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Energy optimized Gaussian basis sets for the atoms Tl–Rn*

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Energy optimized Gaussian basis sets have been derived for the atoms Tl–Rn. Two sets are presented - a (20, 16, 10, 6) set and a (22, 17 13 8) set. The smallest sets yield atomic energies 107 to 123 mH above the numerical Hartree–Fock values, while the larger sets give energies 11 mH above the numerical results. Energy trends from the smaller sets indicate that reduced shielding by *p*-electrons may place a greater demand on the flexibility of *d*- and *f*-orbital description for the lighter elements of the series.

Key words: *Ab initio* LCGO-MO calculations — Gaussian basis sets

1. Introduction

The Gaussian type orbital (GTO), first introduced in quantum chemistry by Boys [1], is today the preferred type of basis function for the overwhelming majority of LCAO-MO calculations. The shortcomings of this type of function in the representation of atomic orbitals, are more than compensated for by its behavior in the evaluation of two-electron integrals - one of the heaviest computational tasks in this type of calculation [2–6].

During the last decade GTO basis sets have been derived for most of the elements of the periodic table, and although the quality may vary somewhat, it is usually possible to find a high-quality basis set for most atoms [7–9]. An exception to this is the post-lanthanide main group elements Tl–Rn. The only basis sets in the literature for these atoms [10] are contracted minimal basis sets with total energies more than 10 Hartrees above the numerical Hartree–Fock results of Froese-Fischer [11]. Although this is a small fraction of the total atomic energy, it is

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very large compared to "normal" chemical energies as manifested in binding energies and activation energies.

With the present advances in supercomputer technology there is no reason why this corner of the periodic table should not be accessible to high-quality LCAO-MO *ab initio* calculations. One objection might be that the relativistic effects play a large role for this group of elements [12–18] and the relativistic energy lowering is almost two orders of magnitude larger than the basis set error referred above. However, for most relativistic molecular calculations it will be of interest to have high-quality non-relativistic calculations available for comparison. Also, a number of groups have successfully used first order perturbation theory to estimate relativistic energy corrections from a non-relativistic wavefunction [18–20]. Finally, the basis sets suggested here are so flexible that good results may be expected also in applications using approximate one-component relativistic schemes [21–24].

On this background, the development of high-quality basis sets for the atoms Tl–Rn has been undertaken. The computational technique and strategy employed are briefly summarised below, followed by a discussion of the properties of the two series of basis sets developed in full. One set contains 20 *s*-orbitals, 16 *p*-orbitals, 10 *d*-orbitals, and 16 *f*-orbitals, denoted (20, 16, 10, 6), the other is a (22, 17, 13, 8) set.

2. Computational details and results

The investigation reported here was carried out using computer programs described previously [25]. These programs use a scaled Newton–Raphson algorithm in the search for a minimum on the energy hypersurface. The Hessian required for these calculations is obtained either analytically (closed shells) or numerically (open shells).

As a first step a number of basis sets of varying size were optimized for Rn. Some results of this variation are presented in Table 1 which shows how the total atomic

Table 1. Variation of total energy with basis set size for the ground state of Rn. ΔE is deviation from the numeric Hartree–Fock result of −21866.772 H (Ref. [11])

Basis set	ΔE (H)	Basis set	ΔE (H)
s-variation		*d*-variation	
23, 18, 10, 7	0.067	21, 17, 13, 7	0.019
22, 18, 10, 7	0.068	21, 17, 12, 7	0.022
21, 18, 10, 7	0.070	21, 17, 11, 7	0.022
20, 18, 10, 7	0.076	21, 17, 10, 7	0.073
p-variation		*f*-variation	
21, 19, 10, 7	0.067[a]	23, 18, 10, 8	0.062
21, 18, 10, 7	0.070	23, 18, 10, 7	0.067
21, 17, 10, 7	0.073	23, 18, 10, 6	0.092
21, 16, 10, 7	0.079	23, 18, 10, 5	0.213

[a] Estimated from unpublished calculations on Pb

energy depends on basis set size. On the basis of this it is possible to choose a set conforming to specified criteria. One obvious criterion is the total energy, which should be as low as possible with the minimum number of basis functions. Two basis sets for comparable atoms are Huzinaga's (16, 12, 8) set for Xe [26], and the Yb (21, 15, 10, 8) set of van Piggelen et al. [27] - these sets yield total atomic energies respectively 0.143 and 0.019 H above the numerical results of Froese-Fischer [11]. By comparison, the total energies of the Wachters' (14, 9, 5) basis sets for Sc and Zn are respectively 0.014 H and 0.089 H above the numerical results.

Another criterion which may be applied to basis set selection is that of energy-balance. The description of orbitals of different symmetry should be of approximately the same quality. In practice this means that adding one basis function to the set should give the same lowering of the total energy regardless of which symmetry the function belongs to. For basis sets in the range presented in Table 1 the total energy is strongly dependent on the number of functions used to describe *d*- and *f*-orbitals. This is unfortunate - basis functions with high angular momentum quantum numbers generally lead to longer integral evaluation times, and it is therefore desirable to keep the number of such functions low. Their energetic importance is due partly to the large number of electrons in *d*- and *f*-shells, and for cases where these would not be expected to be chemically active, *d*- and *f*-shells may possibly be described with less accuracy than the rest of the atom. However, these are high-lying shells, and the possibility of introducing a superposition error should be considered.

One would also like to ensure a certain minimum of flexibility in the wavefunction. A normal requirement is to demand at least a double zeta description of the valence orbitals [29]. The possible effects of multiple minima on the energy hypersurface in this connection has been discussed elsewhere [30].

On the basis of such criteria and the data in Table 1, two sets of GTO basis functions have been derived for the atoms Tl-Rn. The smallest of these - (20, 16, 10, 6) - is slightly unbalanced in the sense that the *d*- and *f*-shells are not as accurately described as *s*- and *p*-shells. Thus, the addition of one more *d*-function leads to an energy lowering of 39 mH, an *f*-function yields 24 mH, whereas *s*- and *p*-orbitals would only contribute 6 mH. Comparing total atomic energies to the numerical results of Froese-Fischer [11] (Table 2) it is seen that the accuracy of this set is slightly poorer than Wachters' transition metal sets [28]. The large set - (22, 17, 13, 8) - is reasonably well-balanced and produces total atomic energies only 11 mH above the numerical reults. An increase of basis set size beyond this should probably concentrate on the addition of polarization functions which may be of greater importance for molecular applications than a further refinement of the description of the atom.

There is a slight difference in the convergence criteria used for the optimizations of the two sets. Optimization is carried out in the space of the logarithm of the orbital exponents as described previously [3]. While the smaller sets have been optimized to the stage where all gradient in this space are smaller than 10^{-5}, the large sets have only been optimized on the basis of a stable energy. Consequently some of the more diffuse orbitals may have gradient components of magnitude

Table 2. Total ground state energies for the atoms Tl-Rn obtained with (20, 16, 10, 6) and (22, 17, 13, 8) basis sets. ΔE is the deviation from the numeric Hartree-Fock values of Froese-Fischer (Ref. [11]). All energy values are in Hartrees

	(20, 16, 10, 6)		(22, 17, 13, 8)	
Atom	$-E$ (GTO)	ΔE	$-E$ (GTO)	ΔE
Tl	18961.70248	0.123	18961.81431	0.011
Pb	19523.89055	0.117	19523.99779	0.011
Bi	20095.47266	0.113	20095.57636	0.010
At	20676.38980	0.111	20676.49061	0.011
Po	21266.77260	0.109	21266.87119	0.011
Rn	21866.66467	0.107	21866.76154	0.011

10^{-3}-10^{-4}. Thus, if the criterion used by Mezey and co-workers [31-33] is applied, the large sets may be regarded as somewhat unbalanced. This is not expected to have any great effects on the quality of the wavefunction.

One interesting feature of Table 2 is the gradual improvement in total energy relative to the numerical results for the (20, 16, 10, 6) sets as the atomic number increases. This is contrary to previous experience with the transition metal basis sets where the increasing number of *d*-electrons leads to a poorer energy value as one moves from Sc to Zn without increasing the number of *d*-orbitals in the basis set [28, 30]. This effect may be further analyzed by considering the energy changes obtained using basis sets derived by substituting the functions of one symmetry from the (22, 17, 13, 8) set into the (20, 16, 10, 6) set to get (22, 16, 10, 6) sets etc. The results from calculations using such basis sets for Tl and Rn are presented in Table 3. The difference in energy when increasing the *s*- or *p*-orbital basis is rather small, and in the expected direction - most important for the heaviest atom. With the relatively large *s* and *p* basis sets, this is not surprising. Increasing the *d*- and *f*-orbital sets, however, gives considerably larger energy shifts for the ligher elements. Considering that the number of *d*- and *f*-shell electrons is the same for Tl and Rn, the nature of this differential energy shift must differ from that of the first-row transition metals where the increase in number of *d*-electrons requires a better *d*-orbital description for heavy elements

Table 3. Energy changes relative to total atomic energy obtained with (20, 16, 10, 6) set for Tl and Rn using derived basis sets and the optimized (22, 17, 13, 8) set. All energies in mH

Basis set	ΔE (Tl)	ΔE (Rn)	ΔE (Tl)-ΔE (Rn)
20, 16, 10, 6	0.00	0.00	0.00
22, 16, 10, 6	6.95	7.42	−0.47
20, 17, 10, 6	3.90	4.58	−0.68
20, 16, 13, 6	66.54	55.06	11.48
20, 16, 10, 8	33.67	29.78	3.89
22, 17, 13, 8	111.83	96.87	14.96

to maintain the same accuracy as for the light ones. Inspection of orbital energies shows that the difference between the (20, 16, 10, 6) and (22, 17, 13, 8) basis values for Tl is 15, 14, and 9 mH for 3d, 4d, and 5d respectively, while the corresponding numbers for Rn are 9, 8, and 6 mH. One possible explanation for this may be that the reduced screening effect of the *p*-electrons in Tl as compared to Rn places a greater demand on the flexibility in the *d*-basis.

No attempts have been made to investigate possible contraction schemes for these basis sets. As they stand they may either be used uncontracted, or with a general Raffenetti type contraction [34]. The use of a segmented contraction for these basis sets is probably unwise, as this may destroy important features of the nodal structure of *L* and *M* shell orbitals.

A copy of the basis sets may be obtained from the author on request.

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