3p is taken out of the contraction (and corresponding contractions are used for 3d).

FIG. 1. Radial density distribution \(\rho(r) = 4\pi r^2 |\varphi(r)|^2\) of the 3p AO of P\((^3S)\) with a near HF basis (17,12) and deviations for the 4-31 G and present SV basis sets.

### SIMPLE MOLECULAR TEST CALCULATIONS

Equilibrium geometry determinations of ethane, ethene, ethine, benzene, and azulene with SV, SVP, DZP and the fullerene C\(_{60}\) with SV and SVP basis sets (with an optimized (4)/\([2]\) basis for H) show the following trends.\(^{16}\)

The SV structure constants differ by at most 1.0 pm and 0.2\° from SVP and by at most 1.4 pm and 0.3\° from DZP results. For C\(_{60}\), e.g., we get the C-C distances 145.7 and 138.1 pm (SV) and 145.1/137.6 pm (SVP) which have to be compared to the TZP MP2 (second order Möller–Plesset) equilibrium distances of 144.6/140.6 pm.\(^{19}\)

As typical examples of molecules with second row atoms we report results for P\(_4\) as a typical covalent molecule and for AlCl\(_3\) and SF\(_6\) as more ionic cases. The following results were obtained for various basis sets in comparison to experiment,\(^{20}\) listed in the order SVP/DZP/TZP/exp (\(d\) exponents: Al 0.3, P 0.4, S 0.6, Cl 0.65, F 1.0)

\[
\begin{align*}
P_4(T_d) &\quad R_\text{c}/\text{pm} = 219.8/219.8/219.5/221, \\
P_4 &\quad \Delta E_{\text{SCF}}/\text{kJ mol}^{-1} = -414/-405/-408, \\
\text{AlCl}_3(D_3h) &\quad R_\text{c}/\text{pm} = 208.0/207.9/208.0/206, \\
\text{AlCl}_3 &\quad \Delta E_{\text{SCF}}/\text{kJ mol}^{-1} = -1057/ -1036/ -1028, \\
\text{SF}_6(O_h) &\quad R_\text{c}/\text{pm} = 154.6/155.2/154.4/156, \\
\text{SF}_6 &\quad \Delta E_{\text{SCF}}/\text{kJ mol}^{-1} = -970/ -923/ -876, \\
\Delta E_{\text{SCF}} &\quad \text{is the SCF bonding energy, i.e.,}
\end{align*}
\]
The results demonstrate the quality of SVP basis sets in SCF treatments, e.g., in comparison to DZP or TZP, and confirms the quantitative accuracy of the SCF approximation as far as structure constants are concerned. The SVP basis also shows no shortcomings with respect to SCF binding energies for P4 or AlCl3. Only for SF6 which shows a rather delicate balance of ionic (\(\pi^+\sigma^-\)) and hypervalent (3d on S) contributions to bonding, a larger basis is required for a quantitative account of energetics of bonding.

Finally we report results for TiCl4 as a transition metal compound which can be treated on the SCF level. The equilibrium geometry was determined with SVP and DZP basis sets \([\eta_p=0.065 \text{ (Ti)}, \eta_d=0.34 \text{ (Cl)}]\) with following results listed in the order SVP/DZP/exp:\n
\[
\text{TiCl}_4(T_i) \quad R_{\text{Ti-Cl}} = 217.3/219.5/219.5 \text{ pm}, \\
\Delta E_{\text{SCF}}/\text{kJ mol}^{-1} = -1081/-1106.
\]

Again the SVP basis shows relatively good accuracy with respect to molecular structure and bonding energy as compared to DZP.

### RECOMMENDATIONS FOR MOLECULAR CALCULATIONS

The use of atom optimized basis sets in molecular calculations requires some modifications and extensions which have been extensively discussed in the literature.\(^\text{1-5}\) We only make a few comments in connection with the basis sets presented in this article.

**Polarization functions** should be added to SV or larger basis sets to obtain a reliable account of bonding effects in SCF calculations. An SVP basis appears to yield equilibrium geometries sufficiently close to the HF limit. Polarization functions for H are here of lesser importance,\(^\text{5}\) and hydrocarbons, benzene or related compounds, and fullerenes can even be treated on the SV level.\(^\text{18}\)

**Alkaline earth metals.** Since it is absolutely necessary to have valence \(p\) functions added to the basis sets of alkaline earth elements in molecular calculations, we have optimized the corresponding SV and DZP basis sets for the excited state \(3P\) (i.e., \(ns^2np^3\)). Alternatively one can add two \(p\) sets to the SV basis obtained for the ground state with exponents similar to those of the valence \(s\) functions.

For **boron** we recommend to scale the \(p\) exponents by a factor of 1.3, since the \(p\) contribution to molecular orbitals (MOs) is always markedly contracted as compared to the (relatively weakly bound) \(2p\) AO of the free atom.

**SVP versus larger basis sets.** If more extended basis sets than SVP are to be used, we recommend to go directly to TZP [or TZDP] for atoms up to Ar and the DZP basis sets for K to Kr. The present SV basis may be decontracted for the shell below the valence shell (by taking out the most diffuse function), but we have not encountered cases so far where this led to marked improvements. We recommend in any case that an SVP treatment for a structure determina-

\[
\Delta E_{\text{SCF}} = E_{\text{SCF}}(\text{molecule}) - \sum E_{\text{SCF}}(\text{atoms}).
\]

### CONCLUSION

Full optimization of all basis set parameters (exponents and contraction coefficients) by means of gradient techniques leads to basis sets of relatively small size with least possible loss in accuracy. These basis sets are expected to be superior to those created by just contracting atom...
optimized GTO sets. The present fully optimized SV basis sets are considered to be the best compromise of expense and accuracy.

AVAILABILITY

The basis sets presented in this article are available via FTP (file transfer protocol) at internet address “tchibm3.chemie.uni-karlsruhe.de” (Internet number 129.13.108.8) with login-ID “anonymous” in the directory “/pub/basis.” Besides those mentioned in Tables I and II, the files include also basis sets of type (7,4), (8,4), (9,5), (9,5)/[5,3]/{51111/311}, (10,6), (11,7), (11,7)/[6,4]/{611111/4111}, (13,9) for first row, (10,7), (11,7), (12,8), (12,9), (13,10), (13,10)/[8,6]/{61111111/511111}, (15,12), (17,12) for second row, (14,9,5) for third row transition metals, and (14,11,5), (14,11,5)/[8,6,2]/{62111111/6111111/41} for third row main group elements.

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