

# ON THE ACCURACY OF THE DISCRETIZATION TECHNIQUES IN APPROXIMATE RELATIVISTIC METHODS

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Several non-singular 2-component methods for relativistic calculations of the electronic structure of atoms and molecules lead to cumbersome operators which are partly defined in the coordinate representation and partly in the momentum representation. The replacement of the Fourier transform technique by the approximate resolution of identity in the basis set of approximate eigenvectors of the  $p^2$  operator is investigated in terms of the possible inaccuracies involved in this method. The dependence of the accuracy of the evaluated matrix elements on the composition of the subspace of these eigenvectors is studied. Although the method by itself appears to be quite demanding with respect to the faithfulness of the representation of the  $p^2$  operator, its performance in the context of the standard Gaussian basis sets is found to be encouragingly accurate. This feature is interpreted in terms of approximately even-tempered structure of the majority of Gaussian basis sets used in atomic and molecular calculations.

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## 1. Introduction

In spite of the progress in the development and implementation of the 4-component methods [1–6] for relativistic calculations of the electronic structure of heavy atoms and molecules, their applications to larger molecules are prohibitively demanding [4, 5, 7, 8]. Hence, a great deal of attention is given to approximate methods which are based on the 2-spinor formalism [6, 9, 10–12]. The 2-component formalism proposed by Douglas and Kroll [9] has been found particularly attractive. Over the past decade the so-called Douglas–Kroll (DK) method became the one of the most successful computational tools of relativistic molecular quantum mechanics and relativistic quantum chemistry. Its implementation by Hess and his

co-workers [13–15] has made the DK approach into one of the basic computational methods in relativistic molecular calculations.

Although the DK method works surprisingly well even for systems involving quite heavy elements [16, 17], the origins of its success are quite puzzling. The formal background of the DK approximation has been explained by Sucher [18] and Hardekopf and Sucher [19], bringing the notion of the “no-pair” approximation. Some further insight into the structure of the DK method has been brought by Barysz et al. [11] who analyzed it in terms of the perturbation theory formalism. The success of the method can be traced to the infinite summation of certain contributions to the so-called positive energy solutions of the Dirac equation. With the formal aspects of the DK method rather well understood [11, 18, 19] one is left with its computational implementation. This brings some further approximations whose nature and accuracy do not seem to have been so far carefully investigated. The most important is the approximate evaluation of matrix elements of the DK Hamiltonian [14].

The evaluation of matrix elements of the DK Hamiltonian, as pioneered by Hess et al. [13], involves a discretization of the Fourier transform of intermediate operators through the use of eigenfunctions of the nonrelativistic kinetic energy operator expressed in terms of basis functions defined in the coordinate representation. The numerical stability and accuracy of this approximation will be investigated in this paper. Some necessary details of the DK and related methods will be briefly described in Sec. 2. The discretization method for the evaluation of matrix elements, which arise in the context of the DK and related approaches, is presented in Sec. 3. Different formal and computational aspects of the discretization scheme are discussed. In Sec. 4 the accuracy of this method is investigated numerically through the evaluation of some representative integrals. Conclusions of this study are summarized in Sec. 5.

## 2. The Douglas–Kroll and related 2-component Hamiltonians

The Douglas–Kroll method is usually considered as an approximation to the Dirac–Coulomb Hamiltonian [9, 13, 18, 19]. For moderately heavy systems the dominant part of the relativistic effect is embedded in the one-electron terms [15]. Thus, the transformation of the 4-component equations to their 2-component approximate forms can be limited to the one-electron terms of the Dirac–Coulomb Hamiltonian. In consequence, the essential issues of the Douglas–Kroll approach can be fully appreciated and analyzed in terms of the hydrogenic Dirac equation. In the usual notation [11, 20] this equation is

$$H_0\tilde{\Psi}_0 = \epsilon_0\tilde{\Psi}_0, \quad (1)$$

where (in atomic units)

$$H_0 = \alpha\mathbf{p} + \beta c^2 + (V - c^2)I = \begin{pmatrix} V & c\sigma\mathbf{p} \\ c\sigma\mathbf{p} & V - 2c^2 \end{pmatrix}, \quad (2)$$

and  $\epsilon_0$  is the particle energy shifted by  $-c^2$ . The potential energy operator  $V$  is assumed here to correspond to the electron–nucleus Coulomb attraction. A similar

formalism holds for  $V$  being a multicenter Coulomb interaction operator or some effective interaction potential.

The most important step [11] in the development of the DK approximation is the preliminary unitary transformation of  $H_0$  with the free particle Foldy-Wouthuysen (fpWF) [20, 21] unitary matrix

$$U_0 = \begin{pmatrix} A & \alpha AB \\ \alpha AB & -A \end{pmatrix}, \quad U_0^\dagger U_0 = 1, \quad (3)$$

where

$$A = \sqrt{\frac{e_p + 1}{2e_p}}, \quad B = \frac{1}{e_p + 1} \sigma p, \quad (4)$$

$$e_p = \sqrt{1 + \alpha^2 p^2}, \quad (5)$$

and  $\alpha$  denotes the fine structure constant (in atomic units  $\alpha = 1/c$ , where  $c \approx 137.036$  a.u. of velocity).

This fpWF transformation of  $H_0$  gives a new fully relativistic Hamiltonian  $H_1$

$$H_1 = U_0^\dagger H_0 U_0, \quad (6)$$

whose spectrum is identical with that of the initial Dirac operator  $H_0$ . However, in comparison with  $H_0$ , the transformed energy operator

$$H_1 = \begin{pmatrix} T_p + A(V + \alpha^2 BVB)A & \alpha A[V, B]A \\ \alpha A[B, V]A & -2\alpha^2 - T_p + A(V + \alpha^2 BVB)A \end{pmatrix} \\ = H_{1,d} + H_{1,od}, \quad (7)$$

where

$$T_p = \alpha^{-2}(e_p - 1), \quad (8)$$

differs from the initial one by the dependence on  $\alpha$  in its diagonal ( $H_{1,d}$ ) and off-diagonal ( $H_{1,od}$ )  $2 \times 2$  blocks [11]. One can show that the (1,1) block of  $H_1$

$$[H_1]_{1,1} \equiv h_2 = T_p + A(V + \alpha^2 BVB)A, \quad (9)$$

is, through terms of the order of  $\alpha^2$ , equal to the (1,1) block of the fully block-diagonalized Dirac Hamiltonian

$$H = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix} = U^\dagger H_0 U, \quad (10)$$

where  $U$  is the Foldy-Wouthuysen transformation which leads to the complete separation of the "positive" and "negative" energy eigenspectra of the Dirac Hamiltonian. Thus,

$$h_+ - [H_1]_{1,1} = o(\alpha^4), \quad (11)$$

and  $[H_1]_{1,1}$  can be considered as a 2-component relativistic Hamiltonian which generates the positive energy eigenspectrum of the Dirac Hamiltonian and is accurate through terms of the order of  $\alpha^2$ . Because of the  $\alpha$ -dependence of the  $A$  and  $B$  operators,  $[H_1]_{1,1}$  contains also some terms of the higher order in  $\alpha^2$ .

The 2-component Hamiltonian (9) can be classified as the lowest-order relativistic Hamiltonian of the Douglas-Kroll type and has been extensively investigated in the early papers of Hess et al. [13]. Though it coincides with the Pauli

operator [20] through terms of the order of  $\alpha^2$ , the presence of the operators  $A$  and  $B$  prevents the appearance of singularities. Moreover  $h_2$  carries the major part of the relativistic contribution to energies and will be of main interest in our investigations.

By successive unitary transformations of  $H_1$  one can achieve its step-by-step partial block-diagonalization [11]. In the original DK method, the next transformation is devised in such a way that the (1,1) block, say  $h_{\text{DK}}$ , of the resulting Hamiltonian contains all terms in the interaction operator  $V$  through the second-order, i.e.,  $h_{\text{DK}}$  is accurate through the second-order in the electron-nucleus interaction. The details of this transformation can be found elsewhere [6, 14].

In the alternative approach proposed by Barysz et al. [11], the successive 2-component Hamiltonians,  $h_4, h_6, \dots$ , are defined by their accuracy with respect to  $\alpha^2$ . In such a way one can derive 2-component relativistic Hamiltonians,  $h_{2k}$ , which are *exact* through the  $k$ -th power of  $\alpha^2$ . However, from the computational point of view, the calculation of matrix elements of  $h_{\text{DK}}$  and  $h_{2k}, k \geq 2$ , leads to integrals which appear already in the case of  $h_2$  [11, 13, 14]. Since the numerical accuracy of approximations involved in this step is of primary concern in this paper, we shall limit our analysis to matrix elements of  $h_2$ . In this context it is worthwhile to note that matrix elements of  $A$  and  $B$  can be easily evaluated in the momentum representation. On the other hand, the  $V$  operator matrix elements have a rather simple form in the basis of functions defined in the coordinate space. Finally, what one needs is the matrix elements of  $h_2$  in the coordinate representation.

### 3. Evaluation of the operator matrix elements

The overwhelming majority of the electronic structure calculations is based on what is called the algebraic approximation, i.e., the solution of differential (integro-differential) equations is replaced by the solution of the finite-dimensional algebraic problem, resulting from the matrix representation of the relevant operators in some finite-dimensional subspace of the Hilbert space of square-integrable functions, say  $g_k, k = 1, 2, \dots$ . Traditionally, the so-called basis set  $\{g_k\}$  is defined in the coordinate representation, i.e., the essential part of the 2-spinors  $\Phi_i^{(2k)}$  which solve the  $2 \times 2$  eigenvalue problem,

$$h_{2k}\Phi_i^{(2k)} = E_i^{(2k)}\Phi_i^{(2k)} \quad (12)$$

is determined by the one-electron functions  $g_i = g_i(\mathbf{r})$  of the position vector  $\mathbf{r}$ . Moreover, from the point of view of our considerations, the spin-dependent parts of operators entering the  $h_2$  and higher-order 2-component Hamiltonians are quite irrelevant. If included, their matrix elements will be calculated in the same way as those arising from the spin-independent parts. Thus, it is sufficient to consider representative diagonal matrix elements arising from the spin-averaged operators in  $h_2$

$$I_1 = \langle g_i(\mathbf{r}) | T_p | g_j(\mathbf{r}) \rangle, \quad (13)$$

$$I_2 = \langle g_i(\mathbf{r}) | A(p)V(\mathbf{r})A(p) | g_j(\mathbf{r}) \rangle, \quad (14)$$

and

$$I_3 = \langle g_i(\mathbf{r}) | A(p) b(p) p_\mu V(\mathbf{r}) p_\mu b(p) A(p) | g_j(\mathbf{r}) \rangle, \quad (15)$$

where

$$b(p) = \frac{1}{e_p + 1}, \quad (16)$$

$p_\mu$  is the  $\mu$ -th component of the momentum operator  $p$ , and the summation over  $\mu = x, y, z$  is assumed. It is important to note that all  $p$ -dependent operators,  $T_p$ ,  $A(p)$ , and  $b(p)$ , are solely determined in terms of the scalar operator  $p^2 = p_\mu p_\mu$ . The largest matrix elements, which are possibly most affected by approximations involved in the evaluation of integrals (13–15), are those for  $g_i = g_j = g$ . For this reason we shall limit our investigation to the diagonal terms only.

The natural approach to the calculation of integrals (13–15) would be to Fourier-transform the basis functions and  $V(\mathbf{r})$  to momentum space [18, 19]. Then, the resulting integrals would have to be calculated numerically. In general one would face the problem of multidimensional integration in momentum space. This problem would be further complicated in the case of multicenter form of the Coulomb interaction operator  $V(\mathbf{r})$ , i.e., in the case of molecular calculations. The competitiveness of the 2-component methods would be lost by the computational effort required in the evaluation of matrix elements.

To avoid the above-mentioned computational problems, Hess et al. [13] proposed a method which can be termed as the discretization of the Fourier transform by generating a discrete basis set  $\{\zeta_s(\mathbf{p})\}$  in the momentum space through the diagonalization of the matrix representation of the  $p^2$  operator in some coordinate-dependent basis  $\{\chi_\alpha(\mathbf{r})\}$  defined in the coordinate space. The functions  $g_i$  are not necessarily in the set  $\{\chi_\alpha(\mathbf{r})\}$ .

In the auxiliary basis set  $\{\chi_\alpha(\mathbf{r})\}$  the matrix eigenvalue problem for the operator  $t = p^2$  becomes

$$t u_s = S u_s \tau_s, \quad (17)$$

where  $\tau_s, s = 1, 2, \dots, N$ , is the  $s$ -th discrete eigenvalue and the eigenvectors  $u_s = \{u_{1s}, u_{2s}, \dots, u_{Ns}\}$  determine the finite discrete basis set in the momentum space

$$\zeta_s = \sum_{\alpha=1}^N u_{\alpha s} \chi_\alpha(\mathbf{r}). \quad (18)$$

In Eq. (17)  $S$  denotes the Gramm (overlap) matrix of the coordinate space basis

$$S: \quad S_{\alpha\beta} = \langle \chi_\alpha(\mathbf{r}) | \chi_\beta(\mathbf{r}) \rangle, \quad (19)$$

and  $t$  is the matrix of elements of the operator  $t = p^2$

$$t: \quad t_{\alpha\beta} = \langle \chi_\alpha(\mathbf{r}) | p^2 | \chi_\beta(\mathbf{r}) \rangle. \quad (20)$$

Note that the boundary conditions which define the "momentum" basis set  $\zeta_s$  are those of the set  $\{\chi_\alpha(\mathbf{r})\}$ . For standard basis sets used in molecular calculations (Gaussian functions, Slater or hydrogenic functions) the integrals in (19) and (20) can be easily evaluated.

The finite discrete basis in momentum space is then used to define the (*approximate*) resolution of identity

$$1 \approx \sum_{s=1}^N |\zeta_s\rangle\langle\zeta_s| \quad (21)$$

which is inserted into integrands in (13–15) between the  $r$ - and  $p$ -dependent terms. In this way one obtains approximate expressions for the diagonal terms ( $g_i = g_j = g$ )

$$I_1 \approx \sum_{s,q=1}^N \langle g|\zeta_s\rangle\langle\zeta_s|T_p|\zeta_q\rangle\langle\zeta_q|g\rangle, \quad (22)$$

$$I_2 \approx \sum_{s,q,t,u=1}^N \langle g|\zeta_s\rangle\langle\zeta_s|A(p)|\zeta_q\rangle\langle\zeta_q|V(r)|\zeta_t\rangle\langle\zeta_t|A(p)|\zeta_u\rangle\langle\zeta_u|g\rangle, \quad (23)$$

and

$$I_3 \approx \sum_{s,q,t,u=1}^N \langle g|\zeta_s\rangle\langle\zeta_s|A(p)b(p)|\zeta_q\rangle\langle\zeta_q|p_\mu V(r)p_\mu|\zeta_t\rangle\langle\zeta_t|b(p)A(p)|\zeta_u\rangle\langle\zeta_u|g\rangle. \quad (24)$$

Let us note that in the finite discrete momentum basis set  $\{\zeta_s\}$  generated by Eq. (17) the  $p$ -dependent operators are diagonal. Thus,

$$\langle\zeta_s|T_p|\zeta_q\rangle = \delta_{sq}T(\tau_s), \quad (25)$$

$$\langle\zeta_s|A(p)|\zeta_q\rangle = \delta_{sq}A(\tau_s), \quad (26)$$

and

$$\langle\zeta_s|A(p)b(p)|\zeta_q\rangle = \delta_{sq}A(\tau_s)b(\tau_s). \quad (27)$$

Moreover, the discrete eigenfunctions (18) are expressed in terms of the coordinate space functions  $\chi_\alpha(r)$ , and thus

$$\langle\chi_\alpha|\zeta_s\rangle = \sum_{\beta=1}^N u_{\beta s}\langle\chi_\alpha|\chi_\beta\rangle = \sum_{\beta=1}^N S_{\alpha\beta}u_{\beta s} \quad (28)$$

$$\langle\zeta_s|V(r)|\zeta_q\rangle = \sum_{\alpha,\beta=1}^N u_{\alpha s}^* u_{\beta q}\langle\chi_\alpha|V(r)|\chi_\beta\rangle = \sum_{\alpha,\beta=1}^N u_{\alpha s}^* V_{\alpha\beta}u_{\beta q}, \quad (29)$$

and

$$\langle\zeta_s|p_\mu V(r)p_\mu|\zeta_q\rangle = \sum_{\alpha,\beta=1}^N u_{\alpha s}^* u_{\beta q}\langle\chi_\alpha|p_\mu V(r)p_\mu|\chi_\beta\rangle = \sum_{\alpha,\beta=1}^N u_{\alpha s}^* W_{\alpha\beta}u_{\beta q}, \quad (30)$$

where the matrices  $\mathbf{V}$  and  $\mathbf{W}$  with elements  $V_{\alpha\beta}$  and  $W_{\alpha\beta}$ , respectively, are built of the standard integrals over the coordinate space basis functions,

$$\mathbf{V}: \quad V_{\alpha\beta} = \langle\chi_\alpha(r)|V(r)|\chi_\beta(r)\rangle, \quad (31)$$

and

$$\mathbf{W}: \quad W_{\alpha\beta} = \langle\chi_\alpha(r)|p_\mu V(r)p_\mu|\chi_\beta(r)\rangle = \langle p_\mu\chi_\alpha(r)|V(r)|p_\mu\chi_\beta(r)\rangle. \quad (32)$$

Owing to the use of the discrete  $p^2$  basis set generated by the algebraic approximation (17) the evaluation of matrix elements of essentially all 2-component Hamiltonians [9, 11, 14] is converted into simple matrix multiplication.

It is important to note that, in general, the eigenvectors of Eq. (17) are not the eigenvectors of the  $p_\mu$  operators. For this reason the matrix elements involving individual components of the momentum operator are either calculated separately (cf. Eq. (32)) or manipulated to such a form that only the  $p^2$ -dependent terms survive [11, 14, 22, 23]. This appears to be a secret of the success of the algebraic approach based on the approximate resolution of identity in terms of eigenvectors of Eq. (21). One should also realize that the discrete basis set generated by Eq. (17) will satisfy the boundary conditions appropriate for the coordinate space basis set  $\{\chi_\alpha(\mathbf{r})\}$ .

The accuracy of the algebraic approach to the calculation of matrix elements which appear in 2-component relativistic Hamiltonians [9, 11, 13, 14] relies on the near-completeness of the  $\{\zeta_s\}$  basis set with respect to the representation of the  $p^2$  operator. In terms of the  $\{\zeta_s\}$  basis set the approximate spectral resolution of this operator,

$$p^2 \approx \sum_{s=1}^N |\zeta_s\rangle \tau_s \langle \zeta_s|, \quad (33)$$

and its functions determine the accuracy of the discretization method. Several numerical examples will be presented in the next section.

#### 4. Numerical studies of the accuracy of the discretization method

The dominant majority of the molecular electronic structure calculations is nowadays carried out in the algebraic form [24] with the one-electron approximation in the background of most of the methods currently in use. Computationally most successful methods with a wide range applications use the expansion of one-electron functions into nucleus-centered Gaussian functions. The same computational techniques are also used in molecular relativistic calculations [2, 5, 6, 13, 14]. For this reason the present numerical studies will be concerned with the evaluation of the relativistic Hamiltonian matrix elements in Gaussian basis sets. To avoid excessive numerical data most of the numerical investigations will be carried out for matrix elements of the following form:

$$I = \langle g(\mathbf{r}) | \hat{O} | g(\mathbf{r}) \rangle, \quad (34)$$

where  $\hat{O}$  stands for an operator encountered in relativistic calculations and  $g(\mathbf{r})$  denotes the normalized primitive Gaussian function,

$$g(\mathbf{r}) = \mathcal{N} \exp(-a r^2), \quad (35)$$

with  $a$  being the orbital exponent and  $\mathcal{N}$  denoting the normalization factor.

In computational applications of the DK and related methods the primary attention is usually focused on the relativistic effects in outer (valence) regions of the electronic distribution. The orbital exponents which are important for the description of valence and next-to-valence shells are typically in the range of 0.1–100.0.

The representative results of our study of the performance of the discretization method based on Eq. (21) in calculations of integrals whose exact values are known will be given for  $a = 10.0$ . The results of the investigation of the (relativistic)  $I_2$  and  $I_3$  integrals will be presented for some values of the orbital exponent  $a$ . However, the conclusions of this study are based on a very extensive scan over orbital exponents of distinctively different magnitude. We shall refer to these additional results whenever appropriate.

The coordinate space basis  $\{\chi_\alpha\}$  is also built of primitive Gaussians of the form (35) with orbital exponents  $a_\alpha$  whose range and density are determined by three parameters  $K_{\min}$ ,  $K_{\max}$ , and  $N_{\text{grid}}$ . These parameters define the minimal ( $a_{\min} = 1/N_{\text{grid}} \times 10^{K_{\min}}$ ) and maximal ( $a_{\max} = 10^{K_{\max}}$ ) values of orbital exponents in  $\{\chi_\alpha\}$  and their distribution (grid). The resulting set of  $N = N_{\text{grid}} \times (K_{\max} - K_{\min} + 1)$  primitive Gaussian functions will correspond to the following set of orbital exponents:

$$\{a_\alpha\} : a_{\min} = \frac{1}{N_{\text{grid}}} \times 10^{K_{\min}}, \frac{2}{N_{\text{grid}}} \times 10^{K_{\min}}, \dots, \frac{N_{\text{grid}}}{N_{\text{grid}}} \times 10^{K_{\min}},$$

$$\frac{1}{N_{\text{grid}}} \times 10^{K_{\min}+1}, \frac{2}{N_{\text{grid}}} \times 10^{K_{\min}+1}, \dots, a_{\max} = 10^{K_{\max}}. \quad (36)$$

The faithfulness of the spectral resolution of the  $p^2$  operator and the accuracy of the discretization will be analyzed in terms of the span of orbital exponents ( $K_{\min}, K_{\max}$ ) and the density of their distribution ( $N_{\text{grid}}$ ).

All numerical results presented in this paper have been obtained by using a Fortran program written in quadruple (real\*16) precision. The usual double (real\*8) precision has been found to be insufficient for accurate enough determination of eigenvalues of the  $p^2$  operator from the matrix eigenvalue problem (17).

#### 4.1. Testing the spectral resolution of identity

The expansion of  $T_p$  into the power series with respect to  $\alpha^2$  leads to successive powers of the  $p^2$  operator. The leading relativistic correction is due to the  $p^4$  term and is usually referred to as the mass-velocity correction [20]. Since this operator is hidden within  $T_p$  it is worthwhile to investigate its accuracy which can be achieved with the use of the spectral resolution (21), i.e.,

$$\langle g(r) | p^4 | g(r) \rangle \approx \sum_{s=1}^N \langle g(r) | p^2 | \zeta_s \rangle \langle \zeta_s | p^2 | g(r) \rangle, \quad (37)$$

where  $\zeta_s$  represents approximate eigenfunctions of the  $p^2$  operator determined in the coordinate space basis set  $\{\chi_\alpha\}$  with exponents selected according to Eq. (36). The exact value of the integral in the l.h.s of Eq. (37) with the Gaussian function  $g(r)$  given by Eq. (35) is equal to  $15a^2$ . The results of the numerical study for the orbital exponent  $a$  equal to 10.0 are presented in Table I.

The analysis of the data of Table I shows certain important features of the accuracy of the discretization method based on Eqs. (17), (18), and (21). First, the basis set used to generate the identity resolution should comprise Gaussian

TABLE I

Accuracy of the expectation value of the  $p^4$  operator calculated by using the approximate spectral resolution of identity in the basis of approximate eigenfunctions of the  $p^2$  operator. See Eq. (37) and Sec. 4.1 for details. All values in a.u.

Exponents in the $\{\chi_\alpha\}$ set			$N$	Integral
$a_{\min}$	$a_{\max}$	$N_{\text{grid}}$		
$\frac{1}{N_{\text{grid}}} \times 10^{-1}$	$10^1$	3	9	1495.857262
		4	12	1499.697920
		5	15	1499.979591
$\frac{1}{N_{\text{grid}}} \times 10^{-1}$	$10^2$	3	12	1499.442530
		4	16	1499.987478
		5	20	1499.999778
$\frac{1}{N_{\text{grid}}} \times 10^{-1}$	$10^3$	3	15	1499.533067
		4	20	1499.990585
		5	25	1499.999852
$\frac{1}{N_{\text{grid}}} \times 10^{-1}$	$10^4$	3	18	1499.540531
		4	24	1499.990832
		5	30	1499.999857
$\frac{1}{N_{\text{grid}}} \times 10^0$	$10^1$	3	6	1495.599396
		4	8	1499.672546
		5	10	1499.977426
$\frac{1}{N_{\text{grid}}} \times 10^0$	$10^2$	3	9	1499.407103
		4	12	1499.986406
		5	15	1499.999754
$\frac{1}{N_{\text{grid}}} \times 10^0$	$10^3$	3	12	1499.503352
		4	16	1499.989778
		5	20	1499.999836
$\frac{1}{N_{\text{grid}}} \times 10^0$	$10^4$	3	15	1499.511288
		4	20	1499.990046
		5	25	1499.999842
$\frac{1}{N_{\text{grid}}} \times 10^1$	$10^1$	3	3	1491.440773
		4	4	1499.221467
		5	5	1499.934406
$\frac{1}{N_{\text{grid}}} \times 10^1$	$10^2$	3	6	1498.828418
		4	8	1499.967067
		5	10	1499.999271
$\frac{1}{N_{\text{grid}}} \times 10^1$	$10^3$	3	9	1499.017516
		4	12	1499.975204
		5	15	1499.999512
$\frac{1}{N_{\text{grid}}} \times 10^1$	$10^4$	3	12	1499.033125
		4	16	1499.975852
		5	20	1499.999530
			Exact	1500.000000

functions with orbital exponents  $a_\alpha$  bracketing the exponent  $a$  of the function  $g(r)$  used to calculate the expectation value. Choosing the range with  $a_{\min}$  and  $a_{\max}$  approximately equal to  $a \times 10^{-1}$  and  $a \times 10^1$ , respectively, gives the about 0.04 per cent accuracy of the approximate integral value for the coarsest grid used in these investigations. Once this range is selected, the density of grid becomes quite important. For the above-mentioned range  $(a_{\min}, a_{\max})$ , passing from the grid parameter  $N_{\text{grid}} = 3$  to  $N_{\text{grid}} = 5$ , i.e., increasing the number of basis functions from  $N = 9$  to  $N = 15$  reduces the inaccuracy of the computed integral to less than  $2 \times 10^{-5}$  per cent. However, this means that the error in the calculated integral will occur already at the fourth decimal places.

A similar pattern of behavior has been obtained for other values of  $a$ . Interestingly enough the percentage of error involved in approximate calculations of the expectation value of  $p^4$  is almost independent of the value of  $a$ . This, however, means that for large orbital exponents, e.g., of the order of  $10^6$  or higher, which are quite common in Gaussian basis sets used in calculations for systems comprising heavy elements [25, 26], the absolute values of the error in approximately computed integrals will be enormous. Some consolation is brought by the fact that the integrals of the  $p^4$  type would be finally multiplied by  $\alpha^2 \approx 5 \times 10^{-5}$ , and thus, their absolute error would be greatly reduced. One more important observation is that the contribution of matrix elements involving Gaussian orbitals with large exponents is further reduced by rather small weights of these orbitals in final one-electron functions.

Another integral of interest for testing the accuracy of the identity resolution (21) is

$$\langle g(r) | p^2 r p^2 | g(r) \rangle \approx \sum_{s,q=1}^N \langle g(r) | p^2 | \zeta_s \rangle \langle \zeta_s | r | \zeta_t \rangle \langle \zeta_t | p^2 | g(r) \rangle. \quad (38)$$

Although this integral does not appear explicitly in relativistic calculations, it has certain interesting features similar to those present in integrals (14) and (15). In both cases the operator in the integrand is composed of terms whose expectation values taken separately would be interchangeably small and large. In other words, for small separations  $r$  from the nucleus the values of  $p^2$  are large and vice versa. A similar feature is characteristic of operators in (14) and (15). Owing to this feature the DK and related approaches do not suffer from singularities which would occur in the case of the usual Foldy-Wouthuysen transformation [20]. It is also of importance that the exact value of the integral in the l.h.s. of Eq. (38) can be easily calculated and is equal to  $12a\sqrt{2a}/\sqrt{\pi}$ .

The results obtained in the approximate evaluation of the integral (38), with different basis sets  $\chi_\alpha$  used for the resolution of identity (21), are presented in Table II. They correspond to the value of the orbital exponent  $a$  in (35) equal to 10. The general pattern of these data is similar to that of the data of Table I. However, the matrix elements of the  $p^2 r p^2$  operator appear to be more demanding with respect to the range  $(a_{\min}, a_{\max})$  of the orbital exponents in the  $\{\chi_\alpha\}$  basis set. Also a finer grid needs to be used to obtain integrals accurate through the given number of decimals. The data for the other, lower and higher, values of  $a$  behave in a similar way. Both the integrals and errors scale approximately as  $a\sqrt{a}$ .

TABLE II

Accuracy of the expectation value of the  $p^2 r p^2$  operator calculated by using the approximate spectral resolution of identity in the basis of approximate eigenfunctions of the  $p^2$  operator. See Eq. (38) and Sec. 4.1 for details. All values in a.u.

Exponents in the $\{\chi_\alpha\}$ set			$N$	Integral
$a_{\min}$	$a_{\max}$	$N_{\text{grid}}$		
$\frac{1}{N_{\text{grid}}} \times 10^{-1}$	$10^1$	3	9	314.984054
		4	12	304.814641
		5	15	303.097837
		6	18	302.828374
$\frac{1}{N_{\text{grid}}} \times 10^{-1}$	$10^2$	3	12	303.346111
		4	16	302.798539
		5	20	302.776130
		6	24	302.775931
$\frac{1}{N_{\text{grid}}} \times 10^{-1}$	$10^3$	3	15	303.244158
		4	20	302.790457
		5	25	302.776197
		6	30	302.775907
$\frac{1}{N_{\text{grid}}} \times 10^{-1}$	$10^4$	3	18	303.234274
		4	24	302.789971
		5	30	302.776181
		6	36	302.775906
$\frac{1}{N_{\text{grid}}} \times 10^0$	$10^1$	3	6	315.293706
		4	8	304.918669
		5	10	303.120183
		6	12	302.832739
$\frac{1}{N_{\text{grid}}} \times 10^0$	$10^2$	3	9	303.340495
		4	12	302.799200
		5	15	302.776143
		6	18	302.775933
$\frac{1}{N_{\text{grid}}} \times 10^0$	$10^3$	3	12	303.238617
		4	16	302.790823
		5	20	302.776212
		6	24	303.775907
$\frac{1}{N_{\text{grid}}} \times 10^0$	$10^4$	3	15	303.238700
		4	20	302.790321
		5	25	302.776196
		6	30	302.775907
			Exact	302.775903

From the point of view of the 2-component relativistic calculations for heavy systems the tests presented in this section do not bring very optimistic conclusions. In most calculations based on the use of Eq. (21) the set  $\{\chi_\alpha\}$  is far from being that dense as it should be according to the present data. The set of exponents in  $\{\chi_\alpha\}$  usually ranges from the lowest to the highest exponent of the uncontracted Gaussian basis set used in calculations [22, 23]. Thus, for the most external exponents, in particular for the highest one, the empirical condition established in this study is never met. There is obviously some damping of inaccuracies by the presence of the  $\alpha^2$  factors and the low amplitudes of the high-exponent Gaussians. However, the overall accuracy of the calculated relativistic energies may be, in general, quite poor.

One more aspect to note is the requirement of very high numerical accuracy. Calculations with the computer program written in double (real\*8) precision were found to be numerically unstable because of a very wide range of eigenvalues of Eq. (17) and the program had to be recompiled in real\*16 precision to attain the desired numerical stability. This remark, however, applies primarily to basis sets with particularly dense distribution of orbital exponents and may not be highly important in calculations with traditional Gaussian basis sets [25, 26].

#### 4.2. Evaluation of relativistic integrals $I_2$ and $I_3$

For the purpose of this study we shall simplify the  $V(r)$  operator in Eqs. (14) and (15) to  $1/r$ . Thus, the integrals  $I_2$  will enter the matrix elements of the  $h_2$  and related 2-component relativistic operators with the factor  $-Z$ , where  $Z$  is the nuclear charge. The  $I_3$  integrals will be additionally multiplied by  $\alpha^2$ . This should be taken into account when discussing the relation between the accuracy of the separate integrals and the accuracy of the corresponding matrix elements of the relativistic one-electron Hamiltonian. For systems exhibiting a significant relativistic effect the value of  $Z$  is of the order of  $10^2$ . Thus, the error  $\epsilon$  in the calculated value of  $I_2$  will contribute about  $10^2\epsilon$  error in the Hamiltonian matrix elements. Because of the  $\alpha^2$  factor, the same error in  $I_3$  will contribute only about  $10^{-3}\epsilon$  error in the final matrix element.

The generation of the  $\{\chi_\alpha\}$  basis set for the resolution of the identity operator (21) has been carried out following our findings described in Sec. 4.1. Thus, most calculations have been performed for a limited range of orbital exponents  $a_\alpha$  with the main attention given to the grid density rather than to the extension of the  $(a_{\min}, a_{\max})$  range. Our results for the integral  $I_2$  of Eq. (14) represented in the form (23) for the exponent values of the Gaussian function (35) equal to 1.0, 10.0, and 100., are presented in Table III. Analogous data for the integral  $I_3$  of Eqs. (15) and (24) can be found in Table IV.

The convergence of the calculated integrals with respect to the grid density for the given range of exponents in the  $\{\chi_\alpha\}$  basis set is a little poorer than that observed for the integral  $I_2$ . A relatively coarse grid in the range of exponents ( $a_{\min} = 0.1 \times a$ ,  $a_{\max} = 10 \times a$ ) is required to achieve the 4 decimals accuracy of  $I_2$  even for  $a = 100.0$ . In the case of  $I_3$  to obtain the same accuracy requires a much

TABLE III

Accuracy of the expectation value of the  $A(p)V(r)A(p)$  operator calculated by using the approximate spectral resolution of identity in the basis of approximate eigenfunctions of the  $p^2$  operator. See Eq. (23) and Sec. 4.2 for details. All values in a.u.

Exponents in the $\{\chi_\alpha\}$ set			$N$	Integral
$a_{\min}$	$a_{\max}$	$N_{\text{grid}}$		
Orbital exponent $a = 1.0$				
$\frac{1}{N_{\text{grid}}} \times 10^{-1}$	$10^1$	2	6	1.59568493
		3	9	1.59568410
		4	12	1.59568418
		5	15	1.59568417
		5	25	1.59568417
Orbital exponent $a = 10.0$				
$\frac{1}{N_{\text{grid}}} \times 10^0$	$10^2$	2	6	5.04360876
		3	9	5.04358311
		4	12	5.04358544
		5	15	5.04358511
		6	18	5.04358514
		6	30	5.04358514
Orbital exponent $a = 100.0$				
$\frac{1}{N_{\text{grid}}} \times 10^1$	$10^3$	2	6	15.87556827
		3	9	15.87489332
		4	12	15.87494396
		5	15	15.87493676
		6	18	15.87493754
		7	21	15.87493746
		7	35	15.87493747
$\frac{1}{N_{\text{grid}}} \times 10^0$	$10^4$	7	35	15.87493747

finer grid. However, let us recall that the contribution of  $I_3$  to the Hamiltonian matrix elements is finally scaled by the factor of about  $-2Z \times 10^{-5}$  while that of  $I_2$  is scaled by  $-Z$ . Once the two integrals are multiplied by the appropriate factors, the inaccuracy brought by  $I_3$  will be considerably reduced. Thus, the inaccuracy of the calculated matrix elements of  $h_2$  and related Hamiltonians will be primarily determined by the accuracy of  $I_2$ .

So far our investigations have been concerned with the calculation of a single integral with a rather artificially chosen structure of the  $\{\chi_\alpha\}$  basis set. The purpose of these studies was to establish certain rules for accurate enough calculations of matrix elements which occur in 2-component relativistic calculations. The present findings are not particularly encouraging from the point of view of the usually adopted methods for the calculation of  $I_2$  and  $I_3$ . According to the method pioneered by Hess et al. [13], the  $\{\chi_\alpha\}$  basis set used to evaluate these integrals

TABLE IV

Accuracy of the expectation value of the relativistic operator  $A(p)b(p)p_\mu V(r)p_\mu b(p)A(p)$  calculated by using the approximate spectral resolution of identity in the basis of approximate eigenfunctions of the  $p^2$  operator. See Eq. (24) and Sec. 4.2 for details. All values in a.u.

Exponents in the $\{\chi_\alpha\}$ set			$N$	Integral		
$a_{\min}$	$a_{\max}$	$N_{\text{grid}}$				
Orbital exponent $a = 1.0$						
$\frac{1}{N_{\text{grid}}} \times 10^{-1}$	$10^1$	2	6	0.79769672		
		3	9	0.79769326		
		4	12	0.79769346		
		5	15	0.79769343		
$\frac{1}{N_{\text{grid}}} \times 10^{-2}$	$10^2$	5	25	0.79769343		
		Orbital exponent $a = 10.0$				
$\frac{1}{N_{\text{grid}}} \times 10^0$	$10^2$	2	6	25.17211430		
		3	9	25.17103544		
		4	12	25.17109583		
		5	15	25.17108540		
		6	18	25.17108658		
		7	21	25.17108645		
		7	35	25.17108646		
$\frac{1}{N_{\text{grid}}} \times 10^{-1}$	$10^3$	Orbital exponent $a = 100.0$				
		2	6	779.73371977		
		3	9	779.43066042		
		4	12	779.44284335		
		5	15	779.44057223		
		6	18	779.44081094		
		7	21	779.44078666		
		8	24	779.44078887		
$\frac{1}{N_{\text{grid}}} \times 10^0$	$10^4$	7	35	779.44078881		
		$\frac{1}{N_{\text{grid}}} \times 10^0$	$10^4$	8	40	779.44078872

is chosen as the primitive Gaussian set which defines the basis set used in the evaluation of matrix elements of the 2-component Hamiltonian, i.e.,  $\{g_i\} = \{\chi_\alpha\}$ .

For most of the Gaussian basis sets used in molecular relativistic calculations neither of the earlier (see Sec. 4.1) established recommendations is met. The basis set exponents are far from forming as dense set as would be required according to our present conclusions. The range of orbital exponents in the  $\{\chi_\alpha\}$  is, by definition, the same as in the original Gaussian set in which the Hamiltonian matrix elements are evaluated. The only advantage is that most of the Gaussian sets used in molecular calculations have an approximately even-tempered structure [27–29].

In order to investigate the accuracy of the evaluation of  $I_2$  and  $I_3$  in routine relativistic calculations we shall compute some of these integrals for Au with a relatively standard set of Gaussian basis functions and compare them with accurate numerical values determined according to the method described in this section.

#### 4.3. Evaluation of relativistic integrals $I_2$ and $I_3$ for Au

The basis set used here in calculations of some of the  $I_2$  and  $I_3$  integrals is the fully uncontracted Gaussian set devised for relativistic calculations on gold on its compounds [30, 31]. In the  $s$  subshell this basis set comprises 21 Gaussian functions with exponents ranging from  $a_{\min} = 0.0107835$  to  $a_{\max} = 9424086.3$ . This set of exponents is relatively uniform on the logarithmic scale. For the illustration of the issues addressed in this paper the relevant relativistic matrix elements will be calculated for five selected Gaussians (35) with orbital exponents  $a$  equal to 0.0285347, 0.5531111, 3.8905484, 19.540386, and 94.866768. These primitive Gaussian functions make the dominant contribution in the description of the electron density distribution in the valence and next-to-valence  $s$  shells of the Au atom.

The calculated  $I_2$  and  $I_3$  integrals are presented in Table V. Simultaneously, their accurate numerical values have been determined by using the method employed in Sec. 4.2, i.e., by the generation of the  $\{\chi_\alpha\}$  set independently of the  $s$  subset of Gaussians available from the Au basis set. These reference values are fully converged through all presented decimals by the use of a rather wide range of exponents ( $a_{\min} = 0.01a$ ,  $a_{\max} = 100a$ , where  $a$  is the exponent in the Gaussian function for which the given integral is evaluated) and a fine grid ( $N_{\text{grid}} = 6$ ).

TABLE V

Representative values of  $I_2$  and  $I_3$  for selected  $s$ -type primitive Gaussian functions of the Au basis set and their comparison with accurately evaluated reference results. All values in a.u.

Exponent <sup>a</sup> $a$	$I_2$		$I_3$	
	Au basis set <sup>b</sup>	Accurate <sup>c</sup>	Au basis set <sup>b</sup>	Accurate <sup>c</sup>
0.0285347	0.26956038	0.26956236	0.00384589	0.00384590
0.5531111	1.18676151	1.18676143	0.32817167	0.32817167
3.8905484	3.14691909	3.14691769	6.11718939	6.11718228
19.5403860	7.04671750	7.04671908	68.59879060	68.59875532
94.8667680	15.46615834	15.46615742	721.05883755	721.04768978

<sup>a</sup>The exponent of the Gaussian function defined by Eq. (35).

<sup>b</sup>The  $\{\chi_\alpha\}$  built of the primitive  $s$  subset of the Au basis set. See the text.

<sup>c</sup>Accurate numerical value converged through all displayed decimals. See the text.

In contrast to what one would have expected on the basis of our earlier investigations, the accuracy of the calculated integrals is quite satisfactory. In particular, the  $I_2$  integral for the highest investigated Gaussian exponent  $a = 94.8667680$  is accurate to almost six decimals. Thus, the inaccuracy brought by

this integral to the corresponding matrix element of the Hamiltonian would be of the order of  $10^{-4}$  a.u. The larger discrepancy found for the  $I_3$  integral is rather irrelevant because of the  $-Z\alpha^2$  factor which multiplies its contribution. One should stress that for the integrals calculated in the primitive Gaussian set of Au the total number of orbital exponents is only 21. The accurate values of integrals presented in Table V are obtained in with the  $\{\chi_\alpha\}$  set comprising 30 Gaussian functions with quite densely distributed orbital exponents.

Somewhat disturbing is the loss of accuracy of the integrals computed in the Au basis set with the increase in the orbital exponent  $a$ . This means that the energy contribution from the core orbitals as well as the total energy may be considerably affected by the use of this particular form of the identity resolution. On the other hand, the total relativistic energy of the given system is usually of little interest. In most applications one looks for energy differences resulting from valence processes. These energy differences will be only marginally affected by the use of the same basis set in calculations of the Hamiltonian matrix elements and in the generation of the approximate resolution of identity in the momentum space.

## 5. Summary and conclusions

We have investigated the accuracy of the discretization method used for the evaluation of certain integrals which appear in 2-component approximate relativistic calculations. The method is based in the approximate resolution of identity in terms of eigenvectors of the  $p^2$  operator. The latter follow from the finite-dimensional approximation to the eigenvalue problem of the  $p^2$  operator. This approach replaces the explicit evaluation of the Fourier transform of functions and operators which enter the integrands by relatively simple integration in the coordinate space and matrix multiplication.

The accuracy investigation has been first carried out for integrals whose exact values are known. This has lead to certain rules and recipes which help to generate the  $(p^2)$  basis set used for the diagonalization of the  $p^2$  operator. Following these findings we have studied the convergence of two basic integrals with respect to the range of orbital exponents and their density in the  $p^2$  basis set. At this level the results seem to be rather discouraging. To obtain the accuracy of 8 decimals one needs in most cases quite extensive  $p^2$  basis sets. For coarse grids in the set of orbital exponents the inaccuracies involved in the spectral resolution of identity were found to considerably affect the computed values of the relativistic integrals.

It should be mentioned that the two relativistic integrals considered in this paper are representative for most of the non-singular 2-component methods. They enter the lowest-order relativistic Hamiltonian  $h_2$  and reappear as a part of the higher order terms [6, 11, 14]. Thus, the study of the accuracy of their evaluation reveals the numerical accuracy problems which are encountered in most successful relativistic schemes currently in use.

Interestingly enough for the  $p^2$  basis set equivalent to the set in which the Hamiltonian matrix elements are computed, the accuracy of the relativistic integrals becomes quite satisfactory. This has been exemplified by our calculations of

$I_2$  and  $I_3$  with the standard Gaussian basis set for Au. At least for orbital exponents in the range of values used to describe the valence and next-to-valence regions, the numerically most important ( $I_2$ ) integrals turn out to be accurate through 6 or more decimals. The contribution from the less accurate ( $I_3$ ) integrals is quenched by the  $\alpha^2$  factor and thus, achieving their high accuracy becomes less important.

Our results for the selected standard Gaussian basis set of Au reveal the reasons for surprisingly high numerical stability of the Douglas-Kroll calculations in the implementation by Hess et al. [13]. However, they simultaneously show that the calculated total DK energies may be considerably affected by the inaccuracy of large integrals resulting from Gaussian functions with very high orbital exponents. Moreover, the success of the discretization method, in which the identity resolution is built in the same primitive basis set in which the Hamiltonian matrix elements are evaluated, can be linked to approximately even-tempered form of most of the Gaussian basis sets used in relativistic atomic and molecular calculations. Investigations relating this observation to the completeness of Gaussians [29] are in progress.

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