Compact Basis Sets for LCAO-LSD calculations.

Part I: Method and Bases for Sc to Zn

J. Andzelm,* E. Radzio, and D. R. Salahub

Département de chimie, Université de Montréal, C.P. 6210 Succ. A, Montréal, Québec, Canada H3C 3V1

A method for preparing compact orbital and auxiliary basis sets for LCAO-LSD calculations has been developed. The method has been applied to construct basis sets for first row transition metal atoms from Sc to Zn for the $3d^{n-1}4s^1$ and $3d^{n-2}4s^2$ configurations. The properties of different expansion patterns have been tested in atomic calculations for the chromium atom.

INTRODUCTION

Recently LCAO-Local Spin Density (LCAO-LSD) methods using Gaussian,[1] Slater,[2] or numerical basis sets,[2] sometimes coupled with the Discrete Variational Method (DVM),[2,3] have proven to be quite successful in the determination of geometries and binding energies for various molecules containing transition metal atoms.[1-4] The LCAO methods offer a significant advantage over the widely used Scattered-Wave (SW) method which, although it provides reasonable one-electron properties, fails to predict molecular geometries. However, both the LCAO Gaussian and DVM methods are more computationally demanding than the SW method, and in the case of LCAO-LSD the size of the calculations increases as $\sim N^3$, where N is the number of basis functions. This is a major obstacle in applying this method to larger systems, so that the largest system studied so far with the LCAO-Xα method is a Ni$_4$ cluster.[5]

The LCAO-LSD method with a variational fit to the coulomb energy[1,6] seems to be very accurate and the agreement with fully numerical Xα calculations is very encouraging.[7]

In order to achieve an N^3 rather than an N^4 LCAO-LSD method, one has to provide an orbital basis set and up to four auxiliary sets, to fit (1) the exchange-correlation potential for spin α(XA), (2) the exchange-

correlation potential for spin β(XB), (3) the exchange-correlation energy (XE) and (4) the charge density (CD). In the scheme of Dunlap et al.[1] Hartree-Fock (HF) uncontracted expansions of Hermite Gaussians are employed for the orbital set, and the auxiliary sets of s and d type are then derived from them by multiplying the exponents by 2 for CD and by $\frac{2}{3}$ for the XA, XB, and XE sets, respectively. An additional set of auxiliary p type functions is also included in the CD and exchange sets. Bond-centered fitting functions also have been advocated.

In most LCAO-LSD calculations rather extended uncontracted HF Gaussian basis sets have been employed. However, using such basis sets severely limits the size of the systems which can be studied. Application of the method to systems containing several heavier atoms is computationally very demanding. Hence, there exists a great need for smaller, highly contracted, basis sets which would perform as well as the extended ones and at the same time reduce the computational time. Such compact basis sets have been successfully developed within the HF scheme[8] and at present most molecular calculations are performed using such expansions. However, it can be risky to apply highly contracted HF optimized basis sets in LSD calculations, since there are quite pronounced differences in the valence region between LSD and HF atoms (see Section II), which of course can influence molecular results. It is also not obvious that Dunlap's recipe for the auxiliary sets will be adequate

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*On leave of absence from the Agricultural and Teacher's University, Siedlce, Poland.

in the case of compact basis sets, especially if one takes into account the possibility of near linear dependencies which may arise if such basis sets are decontracted.

We, therefore, decided to develop both orbital and auxiliary sets within the LSD model from LSD calculations on atoms. In the present paper the method of preparing the basis sets is described and compact basis sets for first row transition metal atoms are constructed. As an example the atomic valence properties of different contraction patterns are examined in detail for the Cr atom. In an accompanying article (Part II) the basis sets are tested in molecular calculations for the Cr_2 and Ni_4 systems.

ORBITAL BASIS SETS

LSD vs. HF orbitals

Numerical spin-polarized calculations for the Cr atom have been performed using Kohn-Sham[9] exchange ($X\alpha$ with $\alpha = \frac{2}{3}$) and also various LSD potentials which take account of electron correlation effects in the underlying calculation of the homogeneous electron gas.[11-14] In Table I the $3d$ and $4s$ orbital energies and expectation values of r are presented for the $3d^5 4s^1$ ground state of chromium, and they are compared with corresponding restricted HF results. The expectation values of r for the core orbitals (from $1s$ to $3p$) are very close to each other for all the LSD potentials considered and they are similar to those from HF calculations.

Clearly, substitution of HF exchange by an LSD potential has significant effects on the valence orbitals; the $4s$ orbital is contracted and the $3d$ orbital expands. This effect is already present for the Kohn-Sham (local) exchange only potential, and the shape of the occupied valence orbitals varies only slightly when correlated potentials are used. The consequences of this are two-fold. First, if close to minimal HF-optimized basis sets are used they may not be flexible enough to provide LSD type orbitals in the most important, valence, region of the atom. Most HF basis sets are optimized within the restricted scheme, and it is not obvious that small bases of this type will also be able to describe spin-unrestricted orbitals. Second, since both valence orbital energies and the shapes of the orbitals are quite close for all LSD potentials one may expect that a basis set optimized for one of those potentials will also be appropriate for the others. We have chosen the potential of Vosko et al.[14] as a reference LSD potential for basis set optimization. This potential approaches very closely the most accurate energy calculation of the homogeneous electron gas,[15] so that it is believed to represent the limit of the local approximation for exchange-correlation energies.

HF Basis Sets for Transition Metals

The most widely employed basis sets for first row transition metals are those of Roos,

Table I. Orbital energies (eV) and radial expectation values $\langle r \rangle$ (Bohr) for the $3d$ and $4s$ orbitals of Cr in the $3d^5 4s^1$ configuration.

	HF[a]	KS[b]	JMW[c]	BH[d]	GL[e]	VWN[f]
$-\varepsilon\ 4s^\uparrow$	3.02	4.11	4.78	4.96	4.82	4.53
$-\varepsilon\ 4s^\downarrow$		0.27	1.82	2.48	2.56	2.55
$-\varepsilon\ 3d^\uparrow$	5.08	3.26	4.17	4.40	4.31	3.98
$-\varepsilon\ 3d^\cdot$			0.16	0.67	0.49	0.31
$\langle r \rangle\ 4s^\uparrow$	3.709	3.376	3.331	3.325	3.290	3.334
$\langle r \rangle\ 4s^\cdot$		5.408	3.903	3.786	3.880	3.868
$\langle r \rangle\ 3d^\uparrow$	1.368	1.494	1.467	1.461	1.456	1.461
$\langle r \rangle\ 3d^\downarrow$			1.746	1.732	1.904	1.998

[a]Spin-restricted calculations for Cr(^7S) taken from ref. 10. Note that HF and LSD orbital energies should not be compared because the self interaction terms are not excluded from the LSD treatment (ref. 27).
[b]Reference 9.
[c]Reference 11.
[d]Reference 12.
[e]Reference 13.
[f]Reference 14.

Veillard, and Vinot[16] and of Wachters.[17] These basis sets can be contracted without any loss of accuracy by the general contraction scheme of Raffenetti,[18] thus providing compact basis sets. However, since these basis sets originate from uncontracted sets they have to possess a sufficiently large number of primitive Gaussian orbitals (GTO) to properly describe both core and valence orbitals. It is known that if small Gaussian expansions are optimized to minimize the total energy, most of the GTOs tend to be spent for the innermost orbitals which seriously diminishes the quality of the valence orbitals.

Recently, minimal STO-3G basis sets have been proposed[19] for transition metal atoms. Similar to their predecessors for lighter elements they were found to be very economical in molecular calculations and some trends in geometries of organometallic compounds were found to be well described. However, we expect a basis set to accurately reproduce not only the geometry but also other molecular properties. The average STO-3G error for the orbital energies is as high as 63% and this is clearly not accurate enough. A method of optimization of minimal basis sets has recently been developed by Huzinaga and co-workers.[20] This approach guarantees that an appropriate number of GTOs is used for the description of outer atomic orbitals, even if core orbitals are described at a lower level of accuracy. These basis sets were found to provide excellent orbital energies for transition metal atoms[21] relative to the (numerical) HF limit, and in the case of copper and zinc clusters[22] they correctly reproduced the potential curves. Basis sets prepared according to this method have recently been published for all atoms up to Rn,[23] so that they can provide a systematic starting point for LSD optimizations.

Method of Optimization of LSD Basis Sets

The method adopted here is based on that developed by Huzinaga et al.[20] and will be described briefly for first row transition metal atoms. We assume the following expansion pattern for a minimal basis set $(k_{s1} \ldots k_{s4}/k_{p1}, k_{p2}/k_{d1})$ where k_{l_i} denotes the number of GTOs in the i-th contracted function (CGTO) of l symmetry. The CGTO can

be expressed as:

$$l_i = \sum_{j=1}^{kl_i} d_{l_i,j} g_{l_i}(\alpha_{l_i},j;r) \qquad l = s,p,d \quad (1)$$

where g_{l_i} denotes a GTO.

Our procedure is as follows, taking the s_4 CGTO as an example. In the first step we freeze all other s, p, and d type CGTOs, decontract s_4, and solve the $3 + k_{s_4}$ dimensional LSD problem. This yields a new set of coefficients $(d_{s_4,j})$ and exponents $(\alpha_{s_4,j})$ which are accepted if the total energy of the atom with a four-dimensional s block is lower than the previous one for the fully contracted case. This procedure is repeated for all CGTOs until the total energy stabilizes within a certain threshold [in the present case 10^{-4} a.u. (hartree)]. We start the optimization from optimal HF type basis sets,[23] so that the main changes occur in the valence contractions. In the case of spin-polarized optimization the linear coefficients are determined as an average of coefficients from solutions for each spin:

$$d_{s4,j} = \frac{N_{4s}^{\uparrow} d_{s4,j}^{\uparrow} + N_{4s}^{\downarrow} d_{s4,j}^{\downarrow}}{N_{4s}^{\uparrow} + N_{4s}^{\downarrow}} \quad (2)$$

where $N_{4s}^{\uparrow}(N_{4s}^{\downarrow})$ denotes the number of electrons for spin $\uparrow$ ($\downarrow$) associated with orbital $4s$.

It should be noted that this optimization procedure does not require any auxiliary basis set since the coulomb and exchange correlation terms are accurately calculated by (one-dimensional) numerical integration. This allows the optimization of orbital and auxiliary basis sets to be treated as two independent problems. We will return to this point in Section III.

From Table II one can see that minimal HF-optimized basis sets cause large errors in the description of the $3d$ orbitals. A basis set of the same size optimized for the LSD Hamiltonian significantly diminishes the error for the valence orbitals. The quality of the valence orbitals depends strongly on the size of the d expansion and the minimal basis set with 7 d GTOs provides orbital energies within 0.02 eV of the numerical values for occupied valence orbitals and within 0.2 eV for unoccupied orbitals.

It has long been recognized that diffuse $3d$ functions are important to provide a flexible basis set which can describe an atom in vari-

Table II. Performance of various basis sets for $Cr(3d^5 4s^1)$. Total energy (TE) in hartrees, orbital energies (ε) in eV.

Basis	$-$TE	$-\varepsilon 4s^\uparrow$	$-\varepsilon 4s^\downarrow$	$-\varepsilon 3d^\uparrow$	$-\varepsilon 3d^\downarrow$
Numerical	1042.2192	4.53	2.55	3.98	0.31
$(5333/53/5)^a$	1041.8698	4.15	2.35	2.52	-1.49
$(53321/53/41)^a$	1041.8764	4.16	2.27	3.25	-0.64
$(5333/53/5)$	1041.9044	4.36	2.21	3.53	-0.32
$(5333/53/6)$	1041.9219	4.45	2.30	3.79	-0.03
$(5333/53/7)$	1041.9271	4.51	2.36	3.96	0.16
$(5333/53/51^+)^b$	1041.9160	4.54	2.38	3.98	0.29
$(4333/43/41^+)^b$	1041.1549	4.62	2.47	3.97	0.30
$(3333/33/41^+)^b$	1037.8287	4.60	2.46	3.99	0.32

^{a}Original HF-optimized basis set taken from ref. 23; all other basis sets are optimized for LSD-VWN Hamiltonian.
^{b}The d-type GTO of smallest exponent (1^+) is not optimized in the atomic optimization (see text).

ous molecular environments.[24] To establish the small d exponent we fit a weighted (see below) valence $3d$ orbital ($3d$) using at least 7 d GTOs. Then the smallest exponent of this expansion is kept frozen in an atomic calculation while all other contractions are reoptimized to minimize the energy of the ground state of the atom.

The reference $3d$ orbital is defined as follows:

$$3d = \frac{N_{3d}^\uparrow 3d^\uparrow + N_{3d}^\downarrow 3d^\downarrow}{N_{3d}^\uparrow + N_{3d}^\downarrow} \qquad (3)$$

where $3d^\uparrow$ and $3d^\downarrow$ denote the numerical radial $3d$ function for majority spin and minority spin, respectively, and $N_{3d}^\uparrow(N_{3d}^\downarrow)$ is the number of electrons associated with the corresponding $3d$ orbital. We decided not to optimize the small exponent since it tends to increase and compensate for insufficiencies of the other contractions. The possibility of its optimization for other excited configurations has been ruled out since this would introduce a dependence on a particular molecular environment. The last three entries in Table II show the importance of the small d exponent. Its inclusion brings about excellent agreement with numerical results for the valence orbitals of both spin manifolds. The important feature of the optimization scheme presented here is that one can limit the accuracy of the inner parts of the orbitals (thus obtaining more economical basis sets) which causes a deterioration in the total energy, but the valence region is described reliably in all cases.

In Table III the performance of various contraction patterns for different configurations of Cr is studied. The minimal basis

sets are not flexible enough to describe the atomic states rich in d electrons. The double zeta d (DZ) sets provide significant improvement for these states; however, unless a small d exponent is used the error is still around 1 eV with respect to the numerical values. A basis set at the triple zeta (TZ) level for the d part, including a small d exponent is necessary to provide, within a couple of tenths of an eV, the correct trends in the various states of Cr. However, unless large changes in occupation of $3d$ and $4s$ orbitals occur in comparison with the ground state configuration $3d^5 4s^1$, we expect that even on the DZ level one can obtain sound molecular results. Once again we note that the error in the description of core orbitals does not propagate to the valence region and our smallest $(3333/33/41^+)$ set has the same valence properties as a set which has a more extended core representation.

Based on the present results and those obtained for molecular calculations (reported in Part II) the $(4333/43/41^+)$ expansion pattern has been chosen for all first row transition metal atoms as that fulfilling reasonable requirements of accuracy and economy. The exponents and contraction coefficients for atoms from Sc to Zn in $3d^{n-2}4s^2$ and $3d^{n-1}4s^1$ configurations are listed in Table IVa and IVb, respectively. The $(4333/43/41^+)$ pattern and the tables should be regarded as providing reference basis sets. In molecular calculations more flexible, e.g., split-valence, sets may be necessary.[20-23] These can readily be constructed by simple decontraction of the valence-like components. For example, split-valence sets such as $(43321/43/41^+)$ have been used

Table III. Ionization energies (I)[a] from LSD-VWN calculations on the Cr atom; energy separation $(\Delta)^b$ between ground $(3d^54s^1)$ configuration and excited states $(3d^44s^2$ and $3d^64s^0)$. All energies are in eV.

Basis	$I(3d^54s^1)$	$I(3d^44s^2)$	$I(3d^64s^0)$	Δ_1	Δ_2
Numerical	9.4	13.8	3.3	2.1	4.1
(5333/53/5)	12.2	20.4	0.3	3.7	7.2
(5333/53/6)	12.4	20.6	0.6	3.9	7.0
(5333/53/7)	12.5	20.6	0.9	4.0	6.9
(5333/53/41)	9.8	16.1	2.4	2.1	5.0
(53321/53/41)	9.4	14.9	2.4	2.1	5.0
(53321/53/311)	9.4	14.6	2.4	2.0	5.0
(53321/431*/311)	9.4	14.5	2.4	2.0	5.0
(5333/53/51$^+$)	10.5	18.1	3.1	2.7	4.3
(53321/53/51$^+$)	10.0	16.6	3.1	2.6	4.3
(53321/53/411$^+$)	9.5	14.6	3.2	2.2	4.3
(53321/531*/411$^+$)	9.5	14.5	3.2	2.1	4.2
(4333/43/41$^+$)	10.3	17.7	3.2	2.5	4.4
(43321/43/41$^+$)	9.9	16.1	3.2	2.4	4.3
(43321/431*/311$^+$)	9.4	14.4	3.3	2.0	4.3
(3333/33/41$^+$)	10.3	17.8	3.2	2.5	4.3
(33321/33/41$^+$)	9.8	16.1	3.2	2.5	4.3
(33321/331*/311$^+$)	9.4	14.3	3.3	2.1	4.2

$^a I(3d^54s^1) = E(3d^44s^1) - E(3d^54s^1)$
$I(3d^44s^2) = E(3d^34s^2) - E(3d^44s^2)$
$I(3d^64s^0) = E(3d^54s^0) - E(3d^64s^0)$
$^b \Delta_1 = E(3d^44s^2) - E(3d^54s^1)$
$\Delta_2 = E(3d^64s^0) - E(3d^54s^1)$

in Part II.

In molecular calculations, polarization functions are usually important and have been found to significantly influence molecular results on Cu clusters.[22] We define a polarization function as a GTO next in symmetry to the outermost valence orbital. In the case of transition metal atoms this is a p type orbital which in the least square (LS) method best fits the weighted radial part

Table IVa. Exponents and coefficients for the transition metal atoms in the $3d^{n-2}4s^2$ configuration. (4333/43/41$^+$) contraction pattern.

Sc		Ti		V	
6199.96250	0.01764	6833.34590	0.01757	7502.39540	0.01750
936.73028	0.12312	1032.25180	0.12271	1133.00280	0.12229
211.69364	0.44264	233.36583	0.44191	256.17808	0.44122
56.37566	0.55186	62.20618	0.55278	68.33577	0.55371
85.27566	−0.10020	94.07541	−0.10115	103.31145	−0.10202
9.00653	0.59845	9.99330	0.60331	11.03640	0.60746
3.60251	0.47270	4.02530	0.46778	4.47090	0.46363
6.34199	−0.21188	7.16844	−0.21450	8.03879	−0.21624
0.97299	0.70877	1.11000	0.71099	1.25376	0.71128
0.38834	0.41489	0.44227	0.41430	0.49794	0.41531
0.60530	−0.16336	0.68868	−0.16148	0.77040	−0.15794
0.07850	0.70392	0.08908	0.68215	0.09862	0.66545
0.03110	0.39463	0.03470	0.41697	0.03778	0.43327
232.94895	0.03048	258.07322	0.03050	287.17682	0.03015
54.37211	0.18854	60.62803	0.18778	67.48680	0.18686
16.41967	0.50343	18.43100	0.50303	20.57121	0.50335
5.30220	0.46123	5.99599	0.46060	6.72819	0.46006
2.24754	0.31193	2.57151	0.31775	2.92429	0.31968
0.83099	0.56866	0.95342	0.56683	1.08743	0.56435
0.30427	0.24390	0.35013	0.23934	0.40003	0.23987
11.94031	0.06136	14.58217	0.06064	17.12858	0.06066
3.09962	0.26051	3.84850	0.26165	4.56585	0.26442
0.91718	0.48761	1.16886	0.48853	1.40513	0.49011
0.24773	0.50790	0.32867	0.49531	0.40126	0.48661
0.05000	1.00000	0.07000	1.00000	0.08600	1.00000

Table IVa *(continued)*

Cr		Mn		Fe	
8201.59770	0.01743	8901.89390	0.01744	9656.88050	0.01739
1238.32040	0.12191	1344.62320	0.12188	1458.53250	0.12160
280.04038	0.44058	304.38663	0.44033	330.26446	0.43982
74.75344	0.55454	81.37078	0.55464	88.35181	0.55527
113.03202	−0.10279	123.11804	−0.10353	133.73201	−0.10416
12.12347	0.61211	13.27275	0.61571	14.46256	0.61976
4.93326	0.45900	5.42141	0.45549	5.92594	0.45150
8.96022	−0.21725	9.92254	−0.21797	10.93447	−0.21882
1.40221	0.71224	1.55897	0.71131	1.72501	0.71055
0.55432	0.41524	0.61372	0.41696	0.67833	0.41835
0.85153	−0.15375	0.93335	−0.14965	1.03827	−0.15121
0.10762	0.65199	0.11633	0.64025	0.12672	0.64111
0.04060	0.44596	0.04326	0.45685	0.04636	0.45683
317.04806	0.02995	347.99049	0.02983	381.59839	0.02956
74.57989	0.18633	81.89399	0.18625	89.82003	0.18552
22.79831	0.50382	25.09950	0.50455	27.58059	0.50481
7.49327	0.45905	8.28786	0.45746	9.13854	0.45715
3.28884	0.32256	3.67201	0.32483	4.07417	0.32758
1.22348	0.56252	1.36582	0.56081	1.51570	0.55990
0.44978	0.23913	0.50138	0.23906	0.55674	0.23717
19.64435	0.06123	22.39314	0.06115	25.09523	0.06167
5.27907	0.26791	6.04799	0.26996	6.80584	0.27275
1.64059	0.49109	1.88864	0.49253	2.12553	0.49409
0.47324	0.47918	0.54549	0.47489	0.60887	0.47198
0.10200	1.00000	0.11600	1.00000	0.12600	1.00000

Co		Ni		Cu	
10472.33200	0.01729	11279.05000	0.01727	12149.60000	0.01720
1580.69830	0.12108	1702.65890	0.12094	1833.26700	0.12056
357.75100	0.43911	385.54172	0.43879	414.99903	0.43826
95.70231	0.55639	103.22650	0.55670	111.12894	0.55751
144.77579	−0.10477	156.21623	−0.10534	168.10397	−0.10588
15.71614	0.62254	17.02205	0.62529	18.38861	0.62729
6.46027	0.44878	7.01489	0.44612	7.59654	0.44421
11.98978	−0.21940	13.09541	−0.21969	14.23753	−0.22002
1.89592	0.71117	2.07346	0.71117	2.26189	0.70903
0.74286	0.41834	0.80980	0.41875	0.88125	0.42137
1.12743	−0.14952	1.22458	−0.14775	1.32343	−0.14568
0.13866	0.62522	0.14895	0.61789	0.15890	0.61136
0.05008	0.47342	0.05308	0.48074	0.05594	0.48705
414.50547	0.02956	452.03793	0.02924	491.19506	0.02894
97.66098	0.18578	106.46562	0.18484	115.69102	0.18386
30.06970	0.50553	32.81248	0.50567	35.69141	0.50567
10.00430	0.45535	10.94126	0.45560	11.92417	0.45609
4.49714	0.32932	4.94138	0.33060	5.40957	0.33110
1.67476	0.55823	1.83973	0.55726	2.01344	0.55644
0.61570	0.23719	0.67576	0.23717	0.73852	0.23788
27.39680	0.06379	30.10542	0.06476	32.89197	0.06571
7.46936	0.27872	8.23645	0.28220	9.02596	0.28557
2.33775	0.49466	2.57967	0.49561	2.82879	0.49634
0.66816	0.46556	0.73415	0.46172	0.80217	0.45806
0.13700	1.00000	0.14800	1.00000	0.15900	1.00000

Zn					
13001.27500	0.01721	0.94979	0.41965	2.18979	0.55542
1962.54310	0.12055	1.42200	−0.14310	0.80205	0.23786
444.61787	0.43808	0.16870	0.60550	36.00687	0.06602
119.18972	0.55755	0.05871	0.49254	9.90494	0.28739
180.51156	−0.10633	527.58803	0.02904	3.10650	0.49697
19.77605	0.63115	124.34763	0.18454	0.87852	0.45596
8.18008	0.44043	38.45237	0.50660	0.17200	1.00000
15.44938	−0.21980	12.89110	0.45382		
2.44824	0.71080	5.88638	0.33253		

Table IVb. Exponents and coefficients for the transition metal atoms in the $3d^{n-1}4s^1$ configuration. $(4333/43/41^+)$ contraction pattern.

Sc		Ti		V	
6224.96180	0.01756	6857.96590	0.01750	7525.10460	0.01743
939.66414	0.12277	1035.23990	0.12239	1135.87720	0.12199
212.12014	0.44235	233.81070	0.44163	256.63382	0.44091
56.43546	0.55254	62.27000	0.55343	68.40618	0.55433
85.32206	−0.10017	94.15526	−0.10109	103.51647	−0.10189
8.99803	0.59984	9.97791	0.60529	10.99341	0.61203
3.59507	0.47135	4.01412	0.46582	4.44364	0.45903
6.36314	−0.20960	7.20071	−0.21205	8.07903	−0.21339
0.96644	0.70524	1.09820	0.71275	1.23855	0.71574
0.37929	0.41807	0.42926	0.41198	0.48218	0.41018
0.54831	−0.15772	0.62977	−0.15747	0.71443	−0.15556
0.07301	0.71230	0.08477	0.67373	0.09537	0.64766
0.02832	0.38703	0.03254	0.42702	0.03609	0.45304
234.95268	0.03010	260.50027	0.03008	289.08692	0.02985
54.76881	0.18718	61.10735	0.18631	67.88636	0.18572
16.50949	0.50302	18.54024	0.50251	20.66549	0.50290
5.31866	0.46332	6.01736	0.46292	6.74660	0.46187
2.27450	0.30162	2.61196	0.30499	2.96166	0.30899
0.83788	0.56341	0.96814	0.56108	1.10031	0.55950
0.30296	0.26326	0.35147	0.26144	0.39965	0.25891
10.20191	0.06813	12.82683	0.06690	15.33416	0.06653
2.61278	0.27033	3.34391	0.27356	4.04356	0.27672
0.74046	0.47121	0.97907	0.47901	1.20521	0.48355
0.18380	0.53746	0.25468	0.51383	0.32053	0.49968
0.03600	1.00000	0.05100	1.00000	0.06400	1.00000

Cr		Mn		Fe	
8202.38570	0.01744	8942.20450	0.01735	9681.55780	0.01734
1236.14170	0.12223	1349.53410	0.12147	1462.93710	0.12116
279.45976	0.44112	305.12756	0.43995	331.23409	0.43915
74.64946	0.55373	81.47958	0.55547	88.51745	0.55636
113.04901	−0.10275	123.18655	−0.10350	133.94476	−0.10404
12.10562	0.61455	13.26301	0.61664	14.41127	0.62402
4.91484	0.45667	5.41452	0.45456	5.89214	0.44721
8.97530	−0.21547	9.96002	−0.21635	11.00896	−0.21648
1.39391	0.71132	1.54559	0.71579	1.70169	0.72007
0.54204	0.41612	0.59852	0.41221	0.65629	0.40801
0.82403	−0.15539	0.89872	−0.15042	1.01804	−0.14875
0.10171	0.66141	0.11325	0.62670	0.11565	0.65458
0.03768	0.43736	0.04148	0.47216	0.04152	0.44114
320.00543	0.02966	350.90076	0.02945	382.54807	0.02946
74.65599	0.18702	82.49562	0.18480	90.12127	0.18452
22.72988	0.50553	25.24733	0.50380	27.72601	0.50310
7.46507	0.45720	8.32031	0.45991	9.18163	0.45977
3.29183	0.32018	3.69644	0.31958	4.12369	0.31849
1.21555	0.56007	1.37024	0.55857	1.53455	0.55679
0.44022	0.24745	0.49698	0.24933	0.55712	0.25213
17.30726	0.06937	19.27490	0.07231	22.20877	0.07059
4.61165	0.28560	5.17497	0.29390	5.98035	0.29262
1.39157	0.48650	1.56964	0.48938	1.81577	0.49204
0.37588	0.48322	0.42489	0.47034	0.48788	0.47008
0.07500	1.00000	0.08200	1.00000	0.09000	1.00000

of the $4s$ orbital defined in a similar manner as the $3d$ orbital given by eq. (3). The exponents of polarization functions for all first row atoms for both configurations are displayed in Table V.

AUXILIARY BASIS SETS

Charge Density Basis Set (CDB)

The variational method of Dunlap et al.[1] allows the calculation of the coulomb energy

Table IVb (continued)

Co		Ni		Cu	
10508.12200	0.01722	11327.28000	0.01719	12142.27200	0.01721
1584.80880	0.12079	1708.59620	0.12054	1832.03920	0.12064
358.34054	0.43888	386.48341	0.43837	414.76010	0.43839
95.78245	0.55694	103.37109	0.55756	111.08396	0.55729
144.70511	−0.10481	156.52892	−0.10520	168.07095	−0.10588
15.72993	0.62195	16.95325	0.63029	18.38177	0.62837
6.46364	0.44944	6.96644	0.44109	7.58397	0.44322
12.03824	−0.21772	13.15577	−0.21772	14.28314	−0.21846
1.87783	0.71714	2.05207	0.71808	2.24355	0.71415
0.72217	0.41217	0.78631	0.41148	0.85829	0.41622
1.06680	−0.14050	1.14100	−0.13476	1.26249	−0.13414
0.12736	0.60863	0.13437	0.59679	0.13855	0.59792
0.04544	0.48696	0.04741	0.49737	0.04856	0.49414
419.66753	0.02906	456.94540	0.02881	490.21874	0.02909
98.51056	0.18419	107.29738	0.18338	115.19785	0.18492
30.27435	0.50453	33.02087	0.50462	35.55666	0.50639
10.05238	0.45827	10.99277	0.45837	11.88484	0.45434
4.53538	0.32277	5.00229	0.32141	5.36513	0.33538
1.68534	0.55604	1.86342	0.55472	1.97971	0.55527
0.61154	0.24878	0.67557	0.25168	0.71494	0.23760
24.30815	0.07308	26.87577	0.07380	28.82532	0.07712
6.57952	0.29938	7.29857	0.30252	7.86096	0.31043
2.00237	0.49319	2.22334	0.49460	2.39787	0.49504
0.53749	0.46150	0.59453	0.45718	0.64104	0.44780
0.09700	1.00000	0.10400	1.00000	0.11000	1.00000

with the positive definite error Δ_c:

$$\Delta_c = \frac{1}{2} \iint (\rho(1) - \tilde{\rho}(1))$$
$$\cdot (\rho(2) - \tilde{\rho}(2))/r_{12}\, d\tau_1\, d\tau_2 \qquad (4)$$

where ρ is the accurate density and $\tilde{\rho}$ is a fit:

$$\tilde{\rho} = \sum_n^M a_n f_n. \qquad (5)$$

In the present case of a spherical atom f_n is a normalized $1s$ GTO:

$$f_n = N \exp(-\alpha_n r^2). \qquad (6)$$

We ruled out the possibility of using ns ($n = 2, 3$) GTOs in eq. (5) since most molecular programs work only with $1s$ GTOs. Having the numerical density ρ for the atom we optimize the exponents α_n and coefficients a_n to minimize the error Δ_c, subject to the normalization constraint:

$$\int \tilde{\rho}(1)\, \delta\tau_1 = N \qquad (7)$$

where N is the total number of electrons.

The LS procedure of obtaining the auxiliary sets through fitting to the charge density and its cube root was already introduced by Dunlap et al.,[25] but was later abandoned

because numerical instabilities were encountered. Since we are dealing with the optimization of a rather large number of nonlinear parameters it turned out to be necessary in the first step to constrain these parameters by an even-tempered expansion:

$$\alpha_i = c\alpha^{i-1}. \qquad (8)$$

The linear parameters are determined from the condition:

$$\frac{\delta\Delta_c}{\delta a_i} = 0 \qquad i = 1, 2 \ldots n. \qquad (9)$$

However, a non even-tempered expansion fits the density much better (Table VI), so

Table V. Polarization functions (p type) for transition metal atoms in $3d^{n-1}4s^1$ and $3d^{n-2}4s^2$ configurations.

		$3d^{n-1}4s^1$		
Sc	Ti	V	Cr	Mn
0.0765	0.0855	0.0951	0.1051	0.1129
Fe	Co	Ni	Cu	
0.1210	0.1266	0.1351	0.1410	
		$3d^{n-2}4s^2$		
Sc	Ti	V	Cr	Mn
0.0833	0.0951	0.1051	0.1183	0.1294
Fe	Co	Ni	Cu	Zn
0.1381	0.1440	0.1531	0.1594	0.1690

Table VI. The effect of CDB optimization on the coulomb energy error (Δ_c), orbital energies and the average value of r for the Cr atom.

Auxiliary Set[a]	Δ_c(eV)	Δ_0[b](eV)	Δ_r(a.u.)[c]
20, even	1.2(−5)[d]	−5.4(−3)	−1.1(−4)
15, even	1.3(−3)	−1.5(−1)	−1.8(−3)
15, full	7.0(−6)	−2.7(−3)	−6.5(−5)
10, even	1.6(−2)	−2.1(−1)	−2.2(−3)

[a]Number means M term expansion in eq. (5), even stands for even-tempered, and full for fully unconstrained optimization.

[b]$\Delta_0 = \max_i (\int \rho_i(1)(\tilde{\rho}(2) - \rho(2))/r_{12}\,d\tau_1\,d\tau_2)$ where i runs over all atomic orbitals.

[c]$\Delta_r = (1/N)\int r(\tilde{\rho}(1) - \rho(1))\,d\tau_1$.

[d]The notation $x\,.\,y(-z)$ means $x\,.\,y \times 10^{-z}$.

in the next step we partially released that constraint, thereby easily obtaining the final fit.

To describe angular deformations of the charge density in molecular environments, additional p and d GTOs have to be used. These were obtained by using the LS procedure to fit the radial functions to the valence charge density. This fit was normalized to the number of electrons associated with the valence orbitals. In our case $3d$ and $4s$ were treated as valence orbitals. Since the valence region of the atom changes most on molecular formation, we expect that this is a proper approach.

One might also consider taking account of angular deformations by introducing off-center auxiliary functions into molecular calculations as advocated, for example, by Dunlap et al.[1] We have elected not to consider this possibility for several reasons. First, the potential danger of introducing an imbalance into the basis sets through the use of bond functions is widely appreciated. Second, there is no obvious way of optimizing such functions; certainly not on the basis of atomic calculations. They are typically introduced in an *ad hoc* fashion. Finally, we simply find no need for the added complications of bond functions. The atom-centered sets proposed here, including the polarization functions, yield an acceptable accuracy for our purposes (see Part II) and they are reasonably economical. If higher accuracy is needed, or if future calculations for other molecules show that they require improvement, they should, and can, be supplemented with further atom-centered functions.
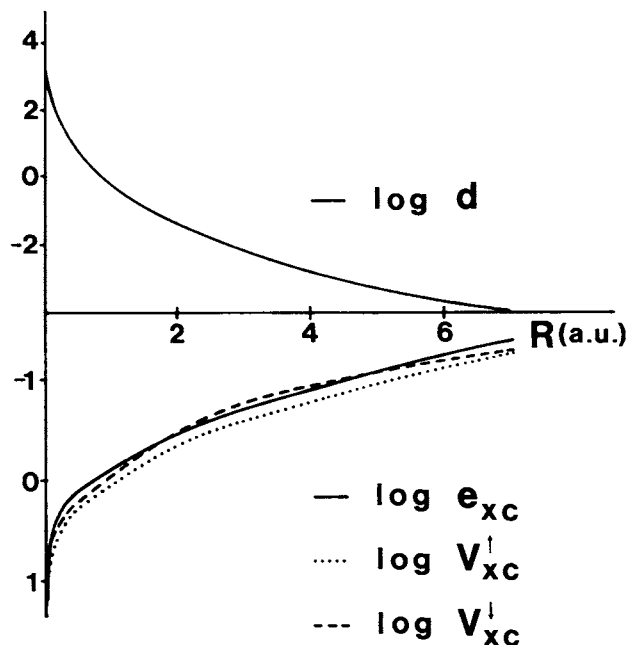

Figure 1. Electron density (d), exchange-correlation potentials (V_{xc}) and exchange-correlation energy density (e_{xc}) vs radius for the chromium atom.

Exchange-correlation Basis Set (XCB)

The LSD-VWN exchange potentials and the corresponding energy density are shown in Figure 1. They are much more slowly varying functions than the density. The fact that the exchange correlation potentials $V_{xc}^{\uparrow}$, $V_{xc}^{\downarrow}$, and energy density e_{xc} plots are close to each other justifies the use of a common set of auxiliary functions to fit all these quantities:

$$\tilde{U} = \sum_n^M a_n f_n \qquad U : \tilde{V}_{xc}^{\uparrow}, \tilde{V}_{xc}^{\downarrow}, \tilde{e}_{xc}. \qquad (10)$$

In the present approach the fitting parameters are found through minimization of the error Δ defined as

$$\Delta = \Delta V_{xc}^{\uparrow} + \Delta V_{xc}^{\downarrow} + \Delta e_{xc} \qquad (11)$$

where

$$\Delta U = \sum_k \int_0^k \rho_u [U(\rho_u) - \tilde{U}(\rho_u)]^2\,d\tau; \qquad (12)$$

k runs over the Herman-Skillman mesh points and U stands for $V_{xc}^{\uparrow}$, $V_{xc}^{\downarrow}$, or e_{xc}, whereas ρ_u is $\rho^{\uparrow}$, $\rho^{\downarrow}$, or the pair $(\rho^{\uparrow}, \rho^{\downarrow})$, respectively. The normalization condition

$$\int \rho_u \tilde{U}(\rho_u)\,d\tau = \int \rho_u U(\rho_u)\,d\tau \qquad (13)$$

is used. The definition of ΔU [eq. (12)] together with the normalization constraint [eq. (13)]

Table VII. The effect of XCB optimization on orbital energies[a] for the Cr atom. Energies are in eV.

Auxiliary Set[b]	$\Delta_o, V_{xc}^{\uparrow}$	$\Delta_o, V_{xc}^{\downarrow}$	$\Delta_{o,e_{xc}}$
15, even	1.8(−3)	−5.4(−3)	−1.9(−3)
12, even	4.8(−2)	8.1(−3)	−3.9(−2)
12, full	−6.2(−3)	−4.9(−3)	3.6(−3)
10, even	4.7(−2)	3.0(−2)	−2.7(−2)

[a] $\Delta_{o,U} = {}^{\max_i} (\int \rho_{i,u}(\tilde{U}(\rho_u) - U(\rho_u)) d\tau)$ where i runs over all atomic orbitals.

[b] See footnote a to Table VI.

assures that the errors in exchange-correlation energies are minimized in eq. (11).

Similar to the case of the charge density fit, an even-tempered expansion is applied in the first step [eq. (8)], whereas the linear coefficients are obtained using the condition that the gradient of the error Δ be zero [eq. (9)]. Non even-tempered expansions appear to yield a better fit to the exchange-correlation potentials and energy density (see Table VII). However, since the fitted curves (see Fig. 1) are now much smoother

than the density curve it was found impossible to perform a fully unconstrained fit. Instead a partially unconstrained fit was done, details of which will be described elsewhere.[26]

In Table VII the quality of the fit measured by the errors in orbital energies is presented. Comparing those errors with corresponding ones from Table VI it can be concluded that a smaller expansion is sufficient for the exchange-correlation (XCB), than for the density (CDB) fit. We adopted the criterion of similarity of errors in orbital energies to combine XCB and CDB fits for molecular calculations.

Analogously to the case of CDB one has to provide d and p type functions for the XCB fit. In the present approach the exchange-correlation potentials and energy are defined for the valence region as a difference:

$$U_v(\rho_{\text{val}}) = U(\rho_{\text{total}}) - U(\rho_{\text{core}}) \qquad (14)$$

Then p and d type contractions are optimized using the LS procedure with a nor-

Table VIII. Density fit bases for atoms in $3d^{n-1}4s^1$, and $3d^{n-2}4s^2$ configurations; c, α represent parameters of even tempered expansion $(c\alpha^{i-1})$ and 1, 11, 12, and 13 are the indices of exponents optimized without the even-tempered constraint.

			$3d^{n-1}4s^1$		
i	Sc	Ti	V	Cr	Mn
1	0.0632	0.0698	0.0765	0.0837	0.0893
c	0.0731	0.0812	0.0901	0.0999	0.1093
α	2.4014	2.4006	2.4000	2.3992	2.4000
11	0.5326(3)	0.5970(3)	0.6690(3)	0.7486(3)	0.8291(3)
12	0.1722(4)	0.1944(4)	0.2197(4)	0.2477(4)	0.2769(4)
13	0.8380(4)	0.9482(4)	0.1075(5)	0.1218(5)	0.1368(5)
i	Fe	Co	Ni	Cu	
1	0.0984	0.1065	0.1142	0.1208	
c	0.1201	0.1309	0.1420	0.1522	
α	2.4001	2.4008	2.4022	2.4070	
11	0.9169(3)	0.1012(4)	0.1111(4)	0.1226(4)	
12	0.3077(4)	0.3425(4)	0.3786(4)	0.4220(4)	
13	0.1523(5)	0.1704(5)	0.1892(5)	0.2121(5)	
			$3d^{n-2}4s^2$		
i	Sc	Ti	V	Cr	Mn
1	0.0900	0.0807	0.0826	0.0895	0.0969
c	0.0993	0.0880	0.0916	0.1004	0.1099
α	2.3424	2.3772	2.3922	2.3945	2.3969
11	0.5179(3)	0.5766(3)	0.6568(3)	0.7351(3)	0.8219(3)
12	0.1588(4)	0.1846(4)	0.2148(4)	0.2423(4)	0.2738(4)
13	0.7616(4)	0.8951(4)	0.1050(5)	0.1188(5)	0.1351(5)
i	Fe	Co	Ni	Cu	Zn
1	0.1066	0.1154	0.1238	0.1325	0.1399
c	0.1212	0.1322	0.1432	0.1549	0.1651
α	2.3953	2.3963	2.3981	2.3992	2.4054
11	0.9060(3)	0.1001(4)	0.1100(4)	0.1205(4)	0.1328(4)
12	0.3030(4)	0.3375(4)	0.3739(4)	0.4123(4)	0.4598(4)
13	0.1497(5)	0.1676(5)	0.1864(5)	0.2064(5)	0.2317(5)

Table IX. Exchange-correlation fit bases for atoms in $3d^{n-1}4s^1$ and $3d^{n-2}4s^2$ configurations; c, α represent parameters of even-tempered expansion $(c\alpha^{i-1})$, and 1 is the first parameter optimized independently.

			$3d^{n-1}4s^1$		
i	Sc	Ti	V	Cr	Mn
1					0.0333
c	0.0173	0.0215	0.0266	0.0281	0.0382
α	2.8388	2.8043	2.7681	2.7915	2.7167
	Fe	Co	Ni	Cu	
1	0.0379	0.0423	0.0459	0.0487	
c	0.0444	0.0509	0.0578	0.0650	
α	2.6986	2.6839	2.6711	2.6610	
			$3d^{n-2}4s^2$		
i	Sc	Ti	V	Cr	Mn
1					0.0331
c	0.0171	0.0209	0.0260	0.0279	0.0401
α	2.8421	2.8149	2.7786	2.7949	2.6994
	Fe	Co	Ni	Cu	Zn
1	0.0362	0.0402	0.0448	0.0479	0.0506
c	0.0461	0.0519	0.0590	0.0651	0.0705
α	2.6848	2.6769	2.6631	2.6618	2.6675

Table X. Density fit bases (p and d functions) for atoms in $3d^{n-1}4s^1$ and $3d^{n-1}4s^2$ configurations.

			$3d^{n-1}4s^1$		
	Sc	Ti	V	Cr	Mn
$p1$	0.1309	0.1599	0.1854	0.2088	0.2275
2	0.4706	0.6343	0.7695	0.8937	1.0141
3	1.8782	2.2456	2.6295	3.0250	3.4409
$d1$	0.2134	0.2898	0.3668	0.4382	0.4985
2	1.2891	1.6390	1.9643	2.2585	2.5452
3	4.2324	5.2981	6.2647	7.1389	8.0287
	Fe	Co	Ni	Cu	
$p1$	0.2497	0.2747	0.3025	0.3315	
2	1.1137	1.2680	1.4101	1.5576	
3	3.8702	4.3212	4.7979	5.2969	
$d1$	0.5660	0.6405	0.7251	0.8175	
2	2.8564	3.1985	3.5755	3.9675	
3	8.9819	10.0139	11.1285	12.2772	
			$3d^{n-1}4s^2$		
i	Sc	Ti	V	Cr	Mn
$p1$	0.1383	0.1558	0.1801	0.1996	0.2178
2	0.3946	0.5211	0.7343	0.8872	1.0219
3	1.8974	2.2302	2.6185	3.0215	3.4355
$d1$	0.2013	0.2801	0.3408	0.3919	0.4478
2	1.6211	1.8340	2.3324	2.4679	2.7048
3	5.7020	6.2011	7.4902	7.7136	8.4123
	Fe	Co	Ni	Cu	Zn
$p1$	0.2414	0.2657	0.2920	0.3183	0.3447
2	1.1524	1.2888	1.4366	1.5870	1.7430
3	3.8715	4.3259	4.8063	5.3073	5.8340
$d1$	0.5084	0.5737	0.6450	0.7243	0.8110
2	3.0013	3.3227	3.6666	4.0313	4.4056
3	9.3316	10.3210	11.3708	12.4717	13.5918

malization constraint [eq. (13) with U replaced by U_v from eq. (14)].

It should be noted that, as was the case for the orbital basis, the optimization of the auxiliary set is based on minimizing errors with respect to atomic data obtained from a numerical calculation. There is hence no direct connection between the orbital set and the auxiliary sets, that is, no "recipe" such as that proposed by Dunlap et al.[1] In

Table XI. Exchange correlation fit bases (p and d functions) for atoms in $3d^{n-1}4s^1$ and $3d^{n-2}4s^2$ configurations.

$3d^{n-1}4s^1$

	Sc	Ti	V	Cr	Mn
$p\,1$	0.0681	0.0783	0.0715	0.0818	0.0862
2	0.2609	0.2937	0.2947	0.3366	0.3696
3	1.0001	1.1016	1.2156	1.3855	1.5839
$d\,1$	0.0899	0.1026	0.0945	0.1058	0.1110
2	0.4091	0.4767	0.4890	0.5566	0.6058
3	1.8615	2.2159	2.5316	2.9262	3.3071

	Fe	Co	Ni	Cu
$p\,1$	0.0944	0.1040	0.1143	0.1252
2	0.4105	0.4556	0.5023	0.5501
3	1.7863	1.9966	2.2085	2.4175
$d\,1$	0.1189	0.1281	0.1371	0.1458
2	0.6645	0.7280	0.7923	0.8563
3	3.7119	4.1369	4.5781	5.0279

$3d^{n-2}4s^2$

	Sc	Ti	V	Cr	Mn
$p\,1$	0.0542	0.0614	0.0677	0.0836	0.0788
2	0.2283	0.2563	0.2858	0.3432	0.3540
3	0.9623	1.0692	1.2064	1.4088	1.5905
$d\,1$	0.0724	0.0819	0.0901	0.1104	0.1047
2	0.3551	0.4131	0.4719	0.5689	0.5865
3	1.7416	2.0841	2.4712	2.9306	3.2863

	Fe	Co	Ni	Cu	Zn
$p\,1$	0.0888	0.1006	0.1131	0.1256	0.1384
2	0.3968	0.4448	0.4946	0.5448	0.5956
3	1.7730	1.9661	2.1630	2.3631	2.5638
$d\,1$	0.1152	0.1268	0.1376	0.1483	0.1581
2	0.6500	0.7193	0.7980	0.8579	0.9260
3	3.6688	4.0798	4.5135	4.9615	5.4228

principle one can merge a given orbital set with any auxiliary set. The accuracy, balance, and economy of the basis sets must ultimately be judged by their performance in molecular calculations. The tests described in Part II show that, for the first row transition metal atoms a (13/3/3) expansion pattern (13s, 3p, and 3d uncontracted functions) for CDB and XCB sets satisfies these criteria.

For the s type density set the even-tempered expansion with the largest and the smallest exponents being optimized has been used. For the exchange set in the even-tempered expansion, the smallest exponent has been allowed to change. The exponents and parameters for CDB and XCB sets for all first row transition metal atoms are displayed in Tables VIII–XI.

CONCLUSION

The compact basis sets introduced here for LSD calculations significantly improve the efficiency of LCAO-LSD calculations, thus extending the scope of these calculations to larger metal clusters. The present method of construction of both orbital and auxiliary sets allows the accuracy of these sets to be increased in a systematic way. Hence, the quality of basis sets used in LCAO-LSD calculations can be judged in a well-defined manner.

Although both the orbital and auxiliary basis sets have been optimized here within the LSD-VWN scheme, we expect that they are also suitable for other LSD potentials. These basis sets may change significantly if more sophisticated extensions of the LSD method such as those corrected for self-interaction[27] or including nonlocal and gradient terms[28,29] are applied. The present method of optimization of both orbital and auxiliary sets can easily accommodate the above mentioned improvements in the LSD scheme, as long as one can define and calculate atomic orbitals.

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