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Relativistic Gaussian basis sets for the atoms hydrogen to neon*

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Gaussian basis sets for use in relativistic molecular calculations are developed for atoms and ions with one to ten electrons. A relativistic radial wavefunction coupled to an angular function of l-symmetry is expanded into a linear combination of spherical Gaussians of the form $r^l \exp(-\alpha r^2)$. One set of basis functions is used for all large and small components of the same angular symmetry. The expansion coefficients and the orbital exponents have been determined by minimizing the integral over the weighted square of the deviation between the Dirac or Dirac-Fock radial wavefunctions and their analytical approximations. The basis sets calculated with a weighting function inversely proportional to the radial distance are found to have numerical constants very similar to those of their energy-optimized non-relativistic counterparts. Atomic sets are formed by combining l-subsets. The results of relativistic and non-relativistic calculations based on these sets are analyzed with respect to different criteria, e.g. their ability to reproduce the relativistic total energy contribution and the spin-orbit splitting. Contraction schemes are proposed.

Key words: Relativistic Gaussian basis sets — Dirac-Fock calculations

1. Introduction

The linear expansion of one-electron wavefunctions into a set of basis functions [1] has become the standard method of obtaining approximate solutions of the

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* Dedicated to Prof. Dr. A. Neckel on occasion of his 60th birthday

Schrödinger equation for molecular systems within the SCF or the MC-SCF approach. Basis sets covering a wide range of accuracy have been elaborated for the most commonly used basis functions, namely Gaussian type functions [2, 3] and Slater type functions [4], and a large amount of experience in choosing basis sets has been accumulated [5, 6]. In striking contrast, relativistic molecular calculations based on the linear expansion method have been reported only in 1980 [7-11] and have remained scarce [12-19]. A main concern of these contributions was to demonstrate and to overcome problems which arise when the Dirac equation is expanded into some basis of conventional functions. These problems are not caused primarily by the increased numerical difficulties posed by the four-component Dirac equation in comparison with the one-component Schrödinger equation. They have two origins:

(1) The Dirac equation expanded into some *incomplete* basis set does not reduce to the representation of the Schrödinger equation in the limit of an infinite velocity of light [20]. Hence, due to different basis set truncation errors in the relativistic and the non-relativistic calculations it is difficult to extract the relativistic effects at all.

(2) Negative energy state solutions may be admixed to the electronic wavefunction, when the Dirac Hamiltonian is used instead of a projected Dirac Hamiltonian [21-23].

Besides these fundamental problems, several difficulties of predominantly technical nature occur which are not encountered in the non-relativistic case:

(1) The number of atomic radial functions to be approximated is almost quadrupled since each relativistic one-electron state is represented by two radial functions and each state with angular momentum quantum number $l > 0$ is relativistically split.

(2) The radial wavefunctions of the states with a total angular momentum quantum number $j = \frac{1}{2}$ become infinite at the origin.

(3) There are more radial functions than in the non-relativistic case which are coupled to the same angular function and which have interlacing nodes.

(4) New types of functions with an pre-exponential factor $r^{(l-1)}$ occur.

(5) Basis functions have to be included into the atomic set with a maximal l-value which is larger by one compared with the non-relativistic case.

Thus, the greater complexity in the functional behaviour requires large and flexible basis sets and the development of computationally economic, i.e., short and accurate sets gains importance. A further aspect of the construction of relativistic basis sets is the fact that the total energy can no longer serve as a guideline as is usual in the non-relativistic case since the Dirac Hamiltonian is not bounded from below.

In the following, relativistic Gaussian basis sets are developed for the atoms of the first and second row by expanding the relativistic atomic radial wavefunctions into linear combinations of spherical Gaussians of the form $r^l \exp(-\alpha r^2)$. The parameters of these expansions, the orbital exponents and the linear combination coefficients, are obtained from a least-squares criterion, namely the minimized weighted square of the deviation between the exact function and its analytical approximation. Since relativistic effects on the wavefunction are small for low atomic numbers, a primary aim is to obtain basis sets which enable one to utilize a part of the acquired knowledge gained from non-relativistic calculations. In comparison with other attempts reported so far where either Slater type functions (STFs) [20, 24, 8, 25, 13, 14, 26–30] or Gaussian type functions (GTFs) [31, 9, 12, 16, 32–35] have been used as basis functions, importance is given to the systematic generation of a large number of sets of different expansion lengths for each atom.

The paper is divided into six sections. In Sect. 2, some well-known properties of relativistic wavefunctions for one- and many-electron atoms are reviewed. The expansion of the radial wavefunctions into spherical Gaussians and the least-squares criterion are formulated in Sect. 3. The dependence of the basis set parameters on the premises of the least-squares approach such as different choices of weighting functions or expansion lengths is analysed in Sect. 4 for hydrogen and helium. In order to appraise the quality of the various basis sets relativistic calculations are performed. They are based on two approaches which at least partially resolve the problems which arise from a straightforward expansion of the Dirac Hamiltonian into an incomplete set of basis functions (for a review see [36]). In the large-c approach [8, 9, 11] the relativistic results are compared with those calculated using the limiting form of the Dirac equation expanded into an incomplete set; this limiting form may be obtained either numerically [8] - by setting the velocity of light c equal to a large number in the computer program - or analytically [9, 11] - by performing the limiting process $c \to \infty$. In the modified kinetic energy approach [15] the matrix representation of the relativistic kinetic energy operator $\vec{\alpha}\vec{p}$ is replaced by a modified one. This representation is constructed such that the modified Dirac-Fock (DF) equations are exactly reduced to the Hartree-Fock-Roothaan (HFR) equations in the limit $c \to \infty$. The generalization of the fit procedure appropriate for the atoms Li to Ne is formulated in Sect. 5. Subsequently, the construction of atomic sets from l-subsets is illustrated for Ne; among the various combinations a small, a medium and a large set are selected. Contraction schemes adequate for calculations by the modified kinetic energy approach are proposed. Finally, some conclusions are summarized in Sect. 6.

The present contribution is mainly intended to describe the method of obtaining the basis sets, and to analyse some of the results for atomic calculations where these sets have been applied. The numerical constants of the sets for the atoms H to Ne are documented in a monograph [37] which is available upon request from the author. There are also basis sets compiled for hydrogen-, helium- and neon-like positive ions in order to demonstrate the dependence of the parameters on the nuclear charge; this subject, however, will not be treated in the following.

2. Some properties of relativistic one-electron wavefunctions for central fields

The components of the relativistic one-electron wavefunctions for a spherically symmetric potential can be factorized into a radial and an angular part (see e.g. [38]) according to

$$\psi_{nl_jm_j}=\begin{pmatrix}\psi^+\\ \psi^-\end{pmatrix}=\begin{pmatrix}r^{-1}P_{nl_j}(r) & \chi_{\kappa m_j}(\theta,\phi)\\ ir^{-1}Q_{nl_j}(r) & \chi_{-\kappa m_j}(\theta,\phi)\end{pmatrix}. \tag{1}$$

The radial function P of the large component ψ^+ and the radial function Q of the small component ψ^- are classified by a label n and a combined label l_j which for $l>0$ distinguishes the relativistic shells $j=l-\frac{1}{2}$ and $j=l+\frac{1}{2}$ originating from the non-relativistic shell l. The angular functions χ are classified by the quantum numbers κ and m_j, where κ is related to l_j in the following way:

$$\begin{aligned}\kappa&=1, &&\text{if } j=l-\tfrac{1}{2}.\\ \kappa&=-(l+1), &&\text{if } j=l+\tfrac{1}{2}.\end{aligned} \tag{2}$$

Each component of the two-component spinors χ is given by a spherical harmonic $Y_{\lambda m_\lambda}$ multiplied by a Clebsch–Gordan coefficient. The degree λ of the spherical harmonic is determined by κ according to $\lambda=j+\frac{1}{2}\operatorname{sgn}(\kappa)$, where $\operatorname{sgn}(\kappa)=\kappa/|\kappa|$. The symbol λ has been introduced in order to distinguish between the angular symmetry of a single spinor in (1) and a state symbolized by l_j. The values of λ appropriate for the large and the small components for the lowest relativistic central field states are indicated in Table 1 by specifying the symmetry symbols $s, p, d, \ldots$ which correspond to $\lambda=0, 1, 2, \ldots$, respectively. It is important to note that members of the set $Y_{\lambda m_\lambda}$ enter into the angular functions of several different relativistic states.

In the case of hydrogen-like atoms with point-like nucleus of charge Z, the functions P and Q can be expressed by confluent hypergeometric functions (see [39]). In the case of many-electron systems, P and Q are solutions of the DF equations. They have been calculated by means of Desclaux's program [40] assuming a point-like nucleus and the LS average of configurations [41].

Close to the origin the radial functions can be represented by power series which are of similar form for the large and the small components:

$$\frac{P_{nl_j}}{r}=r^{\gamma_{\min}-1}(p_0+p_1r+\cdots) \tag{3}$$

$$\frac{Q_{nl_j}}{r}=r^{\gamma_{\min}-1}(q_0+q_1r+\cdots) \tag{4}$$

Table 1. Angular symmetry of the large and small components of relativistic central field states

State classification	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$
Quantum number κ	−1	+1	−2	+2	−3	+3	−4
Large component	s	p	p	d	d	f	f
Small component	p	s	d	p	f	d	g

The power $\gamma_{\min}$ and the coefficients p_i and q_i depend on the central field potential which comprises the contribution from the nucleus and, in the case of a many-electron system, the mean field of all electrons. Table 2 gives the parameters of the power series (3) and (4) for two cases, a point-like nucleus and an extended nucleus [42–44].

3. The expansion of relativistic radial wavefunctions into spherical Gaussians and the least-squares criterion

3.1. *The expansion scheme*

The functions P and Q satisfy a common normalization condition

$$\int_0^\infty \{P^2_{nl_j} + Q^2_{nl_j}\}\, dr = 1, \tag{5}$$

but for their use in the fit procedure each of them individually has been renormalized to unity. Such a renormalized large component wavefunction P_{nl_j}/r is denoted by $d^+(r)$ and a renormalized small component wavefunction Q_{nl_j}/r by $d^-(r)$; the superscript $^\mp$ is employed if no particular component is addressed. In the following, the expression orbital will be used for $d^\mp(r)$, with the specific notation $1s^+$, $1s^-$, $2p^+_{1/2}$, $2p^-_{1/2}$, and so on; the expression radial function will be reserved for $rd^\mp(r)$, with the specific notation P_{1s^+}, Q_{1s^-}, and so on.

An orbital $d^\mp$ characterized by the labels nl_j and coupled to a spherical harmonic of degree λ is approximated by a function $g^\mp$ of the following form:

$$g^\mp(r) = N \sum_{i=1}^{m(\lambda)} c_i(nl_j, \lambda)\phi_i(\alpha_i, \lambda, r). \tag{6}$$

Table 2. Relativistic radial wavefunctions for central field states: power series solutions close to the origin for the large component, $r^{\gamma_{\min}-1}[p_0+p_1 r]$ (*upper row*) and the small component, $r^{\gamma_{\min}-1}[q_0+q_1 r]$ (*lower row*)

State	κ	Angular symm.	Point-like nucleus			Extended nucleus		
			$\gamma_{\min}-1$ [a]	Coefficients [a]		$\gamma_{\min}-1$	Coefficients	
$1s_{1/2}$	-1	s	$-\zeta^2/2$	1	$-Z$	0	1	0
		p		$-\zeta/2$	$w\zeta/3$		0	1
$2p_{1/2}$	$+1$	p	$-\zeta^2/2$	ζ^2	$4Z/3$	0	0	1
		s		2ζ	$-4Z\zeta/2$		1	0
$2p_{3/2}$	-2	p	$1-\zeta^2/4$	1	$-Z/2$	1	1	0
		d		$-\zeta/4$	$w\zeta/5$		0	1
$3d_{3/2}$	$+2$	d	$1-\zeta^2/4$	ζ^2	$8Z/5$	1	0	1
		p		4ζ	$-8Z\zeta/5$		1	0
$3d_{5/2}$	-3	d	$2-\zeta^2/6$	1	$-Z/3$	2	1	0
		f		$-\zeta/6$	$w\zeta/7$		0	1

[a] $\gamma_{\min}$ and the coefficients have been expanded into a power series in $1/c$ and only the leading terms are recorded

Abbreviations: $\zeta = Z/c$; $w = \{Z/|\kappa| - (\varepsilon - V_0/Z)\}$; $V_0 = \lim_{r\to 0} V_e(r)$, where V_e is the mean field of all electrons [20]

The basis functions of the set $\{\phi\}$ are normalized spherical Gaussians

$$\phi_i(\alpha_i, \lambda, r) = \nu_i\, e^{-\alpha_i r^2} r^\lambda \tag{7}$$

with

$$\nu_i = \left\{\frac{2^{(\lambda+5/2)}}{\Gamma(\lambda+3/2)}\right\}^{1/2} \alpha_i^{(2\lambda+3)/4}. \tag{8}$$

The ϕ_i do not depend explicitly on n, but an implicit dependence is introduced by approximating orbitals differing in n by different sets of coefficients. The function N normalizes $g^\mp$ to unity,

$$\int_0^\infty \{g^\mp\}^2 r^2\, dr = 1, \tag{9}$$

and is given by

$$N = 1 \Big/ \left\{\sum_{i=1}^{m} c_i^2 + \sum_{i \neq j}\sum c_i c_j \frac{4\alpha_i\alpha_j^{(2\lambda+3)/4}}{(\alpha_i+\alpha_j)^2}\right\}^{1/2}. \tag{10}$$

The explicit factor r^λ in (7) ensures that a relativistic one-electron wavefunction can be expanded into a set of Cartesian Gaussians $C(\alpha_i, \lambda, \vec{r})$ of the form

$$C(\alpha_i, \lambda, \vec{r}) \simeq x^t y^u z^v e^{-\alpha_i r^2} \tag{11}$$

with $\lambda = t + u + v$. Hence, in the following basis functions with $\lambda = 0$ are referred to as *s*-Gaussians, those with $\lambda = 1$ as *p*-Gaussians, and so on. However, these basis functions which allow a correct description of the angular symmetry of the spinors by Cartesian Gaussians show several deficiencies for small values of r. They are unable to represent properly the eigenfunctions for the central field with point-like nucleus in three aspects:

(1) Since $\gamma_{\min} < 1$ for $|\kappa| = 1$, the power series solutions (3) and (4) approach infinity whereas the approximations (6) remain finite as r tends to zero. The consequences arising from the factor $r^{\gamma_{\min}-1}$ are most pronounced for the states with $\kappa = \mp 1$, i.e. $ns_{1/2}$ and $np_{1/2}$. However, for low values of $\zeta = Z/c$, the approximation $r^{\gamma_{\min}-1} \simeq \exp(-\frac{1}{2}\zeta^2 \ln r)$ holds. Hence, this factor deviates from a constant only within a region which is comparable with the size of the nucleus with radius $R \simeq r_e A^{1/3}$, where A is the nuclear mass and $r_e \simeq (2.65 - 2.84) \times 10^{-5}$ Bohr [45].

(2) More severe than the neglect of a fractional power $\gamma_{\min}$ is the deficiency in the limiting behaviour of the small components for states with $\kappa < 0$. This is due to the fact that a power r^λ is used in the expansion (6) whereas $r^{\lambda-1}$ is demanded (see Table 2). Numerical examples given in Sect. 4.1 will show that basis functions ϕ_i with very large exponents are needed to correct for this deficiency. Hence, these central field functions with pre-exponential factor approximated by $r^{(\lambda-1)}$ will be called "hard" functions. They are represented by "normal" functions of the same symmetry λ even if a large number of them is needed.

(3) "Hard" functions are furthermore required to represent the large components for states with $\kappa > 0$ (see Table 2). However, inspection of the coefficients of the

power series expansion shows that p_0 is smaller than p_1 by a factor ζ^2 and is negligible for small r and low Z.

The aforementioned deficiencies of the functions (7) turn out to be much less important, if the finite size of the nucleus is taken into account. In that case the power series solutions of all large and small components close to the origin [42–44], which are given in Table 2, can be represented exactly by the basis functions (7). Since the region where the "hard" small components have to be approximated by functions with large exponents starts only at r values comparable with those of the nuclear radius, the neglect of a fractional power and of the leading power $(\lambda - 1)$ are less important, at least for low Z values. Indeed, it has been found that smaller basis sets are sufficient to calculate relativistic energy effects when an extended nucleus is assumed [35].

3.2. *The least-squares criterion*

The coefficients $\boldsymbol{c} = c_1, c_2, \ldots c_m$ and the exponents $\boldsymbol{\alpha} = \alpha_1, \alpha_2, \ldots \alpha_m$ of the expansion (6) will be determined by an extremal condition: the integral over the squared deviation $\delta^{\mp} = g^{\mp} - d^{\mp}$ is required to be a minimum,

$$F(\boldsymbol{c}, \boldsymbol{\alpha}) = \int_{r_{\min}}^{\infty} w(r)\delta^{\mp}(r)^2 r^2 \, dr \rightarrow \text{minimum}, \tag{12}$$

subject to the constraint that $g^{\mp}$ remains normalized according to (9). The squared deviation is weighted by a function $w(r)$ to be specified later. The integration is performed over a shell extending from $r_{\min}$ to infinity but it excludes a small region around the origin somewhat larger than the size of the nucleus. A least-squares criterion analogous to (12), but with the choice $r_{\min} = 0$, has been used previously to determine parameters of basis sets, e.g., those of GTFs approximating STFs [46–49] or those of even-tempered sets approximating SCF wavefunctions [50].

Details on the minimization of the functional F and on the non-linear minimum search procedure are given in [37].

4. Gaussian basis sets for hydrogen and helium

4.1. *General behaviour of the analytical approximations*

Qualitative information on the basis sets can be gained by displaying the orbital exponents for sets of different size in a common diagram. Plots of ln α values which were obtained for the hydrogen orbitals $1s^+$ and $1s^-$ with a weighting function $w = 1/r$ are shown in Figs. 1 and 2. The basis functions -2 up to 14 s- and 2 up to 18 p-Gaussians - are numbered such that the first member has the largest exponent; the values of the exponents belonging to a given expansion are connected by straight lines.

First, consider the dashed base lines connecting the smallest exponents α_m^+ or α_m^- of each set. When the ordinate in one of the diagrams is shifted, the two base

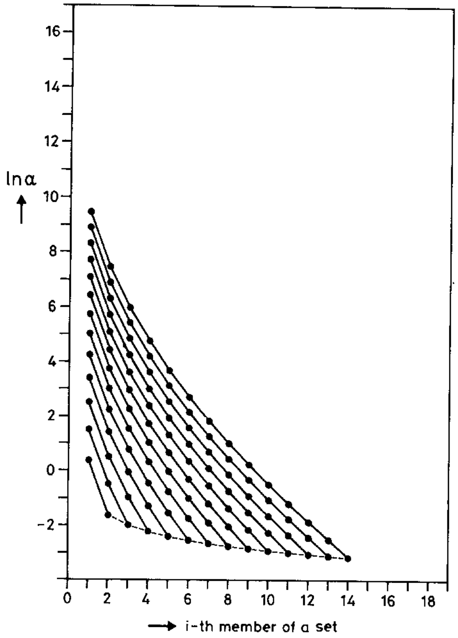

Fig. 1. Basis sets for the large component of the hydrogen ground state wavefunction: logarithm of the orbital exponents α in dependence on the number of s-Gaussians in a set; the values for a set are connected by straight lines

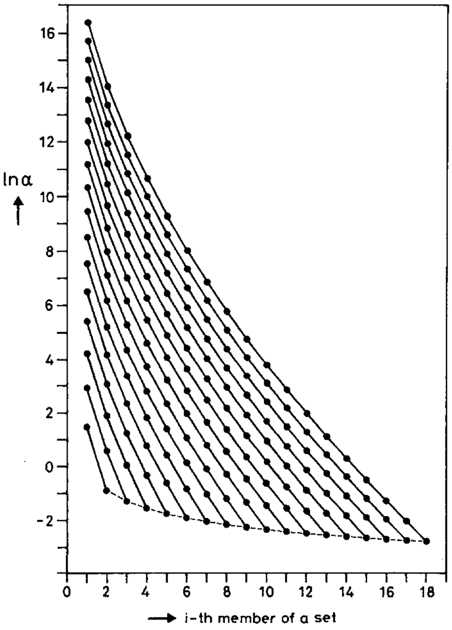

Fig. 2. Basis sets for the small component of the hydrogen ground state wavefunction: logarithm of the orbital exponents α in dependence on the number of p-Gaussians in a set; the values for a set are connected by straight lines

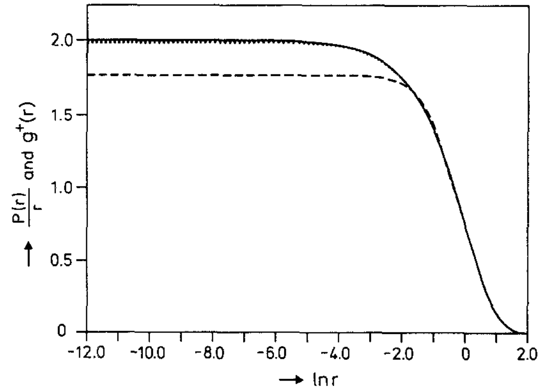

Fig. 3. Hydrogen atom: approximation of the large component orbital $1s^+$ (——) by 3 s-Gaussians (----) and 10 s-Gaussians (· · ·)

lines almost coincide. Thus, the ratio α_m^+/α_m^- is close to a constant value, namely $\simeq 0.5$, corresponding to a ratio $\bar{r}_{1s}/\bar{r}_{2p} = (\alpha_p/\alpha_s)^{1/2} \times 3/4 \simeq 1$ of the mean radii of the outermost functions. Starting from the points at the base lines, the line segments linking the members of the same set first rise with almost constant slope, but then gradually bend upwards. Thus, among the smallest exponents the values for adjacent members are related by an almost constant factor as is characteristic for an even-tempered basis set [51] while the values of the larger exponents deviate increasingly from a rigid geometric series. The slope of the line segments is smaller for the large component than for the small one, so that for the first member of each set the value of α_1^- is much larger than that of α_1^+. Thus, the innermost basis functions of the small component are strongly decaying and approach very much a δ-like character. The different behaviour of the approximations for the large and small components is illustrated in Figs. 3 and 4, respectively.

When the large component is expanded into 3 s-Gaussians, the approximation g^+ deviates from $1s^+$ in the outer part in an oscillatory manner but in a smooth way in the inner part. When more basis functions are used, the deviations are

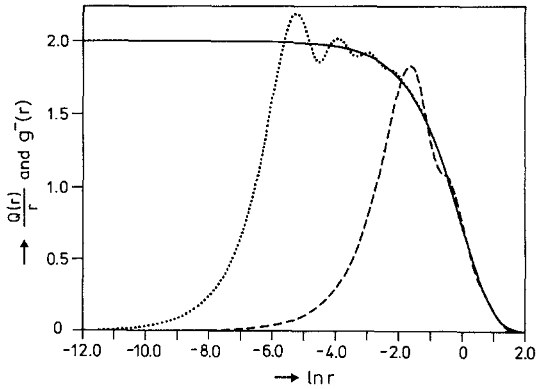

Fig. 4. Hydrogen atom: approximation of the small component orbital $1s^-$ (——) by 3 p-Gaussians (---) and 10 p-Gaussians (· · ·)

reduced to a comparable extent in both regions. In the case of $1s^-$, the p-Gaussians of a small set are positioned in the outer part. The additional p-functions in the larger set mainly correct the wrong limiting functional form for $r \to 0$, shifting the region of large deviations to smaller r values. Evidently, the RMS errors for g^- are much larger and decrease less with m than those for g^+.

Note that indeed the orbitals $1s^+$ and $1s^-$ are almost constant for small r, as stated in Sect. 3. The singular behaviour due to $r^{\gamma_{\min}-1}$ is not yet discernible at the value of $\ln r_{\min}$ which has been chosen in order to cut off the region around the nucleus.

4.2. *Choice of the expansion length for the large and small components*

Comparison of the slope of the line segments connecting the exponent values in Figs. 1 and 2 shows that for a small expansion length the slopes of the approximations g^+ and g^- deviate from each other to a lesser extent than for a large one. This means that for large sets the values of the exponents of the inner p-functions "run away" from those of the corresponding s-functions. This fact induces small matrix elements with respect to $\vec{\sigma}\vec{p}$, the operator coupling the large and small component in the kinetic energy matrix

$$[\vec{\alpha}\vec{p}] = \begin{pmatrix} 0 & [\vec{\sigma}\vec{p}] \\ [\vec{\sigma}\vec{p}] & 0 \end{pmatrix};$$

here, $\vec{\sigma}$ are the Pauli spin matrices and matrix representations are denoted by operators enclosed in square brackets. As a consequence, small kinetic energy eigenvalues arise which cause severe numerical difficulties in calculations based on the large-c and the modified kinetic energy approach. Firstly, the (unphysical) states having no or almost no kinetic energy are usually strongly intermingled with occupied states. It is numerically difficult to preserve orthogonality between these two kinds of states and the SCF process may not converge in this case. Secondly, the evaluation of the inverse of $[\vec{\sigma}\vec{p}]$ needed for the construction of the modified representation $[\vec{\sigma}\vec{p}]^{\mathrm{mod}}$ [15] becomes numerically ill-conditioned.

The conclusions for choosing the expansion lengths for the large and small component are as follows:

(1) For small basis sets the expansion lengths can be chosen to be equal for both components, but for large sets more functions should be used for the small than for the large component.

(2) The basis sets should be decoupled only to such an extent that the $\vec{\sigma}\vec{p}$ overlap between large and small component functions remains appreciable. A measure for a minimal $\vec{\sigma}\vec{p}$ overlap will be given in Sect. 4.3.2.

4.3. *Choice of the weighting function*

Two functions $w(r)$ have been tried, namely $w = 1$ and $w = 1/r$. The values of the obtained parameters using these choices of w are shown in Table 3 for two hydrogen basis sets. The exponents of the $w = 1/r$ approximation are larger and

Table 3. Approximation of the hydrogen ground state radial wavefunctions by s- and p-Gaussians: exponents α and coefficients c obtained for two weighting functions w

	Large component				Non-relativistic energy-optimized 1s orbital[a]	
	$w=1$		$w=1/r$			
Expansion length	α_s	c_s	α_s	c_s	α_s	c_s
3	2.22788	0.154419	4.49172	0.0810391	4.50038	0.07048
	0.405794	0.535640	0.610086	0.457177	0.681277	0.40789
	0.109821	0.444903	0.136959	0.596224	0.151374	0.64767
4	5.21760	10.0567329	12.1918	0.0240949	13.3615	0.01906
	0.954702	0.260048	1.65720	0.169575	2.01330	0.13424
	0.265218	0.532664	0.377861	0.519260	0.453757	0.47449
	0.0880216	0.291535	0.108195	0.428341	0.123317	0.50907

	Small component			
	$w=1$		$w=1/r$	
3	5.68341	0.228167	18.6797	0.116801
	0.840236	0.543671	1.79121	0.440863
	0.182346	0.510147	0.278671	0.719803
4	15.8252	0.108533	68.2539	0.0446025
	2.35882	0.300414	6.57945	0.182941
	0.529726	0.534588	1.05095	0.494705
	0.143035	0.369789	0.213906	0.587178

[a] From [52]

spread over a wider range than those from $w = 1$; the coefficients are less uniformly distributed, being peaked at a few basis functions. The numerical constants of the large component from $w = 1/r$ are similar to those of the non-relativistic 1s orbital which have been obtained from the energy criterion [52].

In the following subsections, the sets obtained from the two weighting functions will be compared with respect to two quantities: the non-relativistic energy E_{nr} and the difference between the relativistic energy E_r and E_{nr}, namely $\Delta E_r = E_r - E_{nr}$, which will be referred to as relativistic energy contribution.

4.3.1. Non-relativistic energies. The deviations between the variational energy and the $1s_{1/2}$ eigenvalue for hydrogen or the ^{1}S SCF energy for helium [53], namely $\delta E_{nr} = E_{nr} - E_{nr}^{\mathrm{exact}}$, are given in Table 4. The values of δE_{nr} are smaller for the $w = 1/r$ sets than those for the $w = 1$ sets; the former require about one or two basis functions less to get comparable accuracy in the non-relativistic energies. The $w = 1/r$ sets give almost the same deviations as the non-relativistic sets whose exponents have been determined from the minimization of the energy expectation value. Since for $c \to \infty$ the large component reduces to the non-relativistic orbital and since for low Z the relativistic effects on the wavefunctions are small [54], the energy criterion is used in an indirect way to appraise the

Table 4. Hydrogen and helium atom; deviation δE_{nr} of the non-relativistic variational energy E_{nr} from the $1s$ eigenvalue or the ^1S SCF total energy: E_{nr} calculated with the relativistic sets obtained from two weighting functions w and with the energy-optimized non-relativistic sets

Number of s-Gaussians	Hydrogen [values in μHa] $w=1$	 $w=1/r$	Non-relativistic energy optimized [a]
3	4989.1	3285.2	3021
4	1505.8	812.0	723
5	492.4	222.0	191
6	172.8	66.1	60
7	64.4	21.2	24
8	25.3	7.2	9
9	10.4	2.6	3
10	4.4	1.00 [c]	1
11	2.0	0.39 [c]	
12	0.9	0.16 [c]	
14		0.03 [c]	
E_{nr}^{exact}		−500 000.00	
	Helium [values in mHa]		
2	151.17	120.82	114.61
3	45.63	28.86	26.00
4	14.62	7.56	6.52
5	4.99	2.16	1.79
6	1.81	0.66	0.56
7	0.69	0.22	0.19
8	0.28	0.08	0.07
9	0.12	0.03	0.03
10	0.05	0.011 [c]	0.01
11	0.02	0.004 [c]	
12		0.002 [c]	
14		0.0004 [c]	
E_{nr}^{HF}		−2861.6800 [b]	

[a] From [52]
[b] From [53]
[c] Segmentally contracted to 9 s-functions using the expansion coefficients from the large component

quality of the relativistic basis sets. It is concluded that the $w=1/r$ sets are preferable to the $w=1$ sets because shorter expansions are needed to get non-relativistic energies with the same given accuracy. A further argument of computational economy favours the $w=1/r$ set in molecular calculations: fewer basis functions with small exponents extend into the bonding region and, therefore, a smaller number of linear combination coefficients must be determined in the variational calculation.

4.3.2. Relativistic energy contribution. The values of the relativistic energy contributions $\Delta E_r = E_r - E_{nr}$ calculated for hydrogen and helium are shown in Table 5. Except for the extended basis sets they deviate so strongly from the exact

Table 5. Hydrogen and helium atom: relativistic energy contributions ΔE_r, $\Delta E_r^{c\to\infty}$ and $\Delta E_r^{\mathrm{mod}}$ calculated with basis sets from two weighting functions w

Number of Gaussians		Hydrogen [values in μHa]							
		ΔE_r		$\Delta E_r^{c\to\infty}$		$\Delta E_r^{\mathrm{mod}}$		$\vec{\sigma}\vec{p}_{\min}$[a]	
s	p	$w=1/r$	$w=1$	$w=1/r$	$w=1$	$w=1/r$	$w=1$	$w=1/r$	$w=1$
3	3	−14 726.3	−7 165.2	−6.551	−6.181	−6.033	−5.387	2.86 −1	4.08 −1
4	4	−3 150.5	−1 928.5	−6.308	−6.378	−6.222	−6.024	9.73 −2	2.69 −1
5	5	−748.7	−482.1	−6.470	−6.448	−6.562	−6.341	2.10 −2	1.41 −1
6	6	−235.8	−109.8	−6.577	−6.518	−6.583	−6.487	3.29 −3	5.65 −2
7	7	−104.5	−28.6	−6.628	−6.657	−6.648	−6.567	4.04 −4	1.82 −2
8	8	−51.8	−11.7	−6.646	−6.610	−6.645	−6.608	4.02 −5	4.98 −3
9	9	−26.2	−8.31	−6.652	−6.630	−6.656	−6.630	3.32 −6	1.19 −3
10	10	−14.9[b]	−7.48	−6.656[b]	−6.642	−6.660[b]	−6.642	2.13 −5[b]	2.50 −4
11	11	−10.0[b]	−7.13	−6.656[b]	−6.648	−6.659[b]	−6.648	3.29 −5[b]	8.07 −6
12	12	−8.15[b]	−6.93	−6.657[b]	−6.652	−6.660[b]	−6.652	4.63 −5[b]	
10	14[b]	−8.15		−6.656		−6.656		1.90 −1	
12	14[b]	−7.17		−6.657		−6.657		2.63 −3	
14	18[b]	−6.72		−6.657		−6.656		2.02 −2	
$\Delta E_r^{\mathrm{exact}}$		−6.657							
3	3	−119.28	−65.38	−0.1231	−0.1151	−0.1185	−0.0973	3.09 −1	5.35 −1
4	4	−25.61	−16.86	−0.1218	−0.1218	−0.1192	−0.1133	8.49 −2	3.13 −1
5	5	−6.70	−4.07	−0.1277	−0.1252	−0.1318	−0.1229	1.58 −2	1.43 −1
6	6	−2.52	−0.97	−0.1310	−0.1283	−0.1312	−0.1275	2.22 −3	5.11 −2
7	7	−1.23	−0.31	−0.1325	−0.1304	−0.1334	−0.1303	2.48 −4	1.51 −2
8	8	−0.63	−0.18	−0.1331	−0.1317	−0.1331	−0.1316	2.27 −5	3.86 −3
9	9	−0.34	−0.15	−0.1332	−0.1324	−0.1334	−0.1324	1.74 −6	8.66 −4
10	10[b]	−0.22	−0.14	−0.1333	−0.1328	−0.1335	−0.1327	1.24 −5	1.73 −4
11	11[b]	−0.17	−0.14	−0.1334	−0.1331	−0.1335	−0.1347	2.03 −5	3.11 −5
12	16[b]	−0.136		−0.1334		−0.1334		6.77 −2	
14	20[b]	−0.133		−0.1333		−0.1334		1.33 −1	
$\Delta E_r = E_r^{DF} - E_r^{HF}$		−0.13334							

[a] Smallest non-zero eigenvalue of $\vec{\sigma}\vec{p}$ matrix representation (absolute value); the decadic exponent is separated by a blank space from the number

[b] Segmentally contracted to 9 s- and 9 p-functions

values that the order of magnitude of the relativistic effect cannot be estimated. This fact makes the slightly better performance of the $w=1$ sets in comparison with the $w=1/r$ sets irrelevant. However, the values of $\Delta E_r^{c\to\infty} = E_r - E_r^{c\to\infty}$ as well as those of $\Delta E_r^{\mathrm{mod}} = E_r^{\mathrm{mod}} - E_{nr}$ clearly indicate that the $w=1/r$ sets are to be preferred, since they lead to a faster convergence towards the exact values.

The smallest non-zero eigenvalue of $[\vec{\sigma}\vec{p}]$ whose absolute value $\vec{\sigma}\vec{p}_{\min}$ is shown in the last two columns of Table 5 illustrates numerically the qualitative arguments given in Sect. 4.2 for choosing the expansion length m and m' for the large and small components, respectively. For $m = m'$, $\vec{\sigma}\vec{p}_{\min}$ becomes smaller with increasing m since the largest exponent α_1^- increases more strongly than α_1^+, as shown in Figs. 1 and 2 for the $w=1/r$ sets. When the exponents of the $w=1$ sets are plotted in analogous diagrams, their line segments have smaller slopes and the α_1^+ and α_1^- values "run away" to a lesser extent. As a consequence, $\vec{\sigma p}_{\min}$ is larger for given m and decreases slower with m than in the case of the $w = 1/r$ sets. A much better matching of the exponents for the s- and p-functions than for a choice $m = m'$ is obtained, when a given set for the large component is combined with a larger one for the small component. In the case of the hydrogen $10s$,$14p$ $w = 1/r$ set, for example, the line segments for the outermost 9 s- and 9 p-functions are almost parallel (see Figs. 1 and 2). If these functions are held uncoupled, a particularly large value of $\vec{\sigma p}_{\min}$ results, which is to be contrasted to that from the $9s$,$9p$ set: here a value smaller by 5 orders of magnitude is obtained and quadruple precision arithmetic is required to calculate $[\vec{\sigma p}]^{\text{mod}}$. Generally, the quantity $\vec{\sigma p}_{\min}$ turned out to be a suitable guideline for combining l-subsets and for fixing the extent of decoupling: the value of $\vec{\sigma p}_{\min}$ should not fall below a threshold value of 5×10^{-4}.

The extended sets which include a larger number of p- than s-functions have been used in calculations on the H_2 molecule [55] approaching closely the DF limit [56] and in a relativistic configuration interaction treatment of the electron correlation in the He atom [57].

4.3.3. Selection of the $w = 1/r$ sets for use in relativistic molecular calculations. Summarizing the results outlined in the preceding subsections, the following arguments are in favour of the basis sets which are obtained with the weighting function $w = 1/r$: compared with the $w = 1$ set,

(1) they are computationally more economic since they need shorter expansions to determine relativistic energy effects and they require less decoupling;

(2) they give lower non-relativistic energies;

(3) their orbital exponents and expansion coefficients are more similar to those of the energy-optimized non-relativistic sets.

The weighting function $w = 1/r$ was also chosen by Bardo and Ruedenberg [50] for deriving non-relativistic even-tempered basis sets. Of all powers of r, $w = 1/r$ was the optimal weighting function to reproduce SCF energies.

5. Basis sets for the atoms lithium to neon

5.1. The iterative self-consistent fit procedure

For the atomic systems considered here ranging from three to ten electrons, the one-electron states $1s_{1/2}$, $2s_{1/2}$, $2p_{1/2}$ and $2p_{3/2}$ have to be approximated. Inspection of Table 1 shows that $1s^+$, $2s^+$ and $2p^-$ are coupled to an angular function of s-symmetry. These three orbitals will be expanded into *one* set of basis functions with $\lambda = 0$; they will have the same exponents but comprise different linear combination coefficients. Similarly, all orbitals coupled to an angular function of p-symmetry, namely $1s^-$, $2s^-$, $2p_{1/2}^+$ and $2p_{3/2}^+$, will be expanded into one common set with $\lambda = 1$. Finally, the orbital $2p_{3/2}^{-}$ which is linked to an angular function of d-symmetry is expanded into a third set with $\lambda = 2$.

An extension of the fit procedure is required for the s- and p-sets, since for a chosen expansion length m and k orbitals to be fitted, m exponents and $k \times m$ coefficients have to be determined. The following strategy has been adopted in these cases: the basis functions are divided into groups using the criterion to which of the k orbitals they contribute most. Then, the exponents of a particular group are adjusted by minimizing the functional (12) for that orbital to which the group has been associated, together with the $m-1$ coefficients; one coefficient is fixed by the normalization condition (9). Starting with the new values for the exponents, those of the next group are optimized, and so on, until all groups are exhausted. This cycle is repeated, until the relative changes in the values of all exponents and all coefficients become sufficiently small.

The criterion adopted for the partitioning of the basis functions into groups will be illustrated by a specific example, the neon atom.

Figure 5 shows plots of the radial functions P_{1s^+}, P_{2s^+} and Q_{2p^-} (all renormalized to unity) and plots of their integrated radial densities $\sigma^{\mp}(r) = \int_0^r d^{\mp 2} r^2 \, dr$. The s-functions of the basis are arranged in decreasing magnitude of the (initially guessed) exponents; they are divided segmentally into 3 groups of t, u and v functions, where $m = t + u + v$, in the following way:

(1) The inner region is mainly filled with density from $1s^+$. Hence, the t functions with mean radii $\bar{r}_{1s}$ less or approximately equal to the value $r_{\max}(1s^+)$ of the maximum of P_{1s^+} are assigned to the first group. This choice does not bias the representations of the inner part of $2s^+$ and of the left wing of $2p^-$; these orbitals are of similar shape as $1s^+$ in the region extending up to $r_{\max}(1s^+)$.

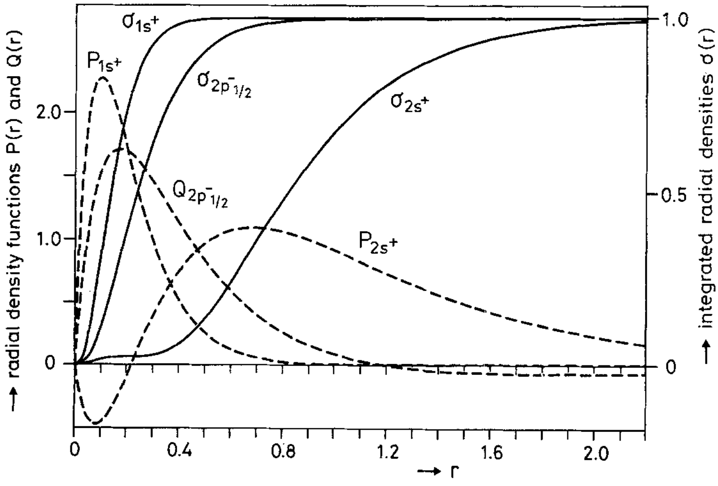

Fig. 5. Neon atom: renormalized radial functions P_{1s^+}, P_{2s^+} and Q_{2p^-} and integrated densities $\sigma(r) = \int_0^r P^2 r^2 \, dr$ or $\sigma(r) = \int_0^r Q^2 r^2 \, dr$

(2) In the range between the maximum of P_{1s^+} and the outer maximum of P_{2s^+} a single function forming the second group is positioned, which accounts for the skewness of the Q_{2p^-} function and the broadening of the maximum in comparison with P_{1s^+}.

(3) The exponents of the remaining v functions having the smallest exponents and forming the third group are determined by minimizing (12) for $2s^+$. At least two functions have to be provided for this group, when besides the outer P_{2s^+} maximum the node in the $2p^-$ orbital has to be represented properly. Hence, at least four functions are needed to describe the functional behaviour of the s-orbitals. However, since only a relatively small amount of charge, namely 15.6%, is contained in the region beyond this node of $2p^-$, a minimal basis of 3 (contracted) s-orbitals may be sufficient to describe the gross features of the spinors of s-symmetry, namely the s-core function, an intermediate function and the s-valence function.

The radial functions Q_{1s^-}, Q_{2s^-}, $P_{2p^+_{1/2}}$ and $P_{2p^+_{3/2}}$ and their integrated radial densities are plotted in Fig. 6. Since the differences between $2p^+_{1/2}$ and $2p^+_{3/2}$ are marginal except very near to the nucleus (see the parameters of the power series solution in Table 2), the same exponents are used for both of them and the basis functions are divided into three groups only according to $m' = t' + u' + v'$. These groups are sufficiently well separated, so that the exponents of the first t' functions can be determined from a fit to $1s^-$, those of the last v' functions from $2p^+_{3/2}$ and the exponent of the intermediate function ($u' = 1$) from $2s^-$. Only the coefficients are optimized for $2p^+_{1/2}$. The minimal p-basis consists of three (contracted) functions, namely the p-core function, and intermediate function and the p-valence function.

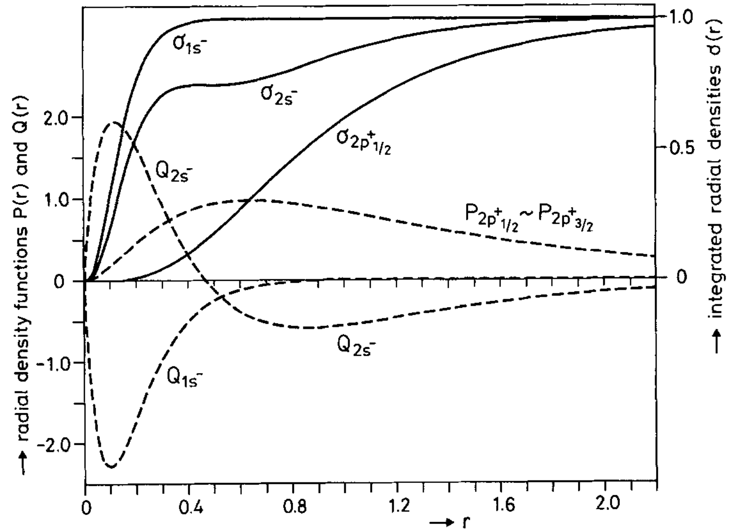

Fig. 6. Neon atom: renormalized radial functions Q_{1s^-}, Q_{2s^-} and $P_{2p^+_{1/2}}$ and integrated densities $\sigma(r) = \int_0^r P^2 r^2\,dr$ or $\sigma(r) = \int_0^r Q^2 r^2\,dr$

5.2. *Construction of relativistic atomic basis sets*

Atomic sets for Li and Be consist of an *s*- and *p*-subset, those for B to Ne contain in addition a *d*-subset. Among the many combinatorial possibilities to form atomic sets, in the following three combinations will be selected for Ne by considering the relativistic effect on the total energy and the spin-orbit splitting of the $2p$ orbital as probes for the core and valence shells, respectively. The closed-shell Ne atom is taken as an example, since our computer program cannot handle relativistic open-shell cases. However, the three Ne sets classified as small, medium and large are expected to be representative for the atoms B to F, since the basis set parameters change gradually along this series.

As a preselection, sets with an equal number of *s*- and *p*-functions or with one *p*-function in excess have been combined. Slightly more than half as many *d*-functions were added to these functions. The so-obtained atomic sets labelled Ba to Bl are listed in Table 6; the notation for the *s*- and *p*-subsets indicates the grouping of the basis functions in the self-consistent fit procedure.

In the large-*c* approach a correction term $\Delta E_r^{\mathrm{corr}} = E_r^{c\to\infty} - E_{nr}$ is subtracted from the relativistic energy contribution $\Delta E_r^{c\to\infty} = \Delta E_r - \Delta E_r^{\mathrm{corr}}$ and a correction term $\Delta_{\mathrm{so}}^{\mathrm{corr}} = \varepsilon(p_{3/2}^{c\to\infty}) - \varepsilon(p_{1/2}^{c\to\infty})$ from the spin-orbit splitting $\Delta\varepsilon_{\mathrm{so}}^{c\to\infty} = \{\varepsilon(p_{3/2}) - \varepsilon(p_{1/2})\} - \Delta_{\mathrm{so}}^{\mathrm{corr}}$ which approximately compensate for the incompleteness of the basis. The values of these corrections which are given in Table 6 are large for all sets Ba to Bi. Since the calculated relativistic effects considerably

Table 6. SCF calculations on Neon atom using different basis sets: errors in total energy δE_r and δE_{nr}, relativistic energy contributions $\Delta E_r^{c\to\infty}$ and $\Delta E_r^{\mathrm{mod}}$, spin-orbit splitting $\Delta\varepsilon_{\mathrm{so}}^{c\to\infty}$ and $\Delta\varepsilon_{\mathrm{so}}^{\mathrm{mod}}$ and large-*c* corrections $\Delta E_r^{\mathrm{corr}}$ and $\Delta\varepsilon_{\mathrm{so}}^{\mathrm{corr}}$ [values in mHa] [a]

Basis set label	Subsets of *s*-, *p*-, *d*-Gaussians	δE_r	δE_{nr}	$\Delta E_r^{c\to\infty}$	$\Delta E_r^{\mathrm{corr}}$	$\Delta\varepsilon_{\mathrm{so}}^{c\to\infty}$	$\Delta\varepsilon_{\mathrm{so}}^{\mathrm{corr}}$	$\Delta E_r^{\mathrm{mod}}$	$\Delta\varepsilon_{\mathrm{so}}^{\mathrm{mod}}$ [b]
Ba	4+1+2, 4+1+2, 4	116.36	233.01	−129.38	−1132.14	4.79	1.04	−145.12	4.25
Bb	4+1+2, 5+1+2, 4	−266.35	195.83	−145.11	−461.93	4.56	−2.21	−144.10	4.35
Bc	5+1+2, 4+1+3, 5	−138.92	39.22	−145.51	−177.50	4.56	−12.42	−144.13	4.52
Bd	5+1+2, 5+1+2, 5	[c]	134.90					−144.99	4.56
Be	6+1+2, 5+1+3, 5	−78.17	10.56	−145.76	−95.85	4.92	−0.65	−144.41	4.52 [d]
Bf	6+1+2, 6+1+2, 5	−109.90	106.62	−142.25	−219.15	4.50	9.34	−145.55	4.37 [d]
Bg	6+1+3, 5+1+4, 6	−28.26	7.27	−144.61	−35.79	4.68	1.84	−144.33	4.56
Bh	6+1+3, 6+1+3, 6	−24.10	12.88	−144.31	−37.54	4.59	−1.33	−145.45	4.55
Bi	7+1+2, 6+1+3, 6	−25.67	10.58	−144.53	−36.59	4.61	−4.43	−144.77	4.54
Bj	7+1+2, 5+1+4, 6	−30.45	4.92	−145.17	−35.07	4.63	0.70	−144.71	4.56
Bk	7+1+3, 6+1+4, 7	−10.19	2.99	−145.56	−13.50	4.62	−0.49	−144.99	4.56
Bl	8+1+3, 7+1+4, 7	−5.52	1.39	−144.73	−7.04	4.62	−0.06	−144.80	4.56
Exact SCF values		$E_r = -128691.97$		$E_{nr} = -128547.10$		$\Delta E_r = -144.87$		$\Delta\varepsilon_{\mathrm{so}} = 4.56$	

[a] The notation for the *s*- and *p*-subsets and the symbols are explained in Sect. 5.1 and 5.2, respectively

[b] The two innermost *s*- and *p*-Gaussians have been contracted in the calculations by the modified kinetic energy approach [15]

[c] No SCF convergence could be achieved in the large-*c* calculation

[d] The 6*d*-subset has been used in the calculations by the modified kinetic energy approach

scatter from set to set and depend strongly on the degree of the contraction, these sets are not adequate for use in large-c calculations. A fairly balanced description of the inner and outer shells has been achieved for set Bj, where moderate values for both correction terms are obtained. Furthermore, the values are the smallest among the four sets Bg to Bj which are combinations of subsets of the same size and which correspond to different least-squares minima. Hence, Bj is proposed to be used as medium-size set. Upon enlarging further the basis, the values of the correction terms and of the total energy errors decrease, but without showing a discriminating jump. Thus, set Bl is termed large even if its sizeable value of $\Delta E_r^{\mathrm{corr}}$ indicates that this basis set is still far from being complete and according to the experience from the expansion of the hydrogen and helium orbitals a larger p- and d-subset would be desirable.

In the modified kinetic energy approach, the error in the total non-relativistic energy is used as a further criterion besides $\Delta E_r^{\mathrm{mod}}$ and $\Delta \varepsilon_{\mathrm{so}}^{\mathrm{mod}}$. The value of δE_{nr} is drastically diminished when going from set Ba to Bc at the expense of a modest increase in computational effort due to the additional basis functions (see Table 6). Hence, Bc is proposed as a small basis set. It is to be preferred over Bd having a different p-subset which gives less energy gain. Furthermore, the value of $\vec{\sigma}\vec{p}_{\min}$ is larger for Bc than for Bd (4.9×10^{-4} versus 2.5×10^{-5}). A marked energy decrease is obtained for set Bj which in addition has the largest $\vec{\sigma}\vec{p}_{\min}$ value among all multiple minima combinations Bg to Bj. Hence, set Bj comprising one more function in the core and in the valence shell than the small set Bc will be classified as medium, in agreement with the conclusions from the large-c calculations. Bl is recommended as large set. Compared with the medium set the s-core and valence shell are augmented each by one s-function whereas the two additional p-functions enter into the p-core only. However, the relative large error in $\Delta E_r^{\mathrm{mod}}$ in contrast to the close agreement for $\Delta \varepsilon_{\mathrm{so}}^{\mathrm{mod}}$ indicates that the basis for the s- and p-core is still not large enough.

5.3. Relativistic contraction schemes

In order to derive contraction schemes appropriate for the modified kinetic energy approach, first some characteristic properties of the relativistic sets will be demonstrated for the case of the small Ne set. It is composed of the subsets $(5+1+2)s$, $(4+1+3)p$, $4d$ and its parameters are given in Table 7; an asterisk in front of the ith coefficient of an orbital indicates that the ith exponent has been optimized for that particular orbital. Dujineveldt's non-relativistic $8s$,$4p$ [58] set is also shown which in comparison with the relativistic set yields a slightly higher non-relativistic energy ($E_{nr} = -128.4817$ Ha vs. -128.5079 Ha) but a virial ratio closer to the exact value (-1.99998 vs. -2.00043).

The values for the exponents of the relativistic set form a more regular progression than those of the non-relativistic set, where a gap exists between the values of the second and third to the last exponent. This gap between the basis functions describing the $1s$ and the outer $2s$ lobe which is observable in many non-relativistic sets (see, e.g., [58]) is filled by a function having appreciable weight in the $2p^-$

Table 7. Gaussian basis sets for the neon atom: orbital exponents α and expansion coefficients c of the relativistic $(5+1+2)s$, $(5+1+3)p$, $4d$ set and of Duijneveldt's non-relativistic $8s$,$4p$ set[a,b]

α_s	$c(1s^+)$	$c(2s^+)$	$c(2p^-_{1/2})$	α_s	$c(1s)$	$c(2s)$
5.31 +3	*3.95 −3	9.62 −4	1.27 −3	8.91 +3	1.76 −3	4.16 −4
7.04 +2	*3.06 −2	7.06 −3	9.84 −3	1.34 +3	1.34 −2	3.13 −3
1.59 +2	*1.37 −1	3.54 −2	4.65 −2	3.04 +2	6.61 −2	1.64 −2
4.58 +1	*3.71 −1	1.01 −1	1.45 −1	8.57 +1	2.26 −1	5.70 −2
1.52 +1	*4.77 −1	2.13 −1	3.28 −1	2.75 +1	4.63 −1	1.58 −1
5.20 +0	1.37 −1	1.19 −2	*4.75 −1	9.45 +0	3.62 −1	1.61 −1
1.45 +0	−3.60 −3	*−6.92 −1	2.44 −1	1.71 +0	2.58 −2	−5.44 −1
4.33 −1	2.60 −3	*−4.78 −1	−1.39 −1	5.02 −1	−5.07 −3	−5.89 −1

α_p	$c(1s^-)$	$c(2s^-)$	$c(2p^+_{1/2})$	$c(2p^+_{3/2})$	α_p	$c(2p)$
2.00 +4	*2.01 −2	1.41 −2	9.04 −6	5.35 −6		
1.93 +3	*8.42 −2	5.92 −2	2.50 −5	9.11 −6		
3.09 +2	*2.55 −1	1.85 −1	1.28 −3	1.22 −3		
6.44 +1	*5.22 −1	4.19 −1	1.04 −2	1.03 −2		
1.59 +1	4.34 −1	*5.27 −1	8.69 −2	8.62 −2	2.84 +1	4.60 −2
4.07 +0	3.10 −2	−4.73 −2	3.34 −1	*3.33 −1	6.28 +0	2.40 −1
1.17 +0	4.27 −3	−4.42 −1	5.20 −1	*5.20 −1	1.70 +0	5.09 −1
3.09 −1	−2.34 −3	−8.81 −2	3.17 −1	*3.19 −1	4.32 −1	4.56 −1

α_d	$c(2p^-_{3/2})$
7.31 +1	8.20 −2
1.34 +1	3.15 −1
3.27 +0	5.68 −1
7.65 +1	4.16 −1

[a] From [58]

[b] For easier legibility, the numbers are rounded to three digits and the decimal exponent is given by $\mp n$. An asterisk preceding the coefficient of an orbital indicates that the exponent has been optimized for that particular orbital

orbital only. Similarly to the s-exponents, the p-exponents are smaller in magnitude compared with the energy-optimized non-relativistic ones. They increase, however, to very large values in order to emulate the "hard" p-functions. The d-set comprises exponents being within a range which is common for polarization functions in non-relativistic calculations, but they reach much larger values.

Now we consider the expansion coefficients, and firstly those of the valence shell. The outermost s-functions which model the valence s-shell have very small coefficients in $1s^+$, but contribute appreciably and with different sign to $2p^-$. Thus, for $1s^+$ and $2s^+$ a similar situation pertains as in the non-relativistic case. Large errors, however, are introduced for $2p^-$ if the outermost s-functions are coupled to a single group according to their weight in $2s^+$. Similarly, a complete contraction of the p-valence shell conflicts with the different characteristics of the large and small components. The outer lobe of the $2s^-$ orbital is only poorly described when the contraction coefficients of the outermost p-functions are taken from the $2p^{+}_{3/2}$ orbital. As a consequence, a minimal basis contraction for the valence shells as realized for set Sa gives only a crude estimate of the relativistic energy contribution and of the spin-orbit splitting (see Table 8). The values of these quantities are improved by splitting the valence shell (set Sb) whereas, as expected, the non-relativistic energy is only marginally lowered. It should be noted, however, that the close agreement with the DF values is accidental, since the core shells are too strongly coupled. This will be shown next, when we concentrate on the contraction of the *s*- and *p*-core.

The coefficients of the innermost *s*-functions parallel each other for all three orbitals $1s^{+}$, $2s^{+}$ and $2p^{-}$, and even more for the larger *s*-sets. With decreasing magnitude of the orbital exponents the ratios of adjacent coefficients differ more and more. Since those for $2p^{-}$ deviate more from $1s^{+}$ than those for $2s^{+}$, the *s*-core has to be decoupled at least as strongly as in the non-relativistic case. The *p*-core orbitals show completely different behaviour in their large and small

Table 8. SCt calculations on the Ne atom by the modified kinetic energy approach[a] using a small, a medium and a large set and different contraction schemes: errors in total energy $\delta E_r^{\mathrm{mod}}$ and δE_{nr}, relativistic energy contribution $\Delta E_r^{\mathrm{mod}}$ and spin-orbit splitting $\Delta\varepsilon_{\mathrm{so}}^{\mathrm{mod}}$ [values in *mHa*]

Basis set label	*s*-, *p*-, *d*-subsets contracted to *s'*, *p'*, *d'* functions[b]	$\delta E_r^{\mathrm{mod}}$	δE_{nr}	$\Delta E_r^{\mathrm{mod}}$	$\Delta\varepsilon_{\mathrm{so}}^{\mathrm{mod}}$
Sa	5+1+2, 4+1+3, 3/3, 3, 1[c]	158.99	155.44	−141.32	3.68
Sb	/4, 4, 2[d]	153.27	153.15	−144.75	4.65
Sc	5+1+2, 4+1+3, 4/4, 4, 2[d]	153.21	153.15	−144.81	4.62
Sd	/5, 5, 2	85.40	85.04	−144.51	4.09
Se	/5, 5, 3	84.90	85.04	−145.01	4.27
Sf	/6, 6, 3	43.56	42.87	−144.19	4.48
Sg	5+1+2, 4+1+3, 5/6, 6, 3	43.56	42.87	−144.19	4.48
Sh	5+1+2, 4+1+3, 5/7, 7, 4	41.04	40.31	−144.14	4.52
Basis set limit			39.22		
Ma	7+1+2, 5+1+4, 4/6, 6, 3	41.56	41.43	−144.74	4.28
Mb	7+1+2, 5+1+4, 5/6, 6, 3	41.54	41.43	−144.76	4.27
Mc	/7, 7, 4	7.24	7.13	−144.76	4.52
Md	7+1+2, 5+1+4, 6/7, 7, 4	7.24	7.13	−144.76	4.52
Me	/8, 8, 5	5.44	5.31	−144.75	4.55
Mf	/9, 9, 6	5.26	5.11	−144.71	4.56
Basis set limit			4.92		
La	8+1+3, 7+1+4, 7/7, 7, 4	10.05	10.19	−145.01	4.50
Lb	/8, 8, 5	2.00	2.29	−145.16	4.55
Lc	/9, 9, 6	1.77	1.71	−144.80	4.56
Basis set limit			1.39		
Exact SCF values					
$E_r=-128691.97$	$E_{nr}=-128547.10$	$\Delta E_r=-144.87$	$\Delta\varepsilon_{\mathrm{so}}=4.56$		

[a] Ref. [15]

[b] segmented contraction of the innermost functions

[c] as [b] and contraction of the outermost 2*s*- and 3*p*-functions

[d] as [b] and splitting of the outermost 3*p*-functions according to 2, 1

components. The coefficients of the innermost p-functions for $1s^-$ and $2s^-$ are to a good approximation constant multiples of each other. Since these high-exponent functions have very small weights in $2p^+_{1/2}$ and $2p^+_{3/2}$, they may be coupled with contraction coefficients taken from $1s^-$. Since the ratios of adjacent coefficients change much more strongly in $2p^+_{1/2}$ and $2p^+_{3/2}$ – and correspondingly also in their non-relativistic $2p$ counterpart – than in the small component orbitals, the extent of p-contraction has to be smaller than suggested by the similarity between $1s^-$ and $2s^-$. Thus, the basis functions of the outer s- and p-core should not be coupled, neither in the relativistic nor in the non-relativistic calculations.

In the three sets Sb, Sd and Sf the s-core is successively decoupled from a single group of five functions into two and finally three groups; the p-core is held contracted to a single group of four functions in the first and second set and opened into two groups in the last one. Along this series, δE_{nr} drops sharply. The first decrease is due to the decoupling of the fifth s-function from the core. The second decrease mainly results from the splitting of the p-core. The splitting of the s-subset is of minor importance, since a contraction $5s,6p$ yields $\delta E_{nr} =$ 46.09 mHa which is only a small loss compared with set Sf having one s-group more. In contrast to the strong decoupling needed in the non-relativistic calculations when weights from $1s^+$ and $1s^-$ are used, the $(5+1+2)s,(4+1+3)p$ set may be contracted to $5s,3p$ when the weights are taken from the non-relativistic $1s$ and $2p$ orbitals, and nevertheless the energy deviates by only 2.33 mHa from the basis set limit. Decoupling of the outer s- and p-core is also of strong influence on $\Delta E_r^{\mathrm{mod}}$ and $\Delta\varepsilon_{\mathrm{so}}^{\mathrm{mod}}$, as shown by the results for the sets Sc and Sd as well as for Se and Sf which pairwise have the same d-basis.

Sets differing in the number of d-functions but having the same number of d-groups give almost the same values for $\Delta E_r^{\mathrm{mod}}$ and $\Delta\varepsilon_{\mathrm{so}}^{\mathrm{mod}}$, as it can be seen from the following pairs Sb,Sc; Sf,Sg; Ma,Mb and Mc,Md. When the sets are too rigidly contracted, however, the calculated relativistic effects strongly scatter, as it is the case for the first and third pair, where values accidentally close and far off from the limits are obtained.

Similarly, as for the small set, a minimal decoupling of the core shells is also required for the medium and large set. There is a sharp reduction of δE_{nr} and of the errors in $\Delta E_r^{\mathrm{mod}}$ and $\Delta\varepsilon_{\mathrm{so}}^{\mathrm{mod}}$ when going from Ma to Mc and from La to Lb. The ultimate convergence towards the basis set limits upon a gradually decoupling of the set is slow, as shown by Md → Me → Mf and Lb → Lc.

Considering the different contractions of the small, medium and large atomic set, a fair compromise between accuracy in the calculated relativistic energy effects and degree of contraction is achieved for the sets Sf, Mc and Lb.

A proposed strategy for choosing a contraction scheme for the relativistic sets may be summarized as follows:

(1) At least a split basis is required for the s-, p- and d-valence shells;

(2) the outer basis functions of the s- and p-core should not be contracted;

(3) the d-set has to be flexibly decoupled while its expansion length is of minor importance.

6. Concluding remarks

The expansion of relativistic orbitals into spherical Gaussians of the form $r^l \exp(-\alpha r^2)$ offers the advantage that the basis set parameters can be used in computer programs based on Cartesian Gaussians whose angular behaviour is given just by r^l times a spherical harmonic of degree l or on their Gaussian lobe approximation [59]. However, there are definite disadvantages of Gaussian type basis functions compared to exponential type ones. Firstly, a large number of spherical Gaussians is needed in order to represent the "hard" functions having an pre-exponential factor $r^{(\lambda-1)}$. Thus, the evaluation of the two-electron integrals becomes much more time-consuming in the relativistic than in the non-relativistic case. This is not only due to the large number of basis functions but also due to the large portion of functions with high l-values. Secondly, "hard" STFs can be easily included in the basis set, since existing computer programs can be adapted to cover these types of functions [60, 13, 14]. In contrast, the formulae for the many-centre one- and two-electron integrals over "hard" Cartesian Gaussians of the form $\exp(-\alpha r^2)x^t y^u z^v/r$ have not yet been published. Furthermore, only approximations to Cartesian Gaussians of degree λ can be constructed from Gaussian lobes [59]. Thirdly, $\vec{\sigma}\vec{p}$ acting on a "normal" STF does not only generate "normal" but also "hard" functions. Thus, the overlap with respect to $\vec{\sigma}\vec{p}$ is large, when the large components are expanded into "normal" and the small components into "normal" as well as "hard" STFs, and less numerical problems from low kinetic energy states are to be expected. Indeed, the relation $\psi^- = \vec{\sigma}\vec{p}\psi^+$ has been adopted by McLean and Lee [13, 14] as a prescription to derive basis sets for the small component; see [32] for details on these sets which have been called kinetically balanced. In contrast to its effect upon an STF, $\vec{\sigma}\vec{p}$ operating on a "normal" spherical Gaussian leads exclusively to functions of the same type.

The large and the small components have been expanded into the *same* set of basis functions. Use of a common set simplifies the organization of the computer program to solve the DF equations. However, the problems related to the non-relativistic limit are exacerbated compared with expansions where different sets of basis functions are used for both components. It has first been pointed out by McLean and Lee [13, 14] that completeness in the basis for the small component alone is sufficient to reduce the DF equations to the HFR equations in the limit $c \to \infty$. The expansions (6) take not advantage of this less stringent requirement on the basis. Hence, the sets developed here are applicable in those approaches where completeness in the small component is enforced by some other means, e.g., by construction of a modified kinetic energy representation [15]. The sets are also appropriate when results of relativistic and quasi-non-relativistic calculations are compared which employ the same basis in both cases, as it is done in the large-c approach.

The optimal parameters which have been obtained from the least-squares criterion with the specific choice $w = 1/r$ of the weighting function closely resemble those obtained by minimizing the total energy of the corresponding non-relativistic functions to which the relativistic functions are reduced in the limit of an infinite velocity of light. These basis sets have already been employed successfully in molecular calculations [15, 17, 18].

Computational details. The calculations have been performed using Gaussian lobes with an off-centre displacement $\Delta R = k/\alpha^{1/2}$ and constants $k = 0.03$ and $k = 0.06$ for the p- and d-functions, respectively. The DF equations within scalar basis sets [11] have been transformed to a basis diagonalizing the $\vec{j}^2$ representation and solved after projecting out higher angular momentum functions not contained in the ground state determinant. The DF equations with modified kinetic energy representation [15] have been transformed to a basis diagonalizing $[\vec{\sigma}\vec{p}]$ and solved after projecting out functions having vanishing kinetic energy. A value of $c = 137.03602$ au for the velocity of light has been taken.

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