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Optimization of Gaussian basis sets for Dirac–Hartree–Fock calculations

Kenneth G. Dyall[1], **Knut Fægri, Jr.**[2]

[1] Thermosciences Institute, NASA Ames Research Center, MS STC 230-3, Moffett Field, CA 94035-1000, USA
[2] Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo 3, Norway

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Abstract. We investigate the optimization of Gaussian basis sets for relativistic calculations within the framework of the restricted Dirac–Hartree–Fock (DHF) method for atoms. We compare results for Rn of nonrelativistic and relativistic basis set optimizations with a finite nuclear-size. Optimization of separate sets for each spin-orbit component shows that the basis set demands for the lower j component are greater than for the higher j component. In particular, the $p_{1/2}$ set requires almost as many functions as the $s_{1/2}$ set. This implies that for the development of basis sets for heavy atoms, the symmetry type for which a given number of functions is selected should be based on j, not on ℓ, as has been the case in most molecular calculations performed to date.

Key words: Basis set optimization – Relativistic basis sets – Dirac–Hartree–Fock

1 Introduction

There has been increasing interest in the past fifteen years in finite basis set approaches to the solution of the Dirac–Hartree–Fock (DHF) equations for molecules [1–12]. The computational demands of finite basis molecular DHF calculations are large, due to the necessity of providing a basis set for the small component as well as for the large component of the wave function. In terms of atomic symmetries, the small component basis requires functions which have one more and one less unit of angular momentum than the corresponding large component functions; thus basis sets for DHF calculations may be approximately four times larger than the corresponding basis sets for nonrelativistic calculations. For atoms, where the spherical symmetry can be fully exploited, this is not a great difficulty, but for molecules it becomes critical, as the number of two-electron integrals required increases as the fourth power of the number of basis functions. Since relativistic effects are most important in heavy atoms, a large number of basis functions will be needed to describe the core region where relativistic effects dominate. It is therefore imperative to minimize the number of basis functions required in DHF calculations, so that the range of problems which can be tackled is not unduly restricted.

There are several issues to be considered when discussing adequacy of basis sets for DHF calculations. The first has been alluded to, namely, the size of the basis set. It is well known that fully optimized basis sets are smaller than even-tempered basis sets for a given accuracy in the total atomic energy, and smaller than the well-tempered sets of Huzinaga [13–15], which mimic the fully optimized sets more closely. A second issue is that unmodified nonrelativistic basis sets are deficient in the core region, particularly for $p_{1/2}$ spinors [16, 17]. The importance of a high-quality description of the core region is also evident from the work of Schwarz et al. [18] which shows that for all orbitals the relativistic effects have their chief contributions near the nuclei. For "normal" heavy elements the addition of a few extra functions remedies the deficiency – but it is likely that re-optimization of the basis will obviate the necessity for the extra functions. For superheavy elements there are computational indications that simple addition of functions without reoptimization is insufficient [19]. It may be argued that the core region is unimportant chemically, and a small deficiency in the core may be tolerable [20], but there is also the possibility of spurious results due to the contribution of a basis function on a neighboring center to the core deficiency, resulting in a large basis set superposition error. A third issue is that even in the outer shells, relativistic effects can cause significant change in the positions of nodes and antinodes. Therefore a function which describes part of a maximum in a nonrelativistic calculation may be of no value in a relativistic calculation because its position is in the region of a node. A fourth issue is that in making comparisons of nonrelativistic and relativistic calculations, equivalent calculations should be done in equivalent basis sets [20]. If a non-relativistic calculation is done with a fully optimized basis set, the relativistic calculation should also, strictly speaking, be done in a fully optimized basis set. The issue of deciding what is an equivalent basis set is a difficult one because of the different requirements of the Dirac and Schrödinger Hamiltonians. In general, the best nonrelativistic basis sets are optimized to obtain similar truncation errors in each of the angular spaces. When using the Dirac Hamiltonian, the angular spaces are defined by the kappa quantum number, and the requirements for spaces of different kappa but the same orbital angular momentum can be quite different. Although the separate optimization of functions for the spin-orbit components of a shell would not lead to efficient basis sets, it is of interest to determine how different the requirements of the spin-orbit components are.

Thus far, few attempts at relativistic basis set optimization for atoms have been published. In the work of Mark [21], Lee et al. [22] and more recently of Minami and Matsuoka [23], exponents were optimized by fitting the basis to numerical atomic DHF functions. Mark's optimizations were limited to the atoms He to Ne; Lee et al. optimized Slater basis sets for highly-charged U, but not for the neutral atoms, which has been done by Minami and Matsuoka for the elements Rn–Pu as well as for some of the positive ions. Ishikawa and coworkers showed that the use of a finite nucleus instead of a point nucleus allowed for more compact basis sets [24] and also eliminated problems with basis set balance close to the nucleus [25]. Visser et al. [26] performed a full relativistic optimization of exponents for the one-electron atoms Sn and U with and without a finite nucleus, showing that the use of a finite nuclear radius significantly decreased the maximum exponent. (This is a general feature of finite nucleus models and not peculiar to relativistic calculations.) In the work of Matsuoka and Huzinaga [27], the parameters of well-tempered sets were optimized for He to Ne and Ar at the DHF level. They found that the nonrelativistically optimized well-tempered sets gave essentially identical energies, and concluded that for atoms up to Xe, nonrelativistic basis sets were adequate. In the past few years, Malli et al. [28] have obtained universal Gaussian basis sets which are essentially even-tempered sets; the optimization is presumably limited to the choice of the range and density of the basis set, though no explicit mention of this is made. Chandra and Hess [29] have recently performed an energy-based basis set optimization on the Au atom with the Douglas–Kroll-transformed Dirac Hamiltonian truncated at second order in the external potential. They found considerable changes in the core exponents, and the necessity for a finite nucleus became apparent in their work.

In order to undertake a more systematic exploration of energy optimized Gaussian basis sets for relativistic calculations we have developed a DHF program using a mixed analytic and numerical approach to exponent optimization. In the next section we provide a brief description of the program and the underlying principles. Some of the issues involved in the selection and optimization of a basis set are discussed in Sect. 3. The Rn atom is used as a test case for demonstrating the effect of the various approaches to energy optimization of relativistic basis sets, and the results are presented in Sect. 4.

2 Theory and implementation

The energy-optimization of the exponents of a basis set in relativistic calculations depends on the existence of some kind of bound on the energy, so that it may be minimized without fear of variational collapse. In many places it is asserted that since the Dirac Hamiltonian is unbounded from below the possibility of collapse is always present. However, Grant [30] has shown that there is a bound on the Dirac–Fock energy in a finite basis, which is the minimum of the potential energy, so that collapse into the negative continuum cannot occur. This is not a very useful bound for the purposes of energy optimization. In fact, it has been pointed out by Talman [31] that the Dirac–Fock energy is a minimum in the space of large component parameters, but a maximum in the space of small component parameters. Equivalently, in a 4-spinor basis, it is a minimum in the space of the parameters of the positive energy states, but a maximum in the space of the parameters of the negative energy states. This means that the orbital Hessian has as many negative eigenvalues as there are negative energy states, and the optimization of the orbitals is equivalent to convergence to an excited state, for which the exact energy is not a lower bound, but for which the energy does not usually go far below the exact energy if orthogonality to the lower states is maintained. In the relativistic case, this is ensured by the application of kinetic balance [32–35].

Kinetic balance has important implications for the exponent space also. Its use to define the small component basis in terms of the large component basis means that there is only *one* exponent parameter space for *both* components. This is in contrast to the work of Talman, who used different exponents for large and small components. With kinetic balance, each basis function can be regarded as a product of a single Gaussian function multiplied by a 4-component vector which contains the angular dependence of the spinor as well as the linear variation parameters (spinor coefficients). This is an implicit projection onto the positive energy states in exponent space. The problem of collapse therefore does not arise in the context of exponent optimization with kinetic balance: the Hessian with respect to the exponents should be positive definite at convergence, corresponding to a minimum in the energy. This has been verified by experience.

The approach to basis set optimization employed in this paper is essentially the same as that of Fægri and Almlöf [36], employing analytic gradients and a scaled Newton–Raphson procedure. Here, the analytic gradient of the energy with respect to the natural logarithms of the basis function exponents is calculated at each point in the optimization process, and the Hessian is evaluated by finite differences of gradients. A search direction is defined by assuming the hypersurface is quadratic in the exponent parameter space and solving the appropriate equation. The Hessian is inverted by first diagonalizing it, then inverting the eigenvalues and back-transforming. By this means, a check can be made on the Hessian index, and directions corresponding to negative eigenvalues of the Hessian excluded from the search, or dealt with in some other manner. A minimum along the search direction is then located, and the procedure repeated until convergence is obtained or the optimization process fails.

The method has been implemented for closed shell systems as a subprogram of the package GRASP [37], and makes use of both the angular momentum algebra packages and the numerical integration routines within the program. The formulation of the energy has been modified so that orbitals from the same shell (same occupation numbers and symmetry) can be derived from a single Fock matrix: thus we write the energy as

$$E = \sum_{a=1}^{n} q_a I(a, a) + \frac{1}{2} \sum_{a,b=1}^{n} q_a q_b F^0(a, b) + \frac{1}{2} \sum_{a,b=1}^{n} \sum_{k} g_{ab}^{k} G^k(a, b) \tag{1}$$

where the (zero) diagonal term

$$q_a(F^0(a, a) - G^0(a, a)) \tag{2}$$

has been added, and the g_{aa}^k are simply related to the f_{aa}^k. The reader is referred to Ref. [37] for definitions of the terms in the energy expression. In the construction of the two-electron part of the Fock matrices in the finite basis, the contraction of the density with the two-electron integrals has been replaced by the numerical evaluation of integrals over the appropriate potentials, with the basis functions tabulated on the grid used in the numerical procedures. The atomic functions a on the first SCF cycle are taken to be the converged numerical solutions. Thereafter they are constructed from the tabulated Gaussian basis functions and their coefficients, after each SCF iteration. The method is therefore equivalent to direct SCF methods [38]. The two-electron Hellmann–Feynmann contributions to the gradients may be evaluated in a similar fashion, by substituting for one of the basis functions its derivative with respect to the natural logarithm of its exponent. The derivative functions are tabulated for this purpose. Use of the converged numerical solutions provides an excellent starting estimate of the wave function for the finite basis calculations: for a basis set of good quality only a few SCF iterations are required to reach convergence in the energy. For numerical accuracy it was found necessary to increase the number of grid points over the GRASP default by a factor of 5, and to converge the eigenvectors to as small a threshold as possible (about 10^{-10}). A Gaussian nuclear charge distribution with RMS radius (in fm) given in terms of the atomic mass number A by $\langle r^2 \rangle^{1/2} = 0.836\, A^{1/3} + 0.570$ [39] has been used in all finite nucleus calculations. All DHF calculations were done with a finite nucleus.

The choice of the starting set of exponents for basis set optimization is critical in obtaining convergence and avoiding the many local minima on the hypersurface. It has been noted that the inner exponents in nonrelativistic optimizations with a point nucleus occur in fixed ratios, essentially independent of atomic number and basis set size [40]. While this behavior is not evident for the finite nucleus, there is still a pattern of decreasing ratios between adjacent exponents with decreasing exponent size among the inner exponents [41]. A simple scaling of the nonrelativistic exponents obtained in finite nucleus optimizations may thus provide a good starting guess for the relativistic optimization. Moreover, reducing the number of parameters in the initial stages of the optimization may help convergence. The program therefore includes an option to minimize the energy with respect to a scaling parameter for each angular type in the basis.

Another important feature built into the program is the ability to force several sets of exponents to be equal. This will enable, for example, a common p set to be determined for $p_{1/2}$ and $p_{3/2}$ spinors, or a common set determined in the valence space where it would be uncontracted in a molecular calculation, with different core exponents for $p_{1/2}$ and $p_{3/2}$, or a completely different set for each spin-orbit component. It also permits a common exponent set for all angular types, or a common set for angular types of the same parity, as is used by Visser et al. [42].

3 Strategy

There are several important considerations in the task of basis set optimization. The most important, from the point of view of the cost of the subsequent molecular integral calculations, is to minimize the number of primitive functions. In doing this, it is important to maintain balance between the different angular symmetries. A balanced basis set is one in which the addition of a function to any of the symmetries (followed by reoptimization) yields the same amount of energy-lowering for all angular symmetries [43]. The minimization of the number of functions must also be weighed against the need to have a sufficient number of functions that there are no major deficiencies in the basis, "major deficiencies" being dependent on the type and quality of calculation aimed for. As noted above, the optimization of relativistic basis sets must observe the kinetic balance condition. For present purposes, it is sufficient to use this condition in the form of the relation

$$\{\psi^{\mathrm{S}}\} \supseteq \{(\sigma \cdot p)\psi^{\mathrm{L}}\} \tag{3}$$

where $\{\psi^{\mathrm{L}}\}$ and $\{\psi^{\mathrm{S}}\}$ are the large and small component basis sets, respectively.

So far the usual approach to optimization of relativistic basis sets has followed the lines used for nonrelativistic primitive sets. The same primitive functions are used for both spin-orbit components of a given ℓ-value in the large component basis, and the small component set is generated by kinetic balance; in other words it contains the derivatives of the large component set. For a full cartesian basis of Gaussian functions the total number of primitive functions in the non-relativistic set is

$$N_{\mathrm{L}} = \sum_{\ell} n_{\ell} \frac{(\ell+1)(\ell+2)}{2} \tag{4}$$

where n_ℓ is the number of different exponents for symmetry ℓ. The strategy above will then yield a relativistic basis with a total of

$$N = 3N_{\mathrm{L}} + \sum_{\ell} n_{\ell} \tag{5}$$

primitive functions. For a "worst case" n^4 dependence in two-electron integral evaluation, this means an increase by a factor greater than 81 relative to the nonrelativistic case.

The number of basis functions may be reduced by introducing so-called "family" basis sets. In one such approach the basis functions are optimized with the constraint that for the large component basis the exponents for the functions of $(\ell + 2)$ symmetry should be a subset of the exponents for ℓ symmetry. This leads to two interleaving families of exponents (for odd and even ℓ respectively), and the $(\ell + 2)$ and ℓ large component functions have common small component basis functions of angular momentum $(\ell + 1)$. The total number of basis functions in this approach is

$$N = 2N_{\mathrm{L}} + \sum_{\ell} n_{\ell}(\ell + 2) + n_p \tag{6}$$

which is a considerable improvement over what we obtained from a simple application of the gradient operator to the nonrelativistic basis set. It should be noted that the reduction comes only in the small component set: the large component set is the same size as the nonrelativistic basis in the previous example.

For relativistic calculations there is really no requirement that the two spin-orbit components of a given ℓ should have the same exponents. An alternative is to optimize exponents for each j-value. This yields the same set of exponents for $s_{1/2}$ and $p_{1/2}$, for $p_{3/2}$ and $d_{3/2}$, etc. The advantage of this approach lies in the fact that the small component corresponding to $s_{1/2}$ is $p_{1/2}$ and vice versa, assuming here that the "contaminant" functions $r^{\ell+2}e^{-\zeta r^2}$ required for strict or minimal kinetic balance can be represented well enough by the "regular" functions $r^{\ell}e^{-\zeta r^2}$. Thus we need not worry about imposing kinetic balance, which will be fulfilled automatically, and the total number of primitive functions is

$$N = 2N_{\mathrm{L}} + \sum_{\ell} n_{\ell}(\ell + 2). \tag{7}$$

A further advantage of this approach derives from the need to increase the size of the $p_{1/2}$ basis set relative to the nonrelativistic p basis set due to the behavior of the $2p_{1/2}$ orbital close to the nucleus [16]. In an ℓ-based approach as described in the first two examples this would also lead to increases of the $p_{3/2}$ large component space and the $d_{3/2}$ small component space. In the j-based approach this feature is included in a natural manner. If the contaminant functions were required, the number of functions in a j-based approach would be similar to that for the ℓ-based approach in which the extra functions needed in the core were added.

The ultimate flexibility would be obtained by optimizing a set of exponents for each κ-value. This would yield basis sets which would rapidly prove prohibitively expensive for actual molecular calculations. However, in a study like this the κ-based sets may be explored for pedagogical purposes. In line with the discussion of the ℓ- and j-based approaches above, it will be of interest to investigate the properties of κ-based sets dimensioned either with equal number of functions for each j-value or for each ℓ-value.

To summarize the discussion in this section and to introduce some terminology which will be used in the discussion of the results, we note that the basic quantum number on which sets of exponents are defined is κ. These sets of exponents may be combined on the basis of the choice of one of the quantum numbers j or ℓ, or on a combination such as even or odd parity of ℓ. Thus, a j-based set will combine the sets for $\kappa = j + \frac{1}{2}$ and $\kappa = -(j + \frac{1}{2})$, and an ℓ-based set will combine the sets for $\kappa = \ell$ and $\kappa = -\ell - 1$. Because of these possible combinations, the selection of sets of exponents for optimization may differ from the distribution of exponents between quantum numbers. For the selection of a set of exponents for optimization, the term "x-based optimization" or "x-optimized" will be used. Thus, in a j-based optimization, functions with the same j value will have common exponents which are optimized. For the distribution of exponents between different quantum numbers the term "x-distributed" will be used. A set which is ℓ-distributed, for example, will have the same number of exponents for $j = \ell - \frac{1}{2}$ as for $j = \ell + \frac{1}{2}$. (Note that the ℓ value is that of the large component: kinetic balance takes care of the small component set.)

4 Results

To demonstrate the development of relativistic basis sets, we have selected the Rn atom, and start with the $22s17p13d8f$ basis set optimized by Fægri [44]. In all calculations, strict or minimal kinetic balance was employed; this corresponds to the equality in Eq. (3). The total energies and the errors in the total energy with respect to the basis set limit (i.e. the numerical HF or DHF value) for a number of basis sets of this structure are reported in Table 1. The nonrelativistic basis sets are accurate to about 10 mE_h. Using these basis sets in the standard way without modification, i.e. using ℓ-distribution, yields large errors. Optimizing the relativistic basis set on ℓ values with ℓ-distribution yields an error of 132 mE_h which shows that the basis set optimized in this way is not of the same quality as the nonrelativistic basis set. Even a κ-based optimization with ℓ-distribution gives an error of 86 mE_h. It is not hard to find the reason. Examination of the exponents reveals that the $p_{1/2}$ exponents are more spread out than the $p_{3/2}$ set, and the need for extra functions in the $p_{1/2}$ set is obvious. The alternative is to use a j-distribution rather

Table 1. Hartree–Fock and Dirac–Fock total energy of Rn atom with a $22s17p13d8f$ basis set optimized in various ways

Basis set description	Total energy (E_h)	Truncation error (E_h)
Hartree–Fock		
NR point nucleus	− 21 866.7614	0.0108
Numerical limit	− 21 866.7722	0.0000
NR finite nucleus	− 21 865.8432	0.0098
Numerical limit	− 21 865.8530	0.0000
Dirac–Fock		
NR point nucleus ℓ-distributed	− 23 600.1404	1.9638
NR finite nucleus ℓ-distributed	− 23 600.0444	2.0598
DF ℓ-optimized ℓ-distributed	− 23 601.9719	0.1323
DF κ-optimized ℓ-distributed	− 23 602.0191	0.0856
NR point nucleus j-distributed	− 23 601.9998	0.1044
NR finite nucleus j-distributed	− 23 601.9072	0.1970
DF j-optimized j-distributed	− 23 602.0836	0.0206
Numerical limit	− 23 602.1042	0.0000

than an ℓ-distribution. Using the nonrelativistic basis sets without reoptimization in this way (i.e. using the non-relativistic s-exponents also for the $p_{1/2}$, the nonrelativistic p-exponents for $p_{3/2}$ and $d_{3/2}$, etc.) gives an order of magnitude reduction in the error over the ℓ-distributed basis sets. Finally, the j-optimized j-distributed set gives a truncation error of 21 mE_h, which is much closer to the nonrelativistic truncation error. A κ-based optimization with j-distribution proved impractical due to the overrepresentation in low-j components of higher ℓ, i.e. $d_{3/2}$ and $f_{5/2}$, and was not explored further.

It is worthy of note that the differences between the numerically determined spinor eigenvalues and the basis set values for the j-optimized set vary by no more than a factor of 2 for all spinors, with values around 3 mE_h, and the differences between the eigenvalues for the spin-orbit components of any orbital differ by only a few hundredths of a millihartree. This is in contrast to the other optimizations, where the $p_{1/2}$ spinors have discrepancies a factor of 5 to 10 larger than the other spinors, and as a consequence the differences between the eigenvalues for the spin-orbit components of an orbital, which are an estimate of the spin-orbit splitting, are underestimated by a considerable amount. The accuracy of the spin-orbit splitting is improved in light atoms such as Ne by the adoption of a j-distributed basis set, but for heavy atoms, the unoptimized j-distributed set gives errors in the eigenvalue differences of the spin-orbit components of the order of a few millihartrees.

In addition to obtaining the best possible energy, we also require that the basis sets be balanced, i.e. the addition of a function to any angular type with reoptimization of the basis gives the same lowering in energy. Given that relativistic effects contract the core regions of the atoms but have much smaller effects on the valence region, it is possible that a basis set which is balanced in a nonrelativistic optimization will be unbalanced in a relativistic optimization. The degree of balance in the Rn basis set has been determined by addition of functions to each space. The calculations were done for ℓ-, j- and κ-based and distributed optimizations, and the results are summarized in Table 2–5.

Table 2 shows that the nonrelativistic $22s17p13d8f$ Rn set is reasonably balanced, perhaps somewhat overrepresented in the s-space, but this is due to the fact that the distribution was originally derived for a point nucleus. A better balance for a finite nucleus would be $21s18p13d8f$. Looking at Table 3 we see that whereas the $22s17p13d8f$ ℓ-distribution still is reasonably balanced for s, d and f orbitals, the p-space is underrepresented, and in the end requires almost as many functions as the s-space for balance to be restored. For the j-based $22j_{1/2}17j_{3/2}13j_{5/2}8j_{7/2}$ distribution, Table 4 shows a much better balance. The main modification required to balance the set is addition of one or two functions to the $j_{1/2}$ and $j_{3/2}$ spaces,

Table 2. Energy lowering $\Delta E = E_n - E_{n-1}$ in E_h for addition of the nth function in each symmetry in nonrelativistic finite nucleus basis set optimizations. Reference set is $22s17p13d8f$

s		p		d		f	
n	ΔE	n	ΔE	n	ΔE	n	ΔE
22	– 0.00153	17	– 0.00451	13	– 0.00384	8	– 0.00524
23	– 0.00056	18	– 0.00281	14	– 0.00138	9	– 0.00116
		19	– 0.00120				

Table 3. Energy lowering $\Delta E = E_n - E_{n-1}$ in E_h for addition of the *n*th function in each symmetry in relativistic ℓ-based finite nucleus basis set optimizations. Reference set is 22*s*17*p*13*d*8*f*

s		*p*		*d*		*f*	
n	ΔE	*n*	ΔE	*n*	ΔE	*n*	ΔE
23	– 0.00304	18	– 0.06184	14	– 0.00310	9	– 0.00154
24	– 0.00101	19	– 0.02816	15	– 0.00155		
		20	– 0.01317				
		21	– 0.00713				
		22	– 0.00464				
		23	– 0.00233				
		24	– 0.00114				

Table 4. Energy lowering $\Delta E = E_n - E_{n-1}$ in E_h for addition of the *n*th function in each symmetry in relativistic *j*-based finite nucleus basis set optimizations. Reference set is $22j_{1/2}17j_{3/2}13j_{5/2}8j_{7/2}$

$j = 1/2$		$j = 3/2$		$j = 5/2$		$j = 7/2$	
n	ΔE	*n*	ΔE	*n*	ΔE	*n*	ΔE
23	– 0.00516	18	– 0.00459	14	– 0.00122	9	– 0.00079
24	– 0.00251	19	– 0.00205	15	– 0.00042		
25	– 0.00136	20	– 0.00098				

which cover the regions most affected by relativistic contraction. Finally, Table 5 shows that if we optimize exponents for each κ-value separately, basis set balance comparable to that obtained for the nonrelativistic set in Table 2 requires one or two more $s_{1/2}$ functions, and at least four more $p_{1/2}$ functions.

Another consideration in the optimization of basis sets is the coefficient distribution. The nonrelativistic 22*s*17*p*13*d*8*f* Rn set has a valence double-zeta distribution in the *s* and *p* spaces, but addition of an extra *p* function changes the *p* space to triple zeta. In the attempt to obtain a balanced relativistic basis set using ℓ-optimization and distribution, the *p* set again becomes triple-zeta in the valence space. In the *j*-optimized and distributed basis set, the $p_{1/2}$ space remains double-zeta until about 24 functions, and is thereafter triple-zeta, whereas the $p_{3/2}$ space becomes triple-zeta with the addition of one extra function. The quality of a basis set for molecular calculations depends not only on the energy balance, but also on the coefficient distribution. Incautious use of ℓ-optimization may introduce a set of different valence quality than the corresponding nonrelativistic set. Any evaluation of relativistic corrections based on such sets would be of dubious value. Here, *j*-optimized sets appear to provide a basis set which is more nearly consistent with the nonrelativistic set, both in terms of the energy balance and the valence coefficient distribution.

Not only is the coefficient distribution of importance, but the relative magnitudes of the coefficients give an indication of the adequacy of the exponent set to describe the orbitals. In a double zeta description the significant antinode for an orbital is described by two Gaussians, and the coefficients for these two functions in

Table 5. Energy lowering $\Delta E = E_n - E_{n-1}$ in E_h for addition of the nth function in each symmetry in relativistic κ-based finite nucleus basis set optimizations. Reference set is $22s17p13d8f$

s		$p_{1/2}$		$p_{3/2}$		$d_{3/2}$		$d_{5/2}$		$f_{5/2}$		$f_{7/2}$	
n	ΔE	n	ΔE	n	ΔE	n	ΔE	n	ΔE	n	ΔE	n	ΔE
22	− 0.00879	18	− 0.03736	18	− 0.00321	14	− 0.00159	14	− 0.00114	9	− 0.00074	9	− 0.00079
23	− 0.00305	19	− 0.01647	19	− 0.00179	15	− 0.00066	15	− 0.00040				
24	− 0.00101	20	− 0.00715	20	− 0.00081								
		21	− 0.00326										
		22	− 0.00174										
		23	− 0.00113										
		24	− 0.00055										

Table 6. Expansion coefficients for the functions describing the outermost antinodes of the valence and outer core s and p orbitals for a variety of $22s17p13d8f$ basis sets

Method	Basis set description	$6s$	$6p_{1/2}$	$6p_{3/2}$	$5s$	$5p_{1/2}$	$5p_{3/2}$
HF	NR point nucleus	0.82		0.67	0.72		0.77
		0.53		0.50	0.82		0.35
DF	NR point nucleus ℓ-distributed	1.00	0.75	0.62	1.07	0.71	0.75
		0.28	0.32	0.53	0.44	0.21	0.34
DF	NR point nucleus j-distributed	1.00	0.75	0.62	1.07	0.81	0.75
		0.28	0.31	0.53	0.44	0.26	0.34
DF	ℓ-optimized	0.82	0.71	0.49	0.66	0.62	0.36
		0.54	0.47	0.69	0.83	0.61	0.80
DF	j-optimized	0.82	0.63	0.62	0.66	0.70	0.69
		0.54	0.50	0.56	0.83	0.40	0.55

the orbital expansion should also be balanced, i.e. the coefficients should be of similar magnitude. If one of these coefficients for a given orbital is quite small, this indicates that the corresponding function has more of a spectator role, and that the orbital description may be closer to single zeta. In Table 6 the coefficients of the two Gaussians describing the outermost parts of the valence and outer core *s* and *p* orbitals are reported for various basis sets. Simple transfer of the nonrelativistic basis gives a poorer description of the valence region, as evidenced by the large ratio of the coefficients. ℓ-optimization improves the valence description for the 6*s*, but cannot meet the different requirements of the $6p_{1/2}$ and $6p_{3/2}$. The *j*-optimized basis set gives valence coefficients which are the most balanced and the most similar to the nonrelativistic coefficients. Similarly, the 5*s* is not well described by the nonrelativistic basis sets, and requires a relativistic optimization to improve the description. The 5*p* orbitals seem to be well described by the nonrelativistic basis sets with either distribution, but ℓ-optimization produces an imbalance, which is restored by *j*-optimization. Here again, *j*-optimized basis sets provide the best description of the orbitals, and one which most closely corresponds to the nonrelativistic basis set.

5 Conclusions

Most available basis sets today have been optimized for nonrelativistic calculations, even those for very heavy atoms. For high quality relativistic work this is an unsatisfactory situation, becoming even more so the heavier the elements involved are. The present study points to some possible strategies to adopt in the optimization of relativistic basis sets. In particular, we believe that the use of *j*-based distributions hold considerable promise for the further development of such basis sets. This, as we have shown, probably also provides the most economical way of handling the problem with the $p_{1/2}$ space – a solution to which is critical to obtain a reliable energy from relativistic calculations, due to the great penetration of the $2p_{1/2}$ orbital. If nonrelativistic basis sets are to be used without modification, we recommend the use of *j*-based distributions rather than ℓ-based distributions. For accurate spin-orbit splittings, however, and for the best balance of the coefficients, *j*-optimization appears to give the best basis sets. In molecular calculations, *j*-distributed sets would be most efficiently implemented by use of a 2-spinor basis, either explicitly or implicitly.

We have not considered the use of "family" basis sets here in any detail. Qualitatively they will be expected to perform slightly poorer than the ℓ-based sets, but with a considerable saving in the number of basis functions as already pointed out. There are a number of variations on the theme of "family" basis sets, one of these being the possibility for a common set of exponents for the entire function space, in the manner used by Huzinaga and coworkers for their "well-tempered" basis sets. This would automatically provide for kinetic balance, and might also give increased efficiency to integral algorithms aimed specifically at this type of basis set. At present, molecular integral codes do not exploit kinetic balance to this extent, but in the future this may well turn out to be an important consideration in designing relativistic integral codes.

The computer program used by us for the present investigation is unfortunately too slow to be used in extensive derivation of energy optimized basis sets for relativistic calculations. We are presently working on a new program which we hope will be ready for production in the not too distant future. With properly optimized relativistic basis sets and integral codes designed to take advantage of the features characteristic of these sets, the field of finite basis molecular relativistic calculations should be strengthened considerably.

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